RETENTION AND RELEASE OF APPLIED PHOSPHORUS BY THE BENCHMARK SOILS OF LESOTHO

by

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A thesis submitted in accordance with the requirements for the Philosophiae Doctor degree in the Department of Soil Science, Faculty of Agriculture at the University of the Orange Free State

MAY, 2000

Promoter: *PROF. C.C. DU PREEZ*

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Dedicated to

My mother, `M`e `Makutloano Molete who looked after my baby for all the years I spent on this study

and

My little boy, Lefa whom I was not able to stay with at the very early age of his life, may this signify the best future for him.

TABLE OF CONTENTS

ABSTRACT

Retention and release of applied phosphorus by the benchmark soils of Lesotho

A lack of information on the behaviour of applied phosphorus (P) in and on the P requirements of the benchmark soils of Lesotho precludes the establishment of proper application recommendations of P fertilizer for crop production. Therefore, the objectives of this thesis were to determine the P retention capacities and P requirement factors of these soils and identify soil properties implicated therein.

Eleven benchmark soil series, each replicated at least five times were sampled in the lowlands and foothills for P retention studies. These soil samples were prepared as usual for laboratory analyses and characterized especially for the soil properties implicated in P retention. The soil series varied with regard to those properties, providing a good indication of their variability in P retention.

A pilot experiment was conducted on some of the soils to investigate an optimum incubation period for P retention and release studies. The soils were incubated with P levels equivalent to 0, 50, 100, 200 and 400 kg P ha^{-1}, respectively at 85% water filled porosity, which was checked fortnightly. The experiment was laid out in a randomized complete block design at room temperature. Phosphorus retention was then determined 7, 14, 21, 28, 42 and 63 days after P application using the Olsen extraction procedure. The results of this experiment indicated an incubation period of 42 days as practically suitable for P retention and release studies on the benchmark soils.

Thereafter a P retention experiment with 11 soil series, five P levels and five soil phases, all replicated three times, was conducted. The soils were incubated with the same levels of P as in the pilot experiment, for 42 days at 85% water filled porosity that was again checked fortnightly. The experiment was set–up in a split–split plot design, at room temperature. After 42 days P was extracted with Bray and Olsen extractants, respectively and retained P was calculated as the difference between applied and extracted P. Percentage of applied P

i

retained against the Bray and Olsen extractants varied from 6 to 97 and 21 to 91, respectively. The slopes of retained P against applied P, viz. P retention indices (PRI's) varied from −0.04 to 0.28 for Bray and 0.07 and 0.27 for Olsen while the respective slopes of retained P against extracted P, viz. P buffering indices (PBI's) varied from 2 to 55 and 12 to 103. The PRI's and PBI's were closely correlated, r = 0.94 and 0.81 (P < 0.0001) for Bray and Olsen, respectively. The series Fusi, Thabana, Machache and Sefikeng had higher PRI's and similarly higher PBI's than the rest of the series, viz. Khabos, Leribe, Rama, Sephula, Tumo, Matela and Berea, particularly according to the Bray method. In the case of the Olsen method however, the series Khabos and Tumo had comparable PBI's with the series Fusi, Thabana, Machache and Sefikeng though their PRI's were significantly lower. The series Fusi, Thabana, Machache and Sefikeng also had the highest P retention capacity at an application of 400 kg P ha^{-1} (PRC at P400) of about 69 to 83% for Bray and 75 to 81% for Olsen. The respective PRC at P400 for the rest of the series were 0 to 39 and 47 to 66%. For all the soils the slopes of applied P against extracted P, viz. P requirement factors (PRF's) ranged from 0.85 to 11.40 (Bray) and 1.45 to 9.07 (Olsen). The high P retaining series (Fusi, Thabana, Machache and Sefikeng) had high mean PRF's of 3.36 to 7.13 for Bray and 3.85 to 5.47 for Olsen.

For both the Bray and Olsen procedures the parameters PRI, PRC at P400, PBI and PRF were with a few exceptions highly correlated (r^2 > 0.60) with sample density, sand, clay, organic carbon, cation exchange capacity, acid ammonium oxalate and citrate bicarbonate dithionite extractable iron and aluminium. Multiple linear regression models were also obtained for each of the parameters with some of the soil properties.

Recommendations were made with regard to reducing P retention and increasing P availability in the high P sorbing soils and hence to improve crop production.

Keywords: Lesotho benchmark soils, phosphorus, retention capacity, retention index, buffering index, requirement factor, incubation period, soil properties, fertility management.

UITTREKSEL

Retensie en vrystelling van toegediende fosfor deur die verwysingsgronde van Lesotho

'n Gebrek aan inligting oor die gedrag van toegediende fosfor (P) in en oor die P behoeftes van die verwysingsgronde van Lesotho kortwiek die instelling van behoorlike toedieningsaanbevelings van P kunsmis vir gewasproduksie. Daarom was die oogmerke van hierdie proefskrif om die P retensiekapasiteite en P behoeftefaktore van die gronde vas te stel en grondeienskappe betrokke daarby te identifiseer.

Elf verwysingsgrondseries wat elk ten minste vyf keer herhaal is, is in die laaglande en voetheuwels vir P retensie studies gemonster. Hierdie grondmonsters is soos gebruiklik vir laboratoriumontledings voorberei en gekarakteriseer veral vir daardie eienskappe wat 'n rol speel by P retensie. Die grondseries het gevarieer met betrekking tot daardie eienskappe wat 'n goeie aanduiding is van hulle varieerbaarheid in P retensie.

'n Loodseksperiment is op sommige van die gronde gedoen om 'n optimum inkubasieperiode vir P retensie en vrystelling te ondersoek. Die gronde is geïnkubeer met P vlakke ekwivalent aan onderskeidelik 0, 50, 100, 200 en 400 kg P ha^{-1} by 'n 85% watergevulde porositeit wat tweeweekliks gekontroleer is. Fosforretensie is 7, 14, 21, 28, 42 en 63 dae na P toediening bepaal deur die Olsen ekstraheringsprosedure te gebruik. Die resultate van hierdie eksperiment het daarop gedui dat 'n inkubasieperiode van 42 dae prakties geskik is vir studies van P retensie en vrystelling op die verwysingsgronde.

Daarna is 'n P retensie eksperiment gedoen met 11 grondseries, vyf P vlakke en vyf grondfases wat alles drie keer herhaal is. Die gronde is geïnkubeer met dieselfde P vlakke soos in die loodseksperiment vir 42 dae by 85% watergevulde porositeit wat weereens tweeweekliks gekontroleer is. Die eksperiment is as 'n verdeelde-verdeelde perseelontwerp by kamertemperatuur uitgevoer. Na 42 dae is P geëkstraheer met onderskeidelik Bray en Olsen ekstraheermiddels en vasgelegde P is bereken as die verskil tussen toegediende en geëkstraheerde P. Persentasie van toegediende P wat nie geëkstraheer is met Bray en Olsen ekstraheermiddels nie varieer van 6 tot 97 en 21 tot 91, respektiewelik. Die hellings van

vasgelegde P teen toegediende P, te wete P retensie-indekse (PRI'e) het gevarieer van –0.04 tot 0.28 vir Bray en van 0.07 tot 0.28 vir Olsen, terwyl die onderskeie hellings van vasgelegde P teen geëkstraheerde P, te wete P bufferindekse (PBI'e) gevariëer het van 2 tot 55 en 12 tot 103. Die PRI'e en PBI'e het goed gekorreleer, r = 0.94 en 0.81 (P < 0.0001) vir Bray en Olsen respektiewelik. Die series Fusi, Thabana, Machache en Sefikeng het hoër PRI'e en dienooreenkomstig hoër PBI'e as die res van die series, te wete Khabos, Leribe, Rama, Sephula, Tumo, Matela en Berea, veral volgens die Bray metode. In die geval van die Olsen metode het die series Khabos en Tumo egter soortgelyke PBI'e as die series Fusi, Thabana, Machache en Sefikeng hoewel hulle PBI'e betekenisvol laer is. Die series Fusi, Thabana, Machache en Sefikeng het ook die hoogste P retensiekapasiteit by 'n toediening van 400 kg P ha^{-1} (PRK by P400) van 69 tot 83% vir Bray en 75 tot 81% vir Olsen. Die onderskeie PRK by P400 vir die res van die series was 0 tot 39 en 47 tot 66%. Vir al die gronde het die hellings van toegediende P teen geëkstraheerde P, te wete die P behoeftefaktore (PBF'e) gevariëer van 0.85 tot 11.40 (Bray) en 1.45 tot 9.07 (Olsen). Die hoë P retensie series (Fusi,Thabana, Machache en Sefikeng) het hoë gemiddelde PBF'e van 3.36 tot 7.13 vir Bray en 3.85 tot 5.47 vir Olsen.

Vir beide die Bray en Olsen ekstraksie prosedures het PRI, PRK by P400, PBI en PBF met enkele uitsonderings hoogs gekorreleer (r^2 > 0.60) met monsterdigtheid, sand, klei, organiese koolstof, katioonuitruilkapasiteit en suur ammonium oksalaat en sitraat bikarbonaat ditioniet ekstraheerbare yster en alumunium. Meervoudige lineêre regressiemodelle is ook verkry vir elk van die parameters met sekere van die grondeienskappe wat 'n rol speel by P retensie.

Aanbevelings word gemaak met betrekking tot die vermindering van P retensie en vermeerdering van P toeganklikheid in die hoë P sorberende gronde ten einde gewasproduksie te verbeter.

DECLARATION

I declare that the thesis hereby submitted by me for the Philosophiae Doctor degree at the University of the Orange Free State is my own independent work and has not previously been submitted by me at another university. I furthermore cede copyright of the thesis in favour of the University of the Orange Free State.

ACKNOWLEDGEMENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1. General

In their native state, most soils contain very little phosphorus (P), mainly as a result of low P levels in their parent materials (Norrish & Rosser, 1983). A small portion of this P is present in a form readily available for plant uptake. The largest part occurs in a less readily available and even unavailable form. Deficiencies of P in soils are, therefore, a common problem worldwide, limiting crop and herbaceous production, particularly in Australia, South Africa and South America. The soils of the Nile Valley which receive annual deposits of phosphate–rich alluvium from basic rocks on the Ethiopian plateau and some soils formed on volcanic lava are, however, exceptions in not being deficient in P (Wild, 1988).

As already mentioned, various fractions of P occur in soils and from a viewpoint of plant nutrition they can be classified into soil solution, labile and non–labile P. Soil solution P is the fraction of soil P, which is directly accessible for absorption by plant roots. This fraction consists of the orthophosphate ions $H_2PO_4^-$ and HPO_4^{2-}, and the soluble organic phosphate compounds like the lower esters of inositol polyphosphates and others, which are in the monophosphate form. Labile P is the readily available fraction, which replenishes P in the soil solution following its uptake by plant roots. This fraction is made up of isotopically exchangeable P adsorbed onto the surfaces of soil colloids, P in the sparingly soluble minerals (e.g. the residual mineral carbonate apatite, pedogenic mineral apatite and secondary mineral dicalcium phosphate) and organically bonded P. Non–labile P is the fraction present in effectively insoluble minerals which is, if at all, very slowly available. Residual minerals, viz. fluoroapatite, plumbogummite, monazite and xerotime and secondary minerals, viz. fluoroapatite, vivianite and hydroxyapatite, all of which have very low solubility (Norrish & Rosser, 1983), represent this fraction.

The content of P in soils varies not only according to the type of parent material, but also according to the organic matter (OM) content and fertilization history thereof. Soils derived from basic igneous rocks such as basalt contain more P than soils derived from siliceous parent materials (Mengel & Kirkby, 1987; Probert *et al.*, 1987; Wild, 1988). There is evidence that soils formed from weathered rocks in which apatite, the main P containing mineral, is dissolved by leaching of acid water before formation of sufficient Fe and Al oxides and clay minerals, onto which orthophosphate ions are adsorbed, are usually low in P (Wild, 1988). In virgin soils with appreciable amount of OM, the proportion of organic P is much larger than in cultivated soils where OM is reduced. The same is also true for soils under no–till with stubble return as opposed to soils under conventional tillage (Lal, 1976; Le Mare, 1982; Guertal *et al.*, 1991). The content of organic P is directly correlated to that of OM content. In most soils it decreases with depth of the soil profile (Anderson, 1980). In contrast, soils with long cropping history are higher than virgin soils in P due to prolonged P fertilizer application (Williams & Raupach, 1983). On average, content of P in soils is in the range of 134 mg P kg^{-1} in Ghana to 700 mg P kg^{-1} in United Kingdom (Nye & Bertheux, 1957; Cooke, 1958).

According to Wild (1988) the concentration of P in the soil solution can be as low as 10^{-8} M or less in very poor soils in the tropical regions. In soils of the temperate regions the concentration of P in the soil solution is in the order of 10^{-6} M for P deficient soils. Most soils with a moderate P fertility status have concentration of P in the soil solution of 10^{-5} M or more. Based on the plant requirements for P (Higinbothan, 1973; Mengel & Kirkby, 1987), these concentrations are too small to effectively support plant growth. The ability of plant roots to absorb P from very low concentrations and the possible replenishment of soil solution P from the labile pool as the former gets depleted by plant uptake are the only mechanisms by which plants are able to survive under such low P concentrations. However, due to the low content of the labile P and other factors such as water content and diffusion rate that determine availability of P in the rhizosphere, replenishment of soil solution P is rarely able to provide sufficient P for a sequence of good crop yields. This has therefore, led to a high dependence on use of P–containing fertilizers to improve the soil P fertility status and agricultural productivity.

2

1.2. Reactions of applied phosphorus in soils

Phosphorus is a highly reactive albeit immobile nutrient in soils. As a result, not all the P in the fertilizer material becomes accessible to plant roots, some of it reacts with the soil and soil constituents and is retained in forms of varying availability. When P fertilizer is added to the soil it first absorbs the soil water and then dissolves, releasing P and other elements. The concentration of P at the site of fertilizer is then increased relative to that in the bulk soil, forming a concentration gradient towards the latter. As a result, P diffuses from the fertilizer site into the bulk soil where it encounters and reacts with soil and soil constituents. The soil type and the extent to which it is saturated with P determine the type and extent of reactions of applied P in the soil, which in turn determine the fertilizer use efficiency. There is a consensus that P reaction in soils is a diphasic process, consisting of an initial rapid phase which lasts for only a few hours followed by a slow phase which continues for a long time, but at a decreasing rate.

The initial rapid phase involves adsorption onto the surface of soil colloids and precipitation with cations present in the soil solution. The mechanism of the initial rapid P adsorption is covered in a wide range of papers (Rajan *et al.*, 1974; Parfitt *et al.*, 1975; Rajan, 1975; Ryden *et al.*, 1977a, b; Parfitt, 1979; Barrow, 1983a; Goldberg & Sposito, 1985; Parfitt, 1989). Adsorption of orthophosphate ions ($H_2PO_4^-$ and HPO_4^{2-}) occurs through a ligand exchange mechanism between $H_2PO_4^-$ or HPO_4^{2-} and hydroxyl groups (OH^- and H_2O) involving formation of phosphate-metal bridging surfaces. Most reactive sites for P adsorption occur at surfaces or defect sites of oxides and hydroxides of Fe and Al and on surfaces of clay and OM associated with Fe and Al. Initial rapid adsorption of $H_2PO_4^-$ and HPO_4^{2-} at these surfaces or defect sites is very strong, limiting availability of P for plant uptake (Parfitt, 1989).

Nevertheless, a less strong adsorption onto less reactive sites on the same soil components also occurs during the initial rapid phase, particularly at high P concentration (Parfitt, 1989). Phosphate adsorbed in this manner is readily available for plant uptake. Adsorption of P onto negatively charged surfaces of crystalline clay minerals and edges of clay micelles is also possible since P is adsorbed irrespective of charge, evidence for specific adsorption of P

3

(Goldberg & Sposito, 1985). The high soil solution P concentration which occurs immediately after dissolution of P fertilizer accompanied by high concentrations of cations in the solution favours precipitation of P as part of the initial rapid P reaction (Tisdale *et al.*, 1985; Wild, 1988). An example is the formation of a dicalcium phosphate precipitate that is fairly soluble and forms immediately after application of monocalcium phosphate fertilizer (Tisdale *et al.*, 1985).

Following this initial rapid adsorption of P is a *continuous* slow process that involves a shift from the initially, physically sorbed form to a more chemically sorbed form (Ryden *et al.*, 1977b). There is a large consensus that this slow P reaction is a diffusion–controlled process (Kuo & Lotse, 1974; Ryden *et al.*, 1977b; Barrow, 1983c; 1985; Parfitt, 1989; Agbenin & Tiessen, 1995). Ryden *et al.* (1977b) described the slow phase process as occlusion or absorption of initially sorbed P into structurally porous short–range order materials, *with increasing reaction time*. This description is consistent with observations that the extent of slow P reaction depends on the crystallinity and porosity of the adsorbent (McLaughlin *et al.*, 1977; Cabrera *et al.*, 1981; Barrow, 1985; Parfitt, 1989). The concept of time defines the importance of this reaction in controlling the effectiveness of P fertilizer over time or its residual value (Barrow, 1974; Munns & Fox, 1976; Barrow, 1980; Farina & Channon, 1987; Parfitt *et al.*, 1989; Dalal, 1997).

Depending on the type of the sorbing species, this slow P reaction could arise from diffusion of orthophosphate ions through a metal–phosphate coating surrounding the sorbing oxide particle (van Riemsdijk *et al.*, 1984), and from diffusive penetration of orthophosphate ions at defect sites of oxide crystals or between aggregates of microcrystals where they adsorb by replacing the terminal hydroxyl groups and the bonding silicates (Barrow, 1987). Parfitt (1989) showed that penetration or diffusion is not possible with minerals like allophane that have all their reactive AlOH groups on the surfaces and also have small particles that cannot support metal–phosphate coatings around them. Instead, slow P sorption on allophane involves precipitation of P with aluminium located on the defect sites, into stable alumino phosphate (e.g. taranakite or non–crystalline aluminium phosphate). As more P is reacted, the allophane structure is disrupted and more reactive sites are exposed. In oxides and hydroxides of Fe, which have defect sites and/or particles large enough to allow formation

of metal–phosphate coatings, diffusion and penetration are possible (Parfitt et al., 1975; Cabrera et al., 1981; Gunjigake & Wada, 1981; Parfitt, 1989).

The mechanisms of diffusion–controlled slow P reaction are solid–state diffusion and diffusion through micropores. Solid–state diffusion includes exchange and vacancy mechanisms (Manning, 1968). In the exchange mechanism phosphate exchanges positions with other ions whereas in the vacancy mechanism phosphate diffuses into vacant or defect sites of the adsorbing matrix. Evidence in support of these mechanisms was shown by Parfitt (1989) where phosphate diffuses at the defect site and adsorbs by replacing the terminal hydroxyl groups and structural silicates on natural ferrihydrite and goethite minerals. Another example of solid–state diffusion mechanism is diffusion of phosphate through metal–phosphate coatings (Parfitt et al., 1975; Cabrera et al., 1981; Gunjigake & Wada, 1981; van Riemsdijk et al., 1984; Parfitt, 1989). The vacancy mechanism is more favourable and plausible in imperfect or poorly crystalline absorbents than the exchange mechanism for phosphate because large ions like those of P desorb more easily (Barrow, 1985).

In the micropore diffusion mechanism phosphate diffuses between microcrystals. Retention of P through this mechanism was observed on lepidocrocite (Cabrera et al., 1981), ferrihydrite (Willett et al., 1988) and ferrihydrite and goethite (Parfitt, 1989). In their studies on P desorption from iron oxides in relation to pH and porosity Cabrera et al. (1981) observed that reaction between P and lepidocrocite lasted longer than reaction between P and goethite. That was ascribed to the difference in the quantity of micropores between lepidocrocite and goethite (Barrow, 1985). Lepidocrocite has small crystals that form large aggregates with a large proportion of micropores (Barrow, 1985) whereas goethite has large crystals and therefore, limited micropores (Cornell et al., 1983). Thus, slow P reaction lasts longer in soils rich in small–sized iron oxides that form large aggregates with abundant micropores than in soils predominated by large–sized oxides where formation of these micropores is limited. A study of P sorption at field capacity and soil ionic strength (Agbenin & Tiessen, 1995) supports the contention that both the diffusion of surface adsorbed P into crystal micropores and precipitation are mechanisms of slow P reaction. Additional mechanisms of slow P retention are microbial immobilization and complexation

5

by OM (Barrow, 1980; Le Mare, 1982; Norrish & Rosser, 1983; Haynes, 1984; Parfitt *et al.*, 1989; Agbenin & Tiessen, 1995).

Based on the concept of diffusive penetration and its wide acceptance as the origin of the slow P reaction that follows adsorption, Barrow (1985) suggested the use of the term 'sorption' or 'retention' to identify the slow P reaction from the initial rapid adsorption. The author showed that if both terms refer to diffusive penetration of initially adsorbed P, either, therefore, include adsorption and penetration, hence for a given period it is greater than adsorption. In this thesis the terms 'retention' and 'sorption' are used interchangeably to describe all processes through which applied P is rendered less or completely unavailable for plant uptake. This quantity is identified as fractions of applied P that cannot be easily extracted with the common extractants used in characterizing plant available P. Adsorption, therefore, refers to a proportion of applied P adsorbed in isotopically exchangeable, hence readily–available form.

1.3. Soil properties influencing fertilizer phosphorus reactions in soils

Reactions of phosphate fertilizers in soils, starting with dissolution of fertilizer material through the diffusion of dissolved phosphoric acid to the subsequent reaction with soil constituents, depend to a large extent on soil type and reaction environment. Soil properties and conditions, singly and together, determine the type and extent of reactions of applied P in soils. Most soil properties and conditions implicated in adsorption and retention of applied phosphate include water content, clay mineralogy, OM, solution pH and P concentration and saturation of the adsorbing matrix. The influence of each of these properties, singly, on phosphate adsorption and/or retention by soils is discussed to elucidate how P retention differs between soils and what soil fertility management strategies can be employed to overcome P retention problems and increase P availability and hence crop yields.

6

1.3.1. Water content

The primary role played by soil water on reactions of applied P is to dissolve the phosphate fertilizer and translocate the phosphate ions from fertilizer sites into the rhizosphere and/or the bulk of the soil. Phosphate fertilizer applied to a wet soil dissolves very easily and releases almost all the soluble P it contains. Diffusion of dissolved phosphate ions under sufficient soil water conditions ensures thorough mixing of added P in the soil. However, if phosphate fertilizer is applied to a dry soil it is not going to dissolve with ease and probably its distribution through the bulk of the soil and perhaps its effectiveness on increasing availability of P for plant uptake will be impeded. According to Fick's Law (Equation 1.1), diffusion coefficient and nutrient concentration, both of which are strongly related to soil water content, have a direct influence on diffusion (Mengel & Kirkby, 1987). In principle, at low soil water content, patches of high P concentration may develop due to disrupted diffusion pathways, promoting localized adsorption or precipitation of the soluble P.

$$F = -D(dc/dx) \qquad 1.1$$

Where F is diffusion rate of a nutrient per unit cross section and per unit time (mol m^{-2} sec^{-1}), D the diffusion coefficient of the nutrient (m^2 sec^{-1}), c is the nutrient concentration in the bulk soil (mol m^{-3}) and x the distance to the root (m).

Soil water content also affects P retention indirectly through its effects on the chemical reactions involving applied P. According to Goldberg & Sposito (1985), adsorption reactions of P at hydroxylated surfaces take place between solid and liquid phases, therefore, require a medium with sufficient water (Equation 1.2). Under low soil water conditions, adsorbed P is replaced with difficulty via simple exchange reactions but rather diffuses into the remote sorption sites that are accessible only to adsorbed P, and is held with very strong chemical bonds (Aharoni et al., 1991; Agbenin & Tiessen, 1995). Barrow (1974) showed that soil water content below permanent wilting point intensified retention and reduced the effectiveness of applied P.

$$aSOH_{(s)} + H_bPO_4^{b-3}{}_{(aq)} + cH^+{}_{(aq)} \leftrightarrow S_aH_cPO_{4(s)} + bH_2O_{(l)} + (a-b)OH^-{}_{(aq)} \qquad 1.2$$

Nevertheless, the impact of low soil water content on retention and release of applied phosphate may not be as strong as that of excessive water content. For instance, Barrow (1974) noted that the magnitude of P retention at saturation increased two fold compared to that at permanent wilting point. Other studies investigating transformations of P in flooded soils indicated that flooding and drying of flooded soils alike enhance P retention reactions (Khalid *et al.*, 1977; Willett & Higgins, 1978, Holford & Patrick, 1979; 1981; Willett, 1983; 1989; Krairapanond *et al.*, 1993; Phillips & Greenway, 1998). Under waterlogged conditions, reduction of stable $Fe(OH)_3$–phosphate to more soluble $Fe(OH)_2$–phosphate may release occluded P and increase P concentration in the soil solution. Most reduced soils exhibit pH values around 7.0. Near that pH the activity of amorphous $Fe(OH)_2$ is increased. As a result, P released by reduction is precipitated by the $Fe(OH)_2$, which have a high affinity for P, hence retained in an unavailable form. On drying of wet soils, $Fe(OH)_2$ is reoxidized to more stable $Fe(OH)_3$ and therefore, soil solution P is occluded in the less soluble $Fe(OH)_3$–phosphate precipitate (Holford & Patrick, 1981; Phillips, 1998).

1.3.2. Clay mineralogy and content

Clay minerals with a low silica:alumina ratio, viz. the 1:1 types like kaolinite and amorphous aluminosilicates like allophane have high P sorption capacities compared to those with a high ratio, viz. the 2:1 types like illite and montmorillonite (Tisdale *et al.*, 1985; Mengel & Kirkby, 1987; Hue, 1991). The high P sorption capacity of the 1:1 clay minerals relative to that of the 2:1 clay minerals is largely attributed to a large number of exposed hydroxyl groups associated with Al, their high content of associated hydrated oxides of Fe and Al and the pH–dependent charge on the edges of mineral lattice. The high sorption of P in allophanic minerals is related to Al balancing the negative charge of these minerals. Variation in P sorption also exists among the clay minerals of 2:1 type. Hall & Baker (1971) observed that the montmorillonitic minerals adsorbed more P as the pH of the soil increased whereas the vermiculitic minerals adsorbed less with an increase in pH. The reduction in P retention in vermiculite clays was associated with the presence of stable interlayer Al polymers that have effectively reduced specific surface of the reactive Al at high pH, which tends to block the interlayer spaces of the minerals. Thus, P sorption by vermiculitic minerals, as pH increases, is limited to the reactive sites at the edges of the

8

crystalline structure only.

The metal oxides and hydrous minerals gibbsite, goethite, hematite, ferrihydrite and lepidocrocite have higher P sorption capacity than either the 2:1 or 1:1 clays (Tisdale et al., 1985; Hue, 1991). These minerals predominate the clay fraction of and determine most of P retention in most acid weathered soils and red soils of the tropics (Syers et al, 1971; Munns & Fox, 1976; Juo & Fox, 1977; Ryden et al., 1977b; Sanchez & Uehara, 1980; Loganathan et al., 1987; Torrent, 1987; Parfitt et al., 1989; Arduino et al., 1993; Agbenin & Tiessen, 1994; Bainbridge et al., 1995) and have been used almost exclusively to model P reactions in soil (Kuo & Lotse, 1974; Parfitt et al., 1975; Ryden et al., 1977a; Barrow, 1983b; van Riemsdijk et al., 1984; Goldberg & Sposito, 1985; Willett et al., 1988; Parfitt et al., 1989; Agbenin & Tiessen, 1995). Phosphate reactions through adsorption, sorption or precipitation on the minerals arise from the presence of Fe– and Al–hydroxyl groups on the surfaces at the defect sites or at the edges of the mineral structure. The poorly crystalline short–range order minerals such as ferrihydrite and lepidocrocite have a larger P sorption capacity than the well crystalline minerals as gibbsite, hematite and goethite (Cabrera et al., 1981; Johnston et al., 1991; Willett et al., 1988; Parfitt, 1989).

In any soil type P retention increases with clay content (Juo & Fox, 1977; Loganathan et al., 1987; Johnston et al., 1991; Arduino et al., 1993; Ritchie & Weaver, 1993; Agbenin & Tiessen, 1994; Bainbridge et al., 1995). The positive correlation for P retention with content of clay relative to that of sand and silt in a soil system is probably due to their small–sized particles and large surface area (Tisdale et al., 1985). The surface area of clay particles is occupied by highly reactive Al–OH or hydroxy–Al polymers, which due to their high affinity for exchange sites, are not easily replaced by simple cation exchange reactions (Norrish & Rosser, 1983). The presence of these reactive groups on the edges of clay micelle and the large proportion of micropores that form between the aggregates of clay particles account for most of the P sorption in clayey soils. The increase in P retention with increasing clay content, is limited however, at very high clay content because of difficult access of phosphate to clay surface (Fox & Kamprath, 1970). This implies that P retention is apparently highest in loamy soils and lowest in sandy or clayey soils.

The calcium carbonate in calcareous soils also contributes about 5% of its surface area to adsorption and precipitation (preferably called nucleation) of P (Griffin & Jurinak, 1973; Tisdale *et al.*, 1985). Considering the high activity of P in soils and the proportion of carbonates to the total soil solids the contribution by carbonates to reactions of P applied to the soil is relatively small. However, as Tisdale *et al.* (1985) explained, a small portion of the total surface of $CaCO_3$ is involved in P reactions so that while reacting with P, $CaCO_3$ can still control the soil pH, which is its main function. This is consistent with reports that even in calcareous soils P reactions are dominantly controlled by the strong P reactive constituents Fe and Al oxides and clay content, rather than carbonates (Holford & Mattingly, 1975c; Castro & Torrent, 1995; Carreira & Lajtha, 1997; Samadi & Gilkes, 1999). In calcareous soils Fe and Al oxides are responsible for retention of P in less available form, viz. high energy P adsorption whereas $CaCO_3$ is responsible for P adsorption in an available form, viz. low energy P adsorption (Holford & Mattingly, 1975c; Samadi & Gilkes, 1999).

Phosphorus is adsorbed on specific sites on the surfaces of carbonates, in the form of clusters of amorphous calcium phosphate which, with time, converts to crystalline forms (Eanes *et al.*, 1965; Tisdale *et al.*, 1985). The crystalline products of P reaction with $CaCO_3$ include dicalcium phosphate, octacalcium phosphate and hydroxyapatite (Cole *et al.*, 1953; Amer & Ramy, 1971; Holford & Mattingly, 1975b; Mattingly, 1975; Tisdale *et al.*, 1985; Samadi & Gilkes, 1999). Dicalcium phosphate is fairly soluble when the soil pH is near neutral. Therefore, it can represent a labile pool of P, at least, before it converts into octacalcium phosphate and hydroxyapatite that have very low solubility. Since reactivity of $CaCO_3$ depends on the specific surface area of carbonates which in turn is determined by its total surface area (Talibudeen & Arambarri, 1964; Holford & Mattingly, 1975a) the amount of P adsorbed by carbonates in calcareous soils also depends on their total surface area.

1.3.3. Organic matter content

In many cases a strong correlation between P retention and soil OM content is observed (Haynes, 1984; Hughes & Hornung, 1987, Nakos, 1987; Soon, 1991; Arduino *et al.*, 1993; Brennan *et al.*, 1994; Bainbridge *et al.*, 1995). Colloidal OM, viz. humus, forms complexes

with amorphous Fe or Al in acid and non–calcareous soils (Appelt *et al.*, 1975; Le Mare, 1982; Parfitt *et al.*, 1989) and with Ca and/or compounds of Ca and Mg in alkaline and/or calcareous soils (Barrow, 1980). Such complexes react with P to form complexes of humic acid Fe/Al phosphate, humic acid Ca/Mg phosphate or humic acid $Ca(Mg)CO_3$ phosphate. The positive correlation often observed for P adsorption or retention with OM indicates an increase in P adsorption or sorption as effected by these complexes (Weir & Soper, 1963; Appelt *et al.*, 1975).

Saunders (1965) reported that the significance of OM in increasing P adsorption arises from the effect of organically bound Al and Fe oxides rather than of OM *per se*. Results from later studies (Le Mare, 1982; Agbenin & Tiessen, 1994) are in agreement with this scenario. Le Mare (1982) further suggested that correlation for P adsorption or sorption with the proportion of metal cations in soil organic matter (Alc/Fec) to organic carbon, viz. atomic ratio of metal:carbon (Alc/Fec:C) is better than with the simple OM–metal complex. A high ratio of Alc/C favours P retention through precipitation of Al phosphate and complexation of organic Al phosphate while a lower ratio favours adsorption through complexation only (Lévesque & Schnitzer, 1967). Soils with low OM content such as virgin soils or cultivated soils where all the stubble is removed will probably have a large proportion of Al or Fe in organic complexes (high ratio) whereas soils with high OM content like cultivated soil under stubble return management will probably have a relatively lower ratio of metal:carbon.

Studies on the effect of OM on retention and release of P fertilizer (Bell & Black, 1970; Giordano *et al.*, 1971) suggest that phosphate fertilizers, particularly those that contain ammonium, solubilize cation–organic complexes with concomitant displacement and increase of di– and trivalent ions (Al, Fe, Ca and Mg) in the soil solution. Those ions then participate in subsequent adsorption/precipitation reactions that sorb applied P. Furthermore, P adsorption may also be enhanced as solubilized OM coatings move from soil minerals and expose new surfaces for P adsorption reactions in soils that have received fresh P fertilization.

On the other hand, OM may reduce adsorption and sorption reactions of P by producing

organic anions that compete with P for adsorption sites and can exchange with adsorbed P by ligand exchange (Moreno *et al.*, 1960; Weir & Soper, 1963; Nagarajah *et al.*, 1970; Holford & Mattingly, 1975c; Lopez–Hernandez *et al.*, 1979). However, there is still some controversy on this subject. Nagarajah *et al.* (1970) reported that citrate, humate, malate and other organic colloids could form complexes with Al and, to some extent with Fe, and decrease the capacity of these metals for P adsorption and sorption. Tisdale *et al.* (1985) and Hue (1991) showed that the same organic anions could specifically replace adsorbed P from Fe and Al hydrous oxides, meaning that those organic anions have stronger affinity than the phosphate anion for reactive sites on oxide surfaces. In contrast, Appelt *et al.* (1975) found that simple organic acids as well as humic and fulvic acids, had no effect on P adsorption by volcanic ash soils. They concluded that P was adsorbed in preference to the organic acids in those soils. According to Lopez–Hernandez *et al.* (1979) the affinity of organic anions for adsorption is stronger than that of the phosphate ions in acid soils but not in alkaline and calcareous soils, which have highly charged organic anions.

Studies on neutral and calcareous soils (Weir & Soper, 1962; 1963; Holford & Mattingly, 1975c) suggest that OM may reduce bonding energy of adsorbed P in some soils but that P adsorption indeed increases with an increase in OM content. These researchers concluded that P adsorbed by colloidal organic matter or cation–organic complexes is readily available. In other studies Le Mare (1982) noted that high content of humic and fulvic constituents in soils increased P adsorbed in an exchangeable form while their low content increased P adsorbed in a non–exchangeable form.

From this discussion, it can be concluded that OM increases P adsorption by forming complexes with cations and producing new surfaces for further sorption. At a low ratio of metal cation to carbon the P is adsorbed by ligand exchange on the surfaces of OM complexes, in an exchangeable form. The contribution of OM to retention of applied P depends among other factors, on the duration of contact between P fertilizer and the soil. On the other hand, P precipitation by cations in complexes with OM at a high ratio of metal cation to carbon facilitates retention of P in a non–exchangeable form.

1.3.4. Soil solution pH

Although significant correlation between P retention and soil solution pH is not always observed, soil solution pH controls P retention through it effects on the relative levels of the orthophosphate ions $H_2PO_4^-$ and HPO_4^{2-} (Mengel & Kirkby, 1987), and the solubility and occurrence of the metal ions aluminium and iron as well as the exchangeable cations calcium and magnesium (Brady & Weil, 1996), which react with orthophosphate ions in soils. Phosphate occurs predominantly as a monovalent ion at acidic pH as a result of protonation of the divalent ion (Equation 1.3), as a divalent ion at alkaline pH due to dissociation of the monovalent ion (Equation 1.4) and in nearly equal proportions of both ions at neutral pH. Thus, $H_2PO_4^-$ is the most active species in acid soils whereas HPO_4^{2-} is the most active species in alkaline soils. Soil solution pH influences the activity of P in soils through its effects on those elements which react with it.

$$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-, \qquad\qquad 1.3$$

$$H_2PO_4^- + OH^- \rightarrow HPO_4^{2-} + H_2O \qquad\qquad 1.4$$
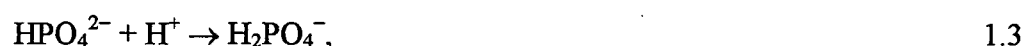
The reactive species of Fe and Al, which provide the most reactive sites for P adsorption and sorption are predominant at pH values below 6.5. Exchangeable Fe (hydroxy–Fe^{3+}) and Al (and Al^{3+} and $Al(H_2O)_6^{3+}$) are most abundant at a pH below 4.7 and the hydrolyzed forms of $Al(OH)_2^+$ are most abundant between a pH of 4.7 and 6.5. $Al(OH)^{2+}$ occurs in the same range of pH as the monovalent hydroxyl–Al but since it is not a stable species its content is always very low. In very acid soils from temperate regions these metal ions precipitate with P to form potassium–aluminium phosphate (taranakite), simple aluminium phosphate compounds and ferric phosphates, with taranakite and simple aluminium phosphates forming in preference to ferric–phosphates unless the soil contains much amorphous ferric hydroxides (Wild, 1988). For example, amorphous iron phosphate is formed in soils rich in ferrihydrite (Nanzyo, 1986) and iron phosphate precipitate tinticite in soils rich in goethite (Jonasson et al., 1988). In temperate soils rich in potassium, taranakite probably precipitates in preference to any other simple aluminium phosphate until all the potassium is used up (Taylor & Gurney, 1965). Phosphate precipitates forming under strongly acid conditions

13

have very low solubility, hence represent retained P.

In moderately acidic soils with pH values of 4.7 to 6.5, P is adsorbed by Al and Fe oxides and their hydroxyl groups at the exchange sites of clay or OM colloids. Phosphate adsorbed by Al and Fe associated with clay and OM may represent a labile pool whereas that adsorbed by hydrous oxides may have little contribution to plant available P (Barrow, 1983c; Willett *et al.*, 1988; Parfitt, 1989; Samadi & Gilkes, 1999). Free Fe oxides, unlike the oxides and hydroxides of Al, have large surface areas that account for most of the P sorption in virgin soils. Therefore, in most agricultural soils with prolonged cropping and P fertilizer history, P sorption capacity contributed by free Fe oxides is already satisfied (Fordham & Norrish, 1974; 1979). As a result, Al oxide accounts for most P sorption (Syers *et al.*, 1971; Wada & Gunjigake, 1979; Loganathan *et al.*, 1987; Brennan *et al.*, 1994; Bainbridge *et al.*, 1995) even though other studies reported strong correlation for Fe rather than Al oxides with P sorption in acid soils, particularly if they have abundant amorphous ferric hydroxides (Ahenkorah, 1968; Juo & Fox, 1977; Arduino *et al.*, 1993). Adsorption of P by Al and Fe oxides decreases with increasing pH. The insoluble $Al(OH)_3^0$ species is predominant at a pH between 6.5 and 8.0. At a pH around 6.5 phosphate adsorption is minimum and its availability is maximum.

In alkaline and calcareous soils the solubility of Al or Fe is depressed in preference to that of exchangeable base cations (Brady & Weil, 1996) and P is principally retained by precipitation in Ca and Mg phosphate compounds or adsorption by Ca and Mg carbonates (Cole *et al.*, 1953; Amer & Ramy, 1971; Kuo & Lotse, 1972; Griffin & Jurinak, 1973; Holford & Mattingly, 1975c). Other researchers (Eanes *et al.*, 1965; Barrow, 1980; Tisdale *et al.*, 1985; Wild, 1988) showed that dicalcium phosphate and other Ca/Mg–phosphate compounds that form near a neutral soil pH are soluble but their solubility decreases with time as they convert to more stable compounds, for example, dicalcium phosphate to hydroxyapatite. Thus, their importance as sources of labile P is time dependent.

Studies using weakly acid soils (Smillie *et al.*, 1987) showed that extractable P declined with increasing time of contact between soil and added P only in the presence of exchangeable calcium. Removal of exchangeable calcium with 0.1M NaCl from the soil

14

system resulted in substantial increases in water extractable P. These results suggest that phosphate reacted with exchangeable calcium to form calcium–phosphate compounds of very low solubility. They were in agreement with results from other studies (Larsen, 1967; Agbenin & Tiessen, 1995; Samadi & Gilkes, 1999). Parfitt (1978) and Wild (1988) showed that phosphate adsorbed by carbonate is slowly converted into apatite, which dissolves very slowly under high soil pH.

When pH of the soil increases in response to liming, P is expected to desorb from Fe and Al oxide surfaces and increase its concentration in the soil solution. However, an increase in available P immediately after liming is seldom observed (Amarasiri & Olsen, 1973; Haynes, 1984; Miles *et al.*, 1985). This is generally ascribed mainly to readsorption of desorbed P by fresh precipitates of Al–hydroxyl polymers that are produced during liming (Amarasiri & Olsen, 1973; Haynes, 1982; 1984; Hall & Baker, 1971; Wild, 1988). These polymers have very strong affinity for P (Norrish & Rosser, 1983) but their capacity for P adsorption decreases with time or may be reduced by the effect of drying following liming (Haynes, 1982; 1984). Therefore, the problem of P retention in limed soils can be reduced by subjecting the limed soil to cycles of wetting and drying prior to application of P fertilizer. Retention of P in limed soils may also result from precipitation of desorbed P by Ca ions from the liming material, into Ca–phosphate compounds not readily soluble at high soil pH (Munns & Fox, 1976; Agbenin & Tiessen, 1995) or from adsorption and precipitation of P by $CaCO_3$ in overlimed soils. The study of Amarasiri & Olsen (1973) showed that liming increased P adsorption maxima from 21.7 to 27.8 mg P 100 g^{-1} soil.

1.3.5. Phosphorus concentration and saturation of the adsorption matrix

It is obvious that reactions between soluble phosphate ions and soil solids are controlled by a shift in equilibrium between the soil solution P and P in the solid phase. A shift in equilibrium can be caused by P inputs (e.g. chemical fertilizers), which increase concentration of P in soil solution and cause a shift towards adsorption and precipitation reactions, and P outputs (e.g. uptake by plant roots), which decrease concentration of P in soil solution and cause a shift towards desorption and dissolution reactions. All P adsorption/sorption studies are based on the concept that an increase in soil solution P

15

concentration increases adsorption of P onto the surfaces, precipitation of P by soluble cations and chemisorption of adsorbed P.

Evidence points that adsorption of fertilizer P is favoured at low concentrations of soil solution P whereas precipitation and sorption/chemisorption are favoured at high soil solution P concentrations (Cole *et al.*, 1953; Griffin & Jurinak, 1973; Le Mare, 1982; Tisdale *et al.*, 1985; Parfitt *et al.*, 1989). In soils that have just received fertilizer the concentration of P is highest in the vicinity of the fertilizer granules or powder or along the fertilizer band and lowest at the periphery of the soil–fertilizer zone (Tisdale *et al.*, 1985). Some studies have specifically noted the importance of P concentration on slow P reaction or chemisorption (Munns & Fox, 1976; Ryden *et al.*, 1977b; Gunjigake & Wada, 1981; Le Mare, 1982; Torrent, 1987; Parfitt, 1989; Agbenin & Tiessen, 1994) and concluded that it is not necessarily the amount of adsorbed P that influences its diffusive penetration into the defect sites and micropores or the build–up of metal–phosphate coatings around the adsorbing metal particles but is the continuous shift towards adsorption which is caused by the relative increase in solution P concentration. This phenomenon can be explained schematically as follows:

$$\text{Soil solution P} \longleftrightarrow \text{Adsorbed P} \longleftrightarrow \text{Sorbed P}$$

Thus, the number of sites available for P reaction referred to as saturation of the adsorption matrix determine the capacity of the soil to retain applied P (Tisdale *et al.*, 1985). This saturation of the adsorption matrix can be expressed as the proportion of P already adsorbed relative to the Fe and Al oxide content of the soil, which is the ratio of adsorbing matrix to P already adsorbed. A narrow ratio indicates that most of the sites for reaction with P are already occupied and only a few sites are still available for additional P, implying that the soil has a low potential to adsorb of applied P, viz. a high saturation of the adsorption matrix. Alternatively, a wide ratio indicates that the soil has a high potential to adsorb applied P, viz. a low saturation of the adsorption matrix. The clayey soils and soils rich in sesquioxide clays, on the account of the large reactive surface area of clay particles and sesquioxide minerals, have a large value of the content of adsorbing matrix. As a result, these soils tend to have a low saturation of the adsorption matrix. In contrast, sandy soils and soils with the predominance aluminosilicate clays like montmorillonite and kaolinite

have a low value of the content of adsorbing matrix and hence a high saturation of the adsorption matrix.

1.4. Motivation and objectives

A knowledge of the extent to which applied P is retained and released by soils is a foundation of fertilizer–crop response trials often utilized to establish proper fertilizer application rate recommendations for correction of P deficiency and optimization of crop yield (Reeve & Sumner, 1970; Guertal *et al.*, 1991; Johnston *et al.*, 1991; Agbenin & Tiessen, 1995; Indiati *et al.*, 1995). An understanding of how soil properties influence the retention and release of P is a vital tool in soil fertility management practices to increase P fertilizer efficiency and to improve agricultural productivity.

Literature on the soils of Lesotho indicates that there is P deficiency in all the benchmark soils of Lesotho (Cauley, 1986). However, correlation of soil fertility test results with fertilizer application rates and crop yields on specific soils has not received sufficient attention. This means that fertilizer application rates presently used in the country are only hypothetical ones. The results of this discrepancy on agriculture in Lesotho are inefficient use of fertilizers, continuing deterioration of the low fertility status of the soils and stagnant agricultural production. With agriculture as the major economic resource in Lesotho, the final impact of this discrepancy is the unrelenting decline of the country's economy.

As a way of approaching this problem therefore, the author undertook a study on all the benchmark soils of Lesotho to characterize their capacity to retain applied P, their potential to release P in plant available form and also to determine the amount of P required to raise the level of plant available P by unity in each of these soils. Because P sorption studies always involve complex techniques and are time consuming the study was also aimed at investigating other soil properties, which are part of routine soil laboratory analysis and can be used to derive information on P retention properties of the soils. *This study, therefore, forms the basis for a number of studies needed to complete a 'soil P fertility study program' that will generate appropriate P fertilizer application rate recommendations.*

17

CHAPTER 2

CHARACTERISTICS OF THE STUDY SOILS

2.1. Introduction

Lesotho has a surface area of about 3.6 million hectares. However, only one third of the country is arable land. This includes the lowlands, the lower foothills and the river valleys in the mountain region. To increase agricultural production from such limited agricultural land requires proper land use and management practices. Thus an intensive soil survey program that can characterize and classify the soils according to their potential capacity and suggest the necessary management practices is a prerequisite. Back in the 1960's, the Government of Lesotho initiated a comprehensive soil survey program to achieve its goal of maximizing agricultural production and conserving the soil resource base of the country. A number of studies have been conducted since then, in collaboration with the overseas soil scientists and agencies.

Among them were the reconnaissance surveys conducted by Carroll & Bascomb (1967), Bawden & Carroll (1968), Binnie & Partners (1972) and the Office of Soil Survey (1979) which identified and categorized the important land and soil resources of Lesotho, and determined the fertility status of the most prominent soils and their potential and limitations for agricultural production. Other studies (FAO, 1972; Powell et al., 1979; Russell, 1979; 1984; Smit, 1984) dealt specifically with project areas but still contributed a great deal to describing the soils of Lesotho. In the early 1980's, another soil survey program was initiated to identify and select the key agricultural soils for detailed description, characterization, classification and interpretation. The work was undertaken under the auspices of the Soil Conservation Division of the Ministry of Agriculture, Lesotho and the United States Department of Agriculture. This work identified eleven soils as the benchmark soils of Lesotho (Cauley, 1986). A complete list of these benchmark soil series of Lesotho is given in Table 2.1, together with their parent materials and some characteristics related to their location in the country according to Cauley (1986) and Schmitz & Rooyani (1987).

18

Table 2.1. Family and series names of the benchmark soils of Lesotho according to the United States Soil Classification System, their parent material and other characteristics related to their locations (Cauley, 1986; and Schmitz & Rooyani, 1987).

Soil family	Soil series	Parent material	Distribution	MAP (mm)[1]	MAT (°C)[2]	Coverage (ha)
Fine loamy, mixed, thermic, pachic argiustoll	Khabos (Khs)	Basalt derived alluvium	Lowlands, Senqu Valley	625 - 800	16	12 000
Fine, mixed, mesic, cumulic hapludoll	Fusi (Fs)	Basalt colluvium and residuum	Lower mountains, foothills	800 - 1100	12	69 000
Very fine, montmorillonitic, mesic, typic pelludert	Thabana (Ta)	Weathered products of basalt colluvium and residuum	Lower mountains, foothills	700 - 950	13	45 000
Fine silty, siliceous, thermic, ultic paleustalf	Leribe (Le)	Ancient basalt alluvium	Lowlands	625 - 800	16	48 000
Fine, mixed, mesic, mollic hapludalf	Machache (Ma)	Basalt residuum	Foothills	700 - 950	13	25 000[3]
Fine loamy, siliceous, thermic, oxic haplustalf	Rama (Rm)	Ancient basalt alluvium	Lowlands	625 - 800	16	4 500
Fine, halloysitic, mesic, mollic paleudalf	Sefikeng (Sg)	Basalt residuum	Foothills	700 - 950	13	25 000[3]
Fine, mixed, thermic, albaquic hapludalf	Sephula (Se)	Purplish shale residuum of Elliot and Molteno Formations	Lowlands	625 - 800	16	42 000
Fine, kaolinitic, mesic, mollic paleudalf	Tumo (Tm)	Weathered products of basalt residuum	Foothills	700 - 950	13	25 000[3]
Fine loamy, siliceous, oxic eutrochrept	Matela (Md)	Alluvium of basalt and sandstone	Foothills, lowlands	625 - 800	16	60 000
Coarse loamy, siliceous, thermic, aquic dystrochrept	Berea (Ba)[4]	Weathered sandstone residuum	Foothills, lowlands	625 - 800	16	125 000

[1]MAP ≡ mean annual precipitation, [2]MAT ≡ mean annual temperature, [3]Total coverage for Machache, Sefikeng and Tumo series, [4]Includes Qalaheng series.

In general, the benchmark soils of Lesotho fall into four soil orders: mollisols (Khabos and Fusi), alfisols (Leribe, Machache, Rama, Sefikeng, Sephula and Tumo), inceptisols (Matela and Berea) and vertisols (Thabana). Detailed studies of these benchmark soils (Cauley, 1986) and less detailed studies on various soils of Lesotho (Carroll & Bascomb, 1967; Powell et al., 1979) indicate that the mollisols and vertisols have a high natural fertility level deriving from their basaltic origin, low degree of weathering, a predominance 2:1 silicate clay minerals and high cation exchange capacity (CEC), base saturation (BS) and OM content. Among the alfisols, the Machache series has a medium natural fertility whereas the rest of the series under this soil order have a low natural fertility status.

The low natural fertility in the alfisols is either a result of a high degree of weathering in some of these soils, especially those derived from basalt rocks in which montmorillonitic minerals have been altered to kaolinitic minerals, or due to some soils being derived from sandstone parent materials with low nutrient elements. The inceptisols are juvenile soils and in the case of the benchmark soils of Lesotho they are derived from sandstone parent materials. Both alfisols and inceptisols of Lesotho are predominated by low activity clays and have, therefore, low CEC's. In addition, they have low soil reaction and BS. The Leribe, Rama, Sephula, Matela and Berea series in particular have low OM content and are severely leached of basic cations. The other three soil series, viz. Machache, Sefikeng and Tumo have a problem of high P retention which is probably due to their high content of iron oxides. Aluminium toxicity is another plant growth limitation but so far only identified in the alfisols (Cauley, 1986).

Although the mollisols and vertisols are considered naturally fertile soils, prolonged cropping has resulted in a reduction of the natural fertility of all the soils in Lesotho, whether mollisols, vertisols, alfisols or inceptisols. Therefore, in order to utilize the potential of those soils for crop production a high level of management, including fertilization, is required for optimum yields. The availability of any plant nutrient added through fertilization, however, does not only depend on its content in the soil but also on its interaction with other biological, chemical and physical soil properties. For example, availability of applied P depends on its reactions with soil constituents like Fe and Al

compounds, silicate clay minerals, carbonates and OM. Thus, soil type plays a key role in determining which principal soil factors control the retention and release of the added nutrient, hence the efficiency of the fertilizer. A thorough knowledge of the chemistry of any particular nutrient in soils is, therefore, a prerequisite for a successful and profitable soil fertility management practice.

The knowledge of soil factors involved in P sorption reactions, for instance, is useful in predicting the P sorption characteristics of the soils (White, 1980; Johnston *et al.*, 1991). In addition, it is also important in decision making for soil management practices that should be employed to increase the recovery of applied P in a plant available form. While the main objective of the studies that constitute this thesis was to investigate the P retention properties of the benchmark soils of Lesotho and identify soil factors that should be considered in soil fertility management practices to increase their P availability, hence improve agricultural production in the country, the aim of the study reported in this chapter was to determine the physical, mineralogical and chemical properties of the soils used in the P studies. The results obtained will be used to elucidate the properties that affect P sorption by the benchmark soils of Lesotho.

2.2. Materials and methods

2.2.1. Site selection and soil sampling

A total of fifty–six soils from different sites in the lowlands and foothills was selected for this study (Figure 2.1 and Table 2.2). All these soils comprise the eleven benchmark soil series of Lesotho. Each benchmark soil series was represented by five soils (soil phases) from different locations with the exception of the Rama series, which was represented by six soils (soil phases). The major reason for concentrating only on the benchmark soils was because they are the key agricultural soils. Selection of sampling sites was made with the aim of covering a wide spectrum for each benchmark soil series in Lesotho.

SCALE 1:800 000

LESOTHO

LEGEND

○	Sampling Sites
Khs5	Soil ID
▢	Lowlands
▨	Foothills
▢	Senqu Valley
▨	Mountains Zone

Maseru

oKhs4

oLe1

Ba3
oSe4

Sg4
oMa3   oMa4

oLe5
oKhs1

Sg5o

Ps5 oSg2
Ta5

Ma2o

oMa5

Tm3
oTm1 oTm2

Sgo oTa2

oTm4

Malo oTa1

oSe1

oBa4

oRm1

Balo

Md2

Khs3o Md1

Khs2o

Le1 Rm3

Le3 Se2

Ba2 oRm2

Md3 Se3

Rm4 Le4

oMd5
oSg3

Fs2o Fs1oTa4

oFs4

oBa5

oSe5 oRm6

Tm5o oTa3
oFs3

oRm5

oMd4

oKhs5

Figure 2.1
Distribution of the fifty six sampling sites

Table 2.2. A list of the study soils, their location and land use at sampling.

Soil Series	Soil ID	Location		Land use
		Site name	Coordination	
Fusi	Fs1	Ha Molengoane	29:24:40 S 27:47:36 E	cropping
	Fs2	Ha Phaloane	29:24:34 S 27:44:53 E	cropping
	Fs3	Matelile, Ha Seeiso	29:49:50 S 27:31:32 E	cropping
	Fs4	Ha Tumaole, Nazareth	29:26:13 S 27:47:33 E	cropping
	Fs5	'Makhoroana, Masetlaokong,	29:10:27 S 28:01:41 E	cropping
Khabos	Khs1	Phuthiatsana (N)	29:05:24 S 27:44:34 E	cropping
	Khs2	Ha James	29:24:07 S 27:32:39 E	cropping
	Khs3	Ha Motloheloa	29:23:59 S 27:34:21 E	cropping
	Khs4	Tlokoeng Butha Buthe	28:46:54 S 28:16:35 E	cropping
	Khs5	Seaka River, Quthing	30:22:00 S 27:35:00 E	cropping/ fallow
Sephula	Se1	Agric. Research plots	29:17:29 S 27:30:30 E	cropping
	Se2	Ha Motloheloa	29:25:00 S 27:35:52 E	cropping/ fallow
	Se3	Ha 'Mantsébo	29:28:18 S 27:32:18 E	Grazing
	Se4	Bela–Bela	28:59:24 S 27:59:34 E	fallow
	Se5	Ha Ramohapi	29:46:07 S 27:17:00 E	cropping
Thabana	Ta1	Phatsa–Kubu, Zenon	29:17:06 S 27:49:05 E	cropping
	Ta2	Ha Sepolo, Sefikaneng	29:15:55 S 27:48:55 E	cropping
	Ta3	Matelile, Ha Seeiso	29:49:19 S 27:30:34 E	cropping
	Ta4	Nazareth	29:24:34 S 27:47:57 E	cropping
	Ta5	'Makhoroana, Masetlaokong	29:10:18 S 28:02:02 E	cropping
Leribe	Le1	Ha Motetepa	28:54:26 S 27:58:35 E	cropping
	Le2	Ha Motloheloa	29:24:51 S 27:35:32 E	cropping
	Le3	Thota–Moli	29:26:32 S 27:33:16 E	cropping
	Le4	Ha 'Mantsébo.	29:28:53 S 27:32:15 E	cropping
	Le5	Kolonyama.	29:04:28 S 27:45:00 E	cropping
Machache	Ma1	Ha Letela	29:17:55 S 27:48:11 E	fallow
	Ma2	Ha Mokhobokoane (TY)	29:10:55 S 28:00:43 E	cropping
	Ma3	Ha Mosekeseke	29:01:56 S 27:57:27 E	cropping
	Ma4	Ha Ntisa	29:02:54 S 28:00:35 E	cropping
	Ma5	Ha Rakoto, Sefikeng	29:12:03 S 27:47:54 E	fallow
Matela	Md1	Ha Mothae	29:24:00 S 27:35:58 E	cropping
	Md2	Ha Rasenkisi	29:22:53 S 27:35:28 E	cropping
	Md3	Ha 'Mantsébo	29:28:18 S 27:31:49 E	cropping
	Md4	Mataoeng, Mohale's Hoek	30:13:02 S 27:25:49 E	cropping
	Md5	Nazareth, Ha Moji	29:22:24 S 27:47:29 E	cropping
Berea	Ba1	Ha Matala	29:22:20 S 27:32:18 E	fallow
	Ba2	Ha 'Mantsébo	29:28:01 S 27:31:58 E	cropping
	Ba3	Bela–Bela	28:59:03 S 27:59:16 E	cropping
	Ba4	Thuathe plateau	29:20:00 S 27:33:23 E	cropping
	Ba5	Masite	29:33:52 S 27:29:37 E	cropping
Rama	Rm1	Ha Leqele	29:21:35 S 27:34:35 E	cropping

Table 2.2. (continues)

Soil series	Soil ID	Location		Land use
		Site name	Coordination	
	Rm2	Ha 'Mantsébo	29:27:22 S 27:32:5 E	cropping
	Rm3	Ha Rathoko	29:25:14 S 27:36:22 E	cropping
	Rm4	Ha 'Mantsébo	29:28:56 S 27:31:23 E	cropping
	Rm5	Silioe	29:57:13 S 27:17:25 E	cropping
	Rm6	Ha Ramokoatsi	29:45:37 S 27:19:51 E	cropping
Sefikeng	Sg1	Sefikeng Ha Fako	29:16:05 S 27:47:56 E	cropping
	Sg2	'Makhoroana, Masetlaokong	29:10:18 S 28:01:47 E	cropping
	Sg3	Nazareth, Agric. Station	29:23:36 S 27:47:47 E	cropping
	Sg4	Ha Lebentlele	29:01:29 S 27:57:40 E	cropping
	Sg5	Mapoteng, Ha 'Matau	29:08:16 S 27:59:21 E	cropping
Tumo	Tm1	Ha Tumo	29:16:00 S 27:41:10 E	cropping
	Tm2	Ha Senekane	29:15:20 S 27:42:59 E	cropping
	Tm3	Ha Senekane	29:15:20 S 27:42:40 E	cropping
	Tm4	Ha Majantsáne	29:17:18 S 27:38:29 E	cropping/ fallow
	Tm5	Matelile, Ha Seeiso	29:49:51 S 27:29:25 E	cropping

The sites were selected on the basis of their P application history. Some had not been fertilized while others only received low levels of P fertilizers in the past. This was to avoid the possibility of having study soils with most of their P sorption capacity already saturated. This was fairly unlikely, however, because little fertilizer is used throughout the country due to lack of knowledge by land–holders of the fertilizer requirements of their fields as well as the economic constraints compounded by escalating fertilizer costs. The only exception was a research site from which Se1 was sampled; this site probably received high levels of P in the past.

At the time of sampling most soils were mono–cropped with maize, sorghum or beans while some were multi–cropped with a sequential combination of cereals and legumes. A few soils were cropped to sunflower or had been cropped to asparagus. There were also other soils that were under fallow or completely withdrawn from cultivation and used for grazing. Samples were taken during the summer growing season of 1997, during March to May. No samples were taken in the first ten weeks after planting which is usually accompanied with fertilizer application. All samples taken from the ploughed soils were taken between rows to avoid direct sampling of fertilizer bands.

Topsoil samples (0 – 300mm depth) were collected randomly from an area of about 1.5 to 3 hectares in size at each sampling site depending on the size of the mapping unit. At least four samples per hectare were taken, with a spade, after removal of surface residue and composited for the entire area. Representative samples (herein referred to as the samples or soil samples) of not less than 10kg were then air–dried and crushed to pass through a 2mm sieve, in preparation for analysis. All the preparations and analyses of the soil samples were done at the laboratories of the Department of Soil Science, University of the Orange Free State, in Bloemfontien.

2.2.2. Soil analysis

All the analyses were done in triplicate by using mostly standard methods. Sample density was determined by recording the mass of a $10cm^3$ scoop of the 2mm size, air–dried soil samples (Johnston $et\ al.$, 1987) and particle size distribution with a modified hydrometer method (Gee & Bauder, 1986). The modified Mebius method of Nelson & Sommers (1982) was used to determine the organic carbon (OC).

Soil pH was determined in distilled water and in 1N KCl suspensions with a soil:solution ratio of 1:2.5 (The Non–affiliated Soil Analysis Work Committee, 1990). Exchangeable basic cations (Ca, Mg, K and Na) were leached with a neutral 1N NH_4OAc (Thomas, 1982) and determined by atomic absorption spectrometry (AAS) according to Knudsen $et\ al.$ (1982). The soil residues from analysis of exchangeable bases were saturated with Na using 1N NaOAc solution with pH of 8.2 (Rhoades, 1982). Excess Na was washed out with concentrated alcohol and then the adsorbed Na was displaced and leached with NH_4OAc. The Na in the leachate was determined by AAS (Knudsen $et\ al.$, 1982) as a measure of CEC. The difference between CEC and the sum of exchangeable bases indicated exchangeable acidity, as acid saturation (AS). The ratio of the total content of basic cations to the CEC gives the BS. The sum of the total exchangeable bases (TEB) was also computed and used to indicate the natural fertility status of the soils according to Berding (1984).

Plant available P was extracted with two methods, one of Bray, using a 0.03N NH_4F and

0.025N HCl solution (Bray & Kurtz, 1945) and another of Olsen, using a neutral 0.5N NaHCO₃ solution (Olsen *et al.*, 1954). The P in the extracts was determined colorimetrical using a slightly modified molybdenum blue colour method of Murphy & Riley (1962).

Amorphous Al and Fe were extracted with a 0.2M acid ammonium oxalate adjusted to pH3.0, in darkness (AAOD) and the crystalline forms were extracted with a buffered neutral citrate bicarbonate dithionite (CBD) according to Jackson *et al.* (1986). The Al and Fe contents were determined by AAS according to Blackemore (1968), Searle & Daly (1977) and Olson & Ellis (1982). Free Al and Fe oxides were estimated as the difference between the CBD and AAOD extractable Al and Fe.

2.2.3. Data analysis

The analysis of variance (ANOVA) technique was employed to test the variations in different properties among the soils, using a personal computer (PC) compatible statistical package, NCSS 2000. Tukey–Kramer multiple comparison test was used to test variations within individual soil series and amongst the soil series. Only where means were variable at 0.050 probability level or less were the variations considered statistically significant unless otherwise stated. Results indicated a great variation in almost all the properties within and amongst the soil series. However, there were some similarities between some soils series in some particular properties.

2.3. Results and discussions

2.3.1. Properties of the study soils in general

The means of the physical, mineralogical and chemical properties of the 56 soils are given in Appendices 2.1, 2.2 and 2.3, respectively. However, the ranges and the means of the individual soil properties determined in this study are presented in Table 2.3. It was clear that all the physical, mineralogical and chemical properties had without exception very wide ranges. In the majority of cases the lowest, highest and mean values were indicative of a good distribution within every soil property.

Table 2.3. The lowest, highest and mean values for the soil properties determined in this study.

Soil property	Lowest value	Highest value	Mean value
Physical properties			
Sample density (kg m^{-3})	1023	1533	1298
Particle size distribution (%)			
Sand	15.93	78.39	45.41
Silt	12.24	37.99	25.01
Clay	8.67	55.67	28.87
Mineralogical properties			
Amorphous oxides (%)			
Al	0.02	0.36	0.15
Fe	0.03	0.71	0.24
Free oxides (%)			
Al	0.00	0.35	0.14
Fe	0.24	5.28	1.84
*Aluminosilicate clays (cmol$_c$ kg^{-1})	19.69	83.03	44.06
Chemical properties			
pH(H$_2$O)	4.48	6.82	5.52
pH(KCl)	3.66	5.46	4.18
Organic carbon (%)	0.19	3.47	1.24
CEC (cmol$_c$ kg^{-1})	2.96	41.74	14.10
Exchangeable bases (cmol$_c$ kg^{-1})			
Ca	0.64	44.17	8.43
Mg	0.22	17.63	3.43
K	0.08	0.60	0.23
Na	0.11	0.24	0.15
Total	1.14	61.06	12.25
Base saturation (%)	13.72	>100	66.01
Acid saturation (%)	0.00	86.28	55.86
Extractable P (mg kg^{-1})			
Bray	0.67	61.52	16.33
Olsen	1.67	23.33	8.36

* Calculated from CEC of soil and clay content.

2.3.2 Properties of the different soil series

2.3.2.1 Physical properties

Amongst the physical properties, viz. sample density, sand, silt and clay fractions, sample

density was the one that was most variable within each and every benchmark soil series (Appendix 2.1). However, when the benchmark soil series were compared, sample density was the same for the Fusi, Khabos, Thabana, Machache and Sefikeng series (1153 to 1230 kg m^{-3}) and also for the Tumo, Leribe, Matela, Rama, Berea and Sephula series (1340 to 1423 kg m^{-3}), indicating only two different groups (Table 2.4). The sample density was significantly correlated with the clay (r = -0.80) and sand (r = 0.71) fractions but not with the silt fraction. However, despite this correlation, there was much greater variation amongst the soil series with respect to particle size distribution than sample density. For instance, there were six, four and seven different groups plus some intermediate ones according to sand, silt and clay fractions, respectively, as opposed to only two groups according to sample density. This variation in the sand, silt and clay fractions resulted in several textural classes, viz. sandy loam (Rama, Sephula and Matela), sandy clay loam (Leribe, Tumo and Berea), clay loam (Khabos and Machache) and clay (Fusi, Thabana and Sefikeng). These results were in agreement with those of Cauley (1986) and Schmizt & Rooyani (1987).

Table 2.4. Variation in mean values of the physical properties between the eleven benchmark soil series.

Series name	Sample density (kg m^{-3})	Particle size distribution (%)		
		Sand	Silt	Clay
Fusi	1184a	26.55ab	34.45 d	42.07 f
Khabos	1230a	40.92cd	27.39 bc	31.29 e
Thabana	1177a	21.17 a	30.30 cd	48.53 g
Leribe	1349b	57.76ef	21.90 ab	20.93 c
Machache	1195a	32.93bc	27.83bcd	38.97 f
Rama	1413b	60.42ef	20.00 a	13.56 a
Sefikeng	1153a	27.81ab	28.04bcd	43.80fg
Sephula	1423b	55.97 e	29.22 cd	15.33ab
Tumo	1340b	47.57 d	24.55abc	27.67 d
Matela	1374b	63.05ef	17.97 a	18.73bc
Berea	1415b	64.47 f	19.63 a	15.73ab

Figures carrying the same letter in a column are not significantly different at 0.050 probability level or less according to Tukey–Kramer multiple comparison test.

28

2.3.2.2 Mineralogical properties

The average mineralogical properties for each benchmark soil series are given in Table 2.5 while the means for each of the 56 soils are given in Appendix 2.2. The mollisols (Fusi and Khabos series) and the vertisols (Thabana series) contained at least twice as much amorphous Fe oxides as amorphous Al oxides. The alfisols (Leribe, Machache, Rama Sefikeng, Sephula and Tumo series) and the inceptisols (Matela and Berea series) contained, however, amorphous Fe and Al oxides in variable proportions which were in some cases equal and in other cases more Al oxides than Fe oxides, and vice versa (Appendix 2.2). On average, the Leribe, Rama, Sephula, Matela and Berea series contained less than 0.08% amorphous Al oxides whereas the Fusi, Thabana and Machache series contained more than 0.25% amorphous Al oxides with the Khabos, Sefikeng and Tumo series intermediate (Table 2.5). According to their amorphous Fe oxide content the soil series can be ranked as follows: Fusi = Thabana > Khabos > Machache = Sefikeng > Tumo > Leribe = Rama = Sephula = Matela = Berea.

Table 2.5. Variation in mean values of the mineralogical properties between the eleven benchmark soil series.

Series	Amorphous oxides (%)		Free oxides (%)		Total oxides of Al & Fe	Aluminosilicate clays
name	Al	Fe	Al	Fe	(%)	(cmol$_c$ kg^{-1})
Fusi	0.28 d	0.59 e	0.04 a	1.77cd	2.68 d	92.18 c
Khabos	0.16 b	0.38 d	0.08 ab	1.36bc	1.98 c	67.31bc
Thabana	0.25cd	0.56 e	0.08 ab	2.09de	2.98 d	68.03bc
Leribe	0.08 a	0.11ab	0.09abc	0.97 b	1.25ab	25.67 a
Machache	0.26cd	0.28 c	0.24 d	4.12 f	4.91 e	40.35ab
Rama	0.06 a	0.05 a	0.11 bc	0.78ab	1.00ab	33.68 a
Sefikeng	0.24 c	0.27 c	0.25 d	4.52 f	5.28 e	38.19 a
Sephula	0.04 a	0.13ab	0.10 bc	0.35 a	0.61 a	48.86ab
Tumo	0.15 b	0.14 b	0.15 c	2.66 e	3.10 d	29.69 a
Matela	0.07 a	0.09ab	0.21 d	1.00 b	1.36bc	30.03 a
Berea	0.06 a	0.07ab	0.24 d	0.78ab	1.15ab	33.79 a

Figures carrying the same letter in a column are not significantly different at 0.050 probability level or less according to Tukey–Kramer multiple comparison test.

The Fusi, Khabos and Thabana series (mollisols and vertisols) were, however, very low in

29

free Al oxides, viz. zero to 0.12% as shown in Appendix 2.2 which were less than 0.1%, on average (Table 2.5). Their free Fe oxide contents of 0.86 to 2.95% were 10 to 30 fold as high as their free Al oxides contents. On average, the free Fe oxide contents of these three soil series were equal to, or more than those of the Leribe, Rama, Sephula, Matela and Berea series (alfisols and inceptisols). The Machache, Sefikeng and Tumo series (alfisols) contained 10 to 40 fold as much free Fe oxides as free Al oxides but the contents of their free oxides far exceeded those of the mollisols and vertisols (Appendix 2.2). As shown in Table 2.5 these series, particularly Machache and Sefikeng, contained the largest amounts of free Fe oxides. Therefore, the 11 soil series can be ranked according to their total oxides of Al and Fe in more or less the following order: Machache = Sefikeng > Fusi = Thabana = Tumo > Khabos = Matela > Leribe = Rama = Berea > Sephula.

Compounds of Fe and Al occur in soils as separate crystalline or noncrystalline particles or as coatings on the interlayer and external surfaces of clay particles. They are not as sticky and plastic as the silicate clays, and therefore soils rich in these compounds are very easy to work even after rainfall. They also have favourable physical properties like high water holding capacity and high aggregate stability. In acid soils, Fe and Al oxides are the chief carriers of variable positive charge on the soil surfaces (Shao & Wang, 1991), hence they participate more in anion exchange reactions rather than cation exchange reactions. The retention of phosphate by the Fe and Al oxides in most red and acid soils is one of the subjects widely researched (Ahenkorah, 1968; Syers et al., 1971; Juo & Fox, 1977; Wada & Gunjigake, 1979; Loganathan et al., 1987; Arduino et al., 1993; Brennan et al., 1994; Bainbridge et al., 1995; Brady & Weil, 1996; Liang et al., 1998). In addition, Fe and Al oxides influence titratable acidity and alkalinity (Shao et al., 1993).

In Lesotho, two of the benchmark soil series, Machache and Sefikeng, had earlier on been identified as high P sorbing soils (Cauley, 1986; Arduino et al., 1993). Their high P sorption is probably due to their high contents of Fe and Al oxides. On account of the contents of Fe and Al oxides, the series Fusi, Thabana and Tumo are presumed to have a high P retention even if not as high as in Machache and Sefikeng series. Soils with low contents of reactive Al and Fe, such as the Sephula, Leribe, Rama, Matela and Berea series, probably have low P sorption capacity. The advantage of high P retention of soils is that such soils normally

retain a large amount of applied P that can be used later to replenish soil solution P for plant uptake during seasons of no P application. The soils with low P retention capacity have limited potential to maintain soil solution P for plant uptake for long periods of time without repeated P applications.

The ranges of the CEC of the clay fraction in the individual soil series indicate that all the series contained mixtures of 1:1 and 2:1 silicate clay minerals (Appendix 2.2). On average, the Fusi series had the highest CEC–clay 92 cmol$_c$ kg^{-1}, followed by the Khabos and Thabana series with a CEC–clay of 68 cmol$_c$ kg^{-1}, indicating that 2:1 silicate clay minerals dominated the clay fraction of these three soil series. Next were the Machache and Sephula series with an average CEC–clay of 40 and 49 cmol$_c$ kg^{-1}, respectively, which can presumably be ascribed to fairly equal mixtures of 1:1 and 2:1 silicate clay minerals. The other six soil series, viz. Leribe, Rama, Sefikeng, Tumo, Matela and Berea had CEC–clay of less than 38 cmol$_c$ kg^{-1}, therefore, were probably dominated by 1:1 silicate clay minerals. These results were consistent with those of Cauley (1986). The 2:1 as opposed to 1:1 silicate clay minerals have large surface areas and are very reactive in adsorption and exchange reactions, hence signify high fertility potential of the soils. Therefore, the high CEC–clay of the Fusi, Khabos and Thabana series confirmed the reports that the mollisols (e.g. Fusi and Khabos) and vertisols (e.g. Thabana) have high natural fertility status compared to other soil orders (alfisols and inceptisols) found in Lesotho (Carroll & Bascomb, 1967; Powell et al., 1979; Cauley, 1986).

2.3.2.3 Chemical properties

The chemical properties of the 56 soils are displayed in Appendix 2.3 while the averages for each soil series are shown in Table 2.6. The soils were neutral to acidic with average pH(H$_2$O) ranging between 4.74 and 6.59 and pH(KCl) ranging between 3.73 and 5.15. The Tumo series had the lowest and the Khabos series had the highest values, with other series intermediate. Differences between pH(H$_2$O) and pH(KCl) were 1 to 2 pH units, on average. These differences were largest in the Fusi series and smallest in Tumo series. The correlation coefficient between pH(H$_2$O) and pH(KCl) was, furthermore 0.93.

Table 2.6 Variation in mean values of the chemical properties between the eleven benchmark soil series.

Series Name	pH (H$_2$O)	(KCl)	CEC	Ca	Mg	K	Na	TEB	BS	AS	OC	P (mg kg^{-1}) Bray	Olsen
			(cmol$_c$ kg^{-1})						(%)				
Fusi	6.53 f	4.69 c	32.75 e	26.07c	11.77c	0.24 bc	0.20 d	38.27c	>100 d	0.00 a	2.52d	3.27 a	5.57 ab
Khabos	6.59 f	5.15 d	22.49 d	19.61b	8.08b	0.37 d	0.18bcd	28.23b	>100 d	0.00 a	1.65c	20.60 cd	14.74 d
Thabana	6.15 e	4.62 c	33.29 e	29.19c	11.90c	0.29 cd	0.20 cd	41.58c	>100 d	0.00 a	2.78e	5.93 ab	6.93 abc
Leribe	5.31bcd	4.01ab	5.30ab	2.58a	0.69a	0.27 cd	0.13 a	3.67a	68.80 c	32.72 b	0.53a	27.68 d	10.25 bcd
Machache	5.01 ab	3.83 a	15.75 c	4.90a	1.74a	0.28 cd	0.13 a	7.04a	42.46ab	57.54cd	1.71c	4.63 ab	4.19 a
Rama	5.37 cd	3.99 a	4.42 a	1.36a	0.48a	0.14 a	0.15 ab	2.12a	48.68bc	51.32 c	0.42a	24.88 d	9.01 abc
Sefikeng	5.05abc	3.79 a	16.64 c	4.06a	1.67a	0.35 d	0.14 a	6.22a	37.19ab	62.81cd	1.76c	7.22 abc	5.65 ab
Sephula	5.57 d	4.25 b	7.61ab	2.07a	0.71a	0.12 a	0.17 bc	3.07a	46.35ab	53.65 c	0.51a	15.13abcd	8.12 abc
Tumo	4.74 a	3.73 a	8.30 b	1.51a	0.43a	0.21abc	0.14 a	2.29a	26.65 a	73.35 d	0.93b	23.96 d	9.63abcd
Matela	5.24bcd	3.99ab	5.71ab	1.37a	0.46a	0.16 ab	0.13 a	2.12a	41.60ab	58.40cd	0.54a	18.55 bcd	6.47 abc
Berea	5.20 bc	3.95 a	5.22ab	1.43a	0.44a	0.15 ab	0.13 a	2.14a	43.04ab	56.96 c	0.41a	26.06 d	11.28 cd

Figures carrying same letter in a column are not significantly different at 0.050 probability level or less according to Tukey–Kramer multiple comparison test.

The OC content of the soil series varied on average from 0.41 to 2.78 %. On the basis of their OC content the soil series can be ranked as follows: Thabana > Fusi > Khabos = Machache = Sefikeng > Tumo > Leribe = Rama = Sephula = Matela = Berea (Table 2.6). On the other hand, the CEC of the soil series ranged from 4.42 to 33.29 $cmol_c$ kg^{-1}. The Rama series had the lowest while the Thabana series had the highest values with the other soil series intermediate. The soils series were ranked according to their CEC in more or less the same order as according to OC above: Thabana = Fusi > Khabos >Machache = Sefikeng >Tumo ≥ Leribe = Sephula = Matela = Berea ≥ Rama.

The total exchangeable bases contained by the Fusi and Thabana series, which were not significantly different, amounted to 38.3 and 41.6 $cmol_c$ kg^{-1}, respectively (Table 2.6). Significantly less TEB was contained by the Khabos series, viz. 28.2 $cmol_c$ kg^{-1}. The other eight soil series contained only between 2.12 to 7.04 $cmol_c$ kg^{-1} TEB and were significantly similar. The variation in exchangeable Ca and Mg between the soil series followed exactly the same pattern as the TEB, which was not necessarily the case with K and Na (Table 2.6). As expected, Ca made the largest contribution to the TEB followed by Mg, K and Na, irrespective of the soil series.

The mollisols (Khabos and Fusi series) and vertisols (Thabana series) had a BS of more than 100% and therefore, an acid saturation of 0% (Table 2.6). In contrast, the alfisols (Leribe, Machache, Rama, Sefikeng, Sephula and Tumo series) and the inceptisols (Matela and Berea series) had a BS of 27 to 67% and therefore, an AS of 32 to 73%. On the basis of acid saturation, the soil series belonging to the mollisols and vertisols had no lime requirement while the soil series belonging to the alfisols and inceptisols had a high lime requirement when used for crop production. These results were in agreement with the lime requirement guidelines given by Carroll & Bascomb (1967) even though at that stage the soils of Lesotho were not as fully defined as they are today.

The level of extractable P from both Bray and Olsen methods was very variable within and among the series (Appendix 2.3 and Table 2.6). The variation within a series was possibly an indication of either different cultural practices from different areas in the country or lack

33

of proper recommended P fertilizer application rates for the soils of Lesotho. According to the Bray method, the Fusi, Thabana, Machache and Sefikeng series had the lowest extractable P while the Khabos, Leribe, Rama, Tumo, Matela and Berea series had the highest extractable P (Table 2.6). The Sephula series had an intermediate amount of extractable P. According to the Olsen method, the Fusi, Thabana, Machache and Sefikeng series, together with the Rama, Sephula and Matela series, still showed low levels of extractable P while the Khabos series showed the highest level of extractable P with the Leribe, Tumo and Berea series intermediate. The correlation coefficient between Bray and Olsen extractable P was 0.85.

The samples Fs3, Ta3, Rm1 and Se1 had extraordinarily high levels of extractable P (Appendix 2.3) which could not confidently be accounted for. It was, however, probable that these four soils had received large applications of P fertilizer in the past. The Fs3 and Ta3 samples were collected from the same area, Matelile. Therefore, it was possible that they were subjected to similar cultural practices that increased their soil P test values. On the other hand, the Se1 sample was taken from a research site, which should explain its high level of extractable P, and the Rm1 sample was collected from a field previously planted to asparagus which is an intensive crop in Lesotho, therefore it should have received large P fertilizer inputs previously. Both sites, respectively represented typical pedons for the Sephula and Rama series *as per* the basic study on the benchmark soils of Lesotho (Cauley, 1986), and therefore could not be excluded.

2.3.3 Soil fertility implications of the physical, mineralogical and chemical properties

In accordance with pH, organic matter and clay which are indicative measurements of the fertility status of soils, and consistent with the reports of Carroll & Bascomb (1967), Powell *et al.* (1979), Cauley (1986) and Schmitz & Rooyani (1987) Fusi, Khabos and Thabana series exhibited higher soil fertility characteristics while Leribe, Machache, Rama, Sefikeng, Sephula, Tumo, Matela and Berea series exhibited lower soil fertility characteristics. For instance, the former three soil series had larger CEC, more exchangeable bases and higher BS than the latter eight soil series (Table 2.6). The good

correlations between pH, OC and clay, respectively with CEC, TEB and BS were therefore, not surprising (Table 2.7). The TEB was recommended by Berding (1984) as a measure of natural fertility status of soils and it indeed seemed a good index even in this study.

The considerably higher fertility status of the Fusi, Khabos and Thabana series is probably due to their basaltic origin, lesser degree of weathering and hence the dominance of 2:1 silicate clay minerals as well as high clay content. The 2:1 silicate clay minerals have a large reactive surface area and therefore, play a significant role in adsorption and exchange reactions of bases. In addition to its contribution towards a large CEC, a high clay content slows down the decomposition rate of organic materials and increases stability of humus and other organic fractions, which constitute OM. The evidence in support of this scenario is a strong correlation between OC and clay content ($r = 0.88$; $P < 0.001$ for $n = 56$). Like clay, the OM also provides adsorption sites for cation exchange reactions. Additionally, due to their colloidal nature, both clay and OM (humus) act as binding agents between soil aggregates and hence encourage the development of a good soil structure that restricts excessive percolation of rainwater and the leaching of bases.

Table 2.7 Correlation coefficients* between the soil fertility characteristics, viz. CEC, TEB and BS and the pH, AS, OC , clay and CEC–clay.

Soil fertility characteristics	pH(H_2O)	AS	OC	Clay	CEC–clay
CEC	0.44	0.47	0.91	0.75	0.75
TEB	0.64	0.67	0.74	0.50	0.76
BS	0.82	0.94	0.41	0.23	0.55

*All the correlations were significant at $P < 0.001$, $n = 56$.

Furthermore, given their landscape position (Cauley, 1986), the Fusi, Khabos and Thabana series benefit from material inputs by way of deposition of debris from upper landscape positions whereas the other series, viz. Leribe, Machache, Rama, Sefikeng, Sephula, Tumo, Matela and Berea loose most of their colloidal materials and the nutrients through the running water. This is thought to partially explain the observed accumulation of OM and exchangeable bases in the Fusi, Khabos and Thabana series relative to the other eight series. The high proportion of OC to clay in the Khabos, Fusi and Thabana series (0.04 to 0.07) as opposed to the other series, especially the Machache, Sefikeng and Tumo series (0.03 to

35

0.05) which had a comparable clay content to the Khabos, Fusi and Thabana series supported the argument that the Khabos, Fusi and Thabana series, by virtue of their landscape position, had advantage over the other series of accumulating more organic material. This proportion was as low as 0.02 in the remaining series, viz. Leribe, Rama, Sephula, Matela and Berea. Furthermore, the Khabos and Thabana series benefit from their proximity to rivers and streams by way of getting an adequate supply of water which is of course, a driving force for biological, chemical and physical soil processes which in turn determine the fertility status of the soils.

All the soil series that exhibited lower fertility characteristics, viz. Leribe, Machache, Rama, Sefikeng, Sephula, Tumo, Matela and Berea had a considerable acid saturation (Table 2.6). The Machache, Sefikeng and Tumo series respectively, had however, a high OC and CEC as opposed to the other series in this group. Therefore, they comprise an intermediate group regarding soil fertility status. They had, however, lower pH values and higher acid saturation than their counterparts, which were probably the major factors limiting their fertility status.

These three series, Machache, Sefikeng and Tumo, share parent materials with the Fusi, Khabos and Thabana series. The former had, however, been subjected to more intense weathering and as a result, their mineralogy is dominated by 1:1 silicate clay minerals (Cauley, 1986). The 1:1 as opposed to the 2:1 silicate clay minerals have limited reactive surface area, hence their participation in adsorption and exchange reactions is very small. The low CEC and hence low TEB and BS in the Machache, Sefikeng and Tumo series as opposed to those of their counterparts in terms of clay content was evidence of the predominance and impact of low activity clays.

Although the Machache and Sefikeng series had a comparable clay content to the Fusi and Thabana series, their clay fraction, more than that of the latter, was dominated by free Fe and Al oxides. On the other hand, the Fusi and Thabana series contain more amorphous Fe and Al oxides than the Machache and Sefikeng series. Nevertheless, since the contents of amorphous oxides in all the soil series were very small, relative to those of the free oxides, their contribution to the total oxide contents is minimal. Therefore, the Machache and

Sefikeng series contained more oxides of Fe and Al than the Fusi and Thabana series in the clay fraction (Table 2.5). As a result, the Machache and Sefikeng series have a better chance for more favourable physical properties, viz. aggregate stability and water holding capacity. In addition, these two soil series are likely to have a high capacity for anion exchange reactions as well as anion retention, since Al and Fe oxides are the chief carriers of variable positive charge on the soil surface (Shao & Wang, 1991; Brady & Weil, 1996).

The remaining series, Leribe, Rama, Sephula, Matela and Berea ranked lower in terms of soil fertility characteristics, viz. CEC, TEB and BS (Table 2.6). This was in agreement with their low pH, organic matter and clay content. These soils were formed from different parent materials (Table 2.1) but had, as would be expected, a common deficiency of essential plant nutrients that was either an inherent property from the parent material (Sephula, Matela and Berea) or a result of prolonged weathering (Leribe and Rama). Additionally, due to their high proportion of sand relative to clay, these five soil series were more susceptible to leaching; a phenomenon associated with their low total exchangeable bases and base saturation.

After categorizing the benchmark soil series according to the present natural soil fertility status, it was considered interesting to establish which factors collectively determine the fertility status. One soil fertility characteristic, for instance, CEC, was chosen for this investigation. The CEC rather than either TEB or BS was considered a better natural soil fertility index since both TEB and BS are dependent on CEC whereas the latter is at least independent of the TEB and BS. Therefore, it is argued that there was a variation in CEC between the soil series with a higher fertility status and those with a lower fertility status, irrespective of their comparable clay contents in some cases, which, as previously mentioned, indicated that clay content was not the only factor determining CEC. According to the correlation statistics shown in Table 2.7, pH(H_2O), AS, OC, clay and CEC–clay had a strong correlation with the CEC of the soils. Furthermore, a multiple regression analysis showed that when other factors were kept constant, then OC, CEC–clay and clay content, singly, explained respectively 91, 75 and 75% of the variation in CEC of the soils. This suggested that the CEC of the study soils was more attributed to OM rather than to either clay content or clay type, the latter being equally important.

The stepwise multiple regression analysis based on the pH(H_2O), AS, OC, clay content, CEC–clay and Fe and Al oxide contents selected five factors, viz. OC, CEC–clay, clay content, AS and free Fe oxides (Fe_d)as factors which collectively determine the CEC of the study soils. This was supported by the residual sum of squares and r^2 statistics shown in Table 2.8. A full regression model, viz. 31 with all five selected factors had the smallest residual sum of squares and the largest r^2 value. The residual mean square (residual sum of squares divided by the error degrees of freedom) for this model was 87.74/50 = 1.75. This value was an estimate of variation of observations around the fitted model and was used to assess the importance of including or excluding one or more factors from the regression model (Mead & Curnow, 1983). If the difference between the residual sum of squares of two models, where one model was a subset of another, was greater than the residual mean square for the full model then it would mean that it was worthwhile to include the other factor(s) in the model. It was obvious that the differences between the residual sum of squares of any pairs of comparable models like model ABCDE and either ABC, ACE, ABCD, ABCE or ACDE were greater than 1.75. This, therefore, indicated that the CEC and hence fertility status of the study soils was determined by all five factors together, viz. OC, CEC–clay, clay content, AS and free Fe oxides.

The following multiple linear regression model was established for CEC: CEC = –8.501 + 2.859 OC + 0.4695 clay + 0.2039 CEC–clay – 0.01927 AS – 1.461 Fe_d. Organic carbon, CEC–clay and clay content have a positive effect on CEC of the soils while acid saturation and free Fe oxides have a negative effect. The significance of free Fe oxides in the model describing CEC of the soils explains the difference in CEC between the series Machache, Sefikeng and Tumo and the series Fusi, Khabos and Thabana, irrespective of similar proportions of clay in these two groups of series. Iron and Al oxides are more important in anion than in cation exchange reactions, hence their high proportions in the clay fraction negatively affect CEC of the soils. Further, it also supports the consideration that Machache and Sefikeng series more than any other series have more favourable physical properties as well as higher capacities for anion exchange reactions and anion retention due to their larger contents of Fe and Al oxides.

Table 2.8. Stepwise multiple regression report for the five factors determining CEC of the study soils.

Regression model*	Variables included*	Residual sum squares	r^2 value	Error degrees of freedom
1	A	1576.89	0.75	54
2	B	5831.09	0.08	54
3	C	1610.59	0.75	54
4	D	584.01	0.91	54
5	E	3384.73	0.47	54
6	AB	560.76	0.92	53
7	AC	226.27	0.96	53
8	AD	550.88	0.91	53
9	AE	801.93	0.87	53
10	BC	997.35	0.84	53
11	BD	332.67	0.95	53
12	BE	2293.42	0.64	53
13	CD	244.96	0.96	53
14	CE	1487.42	0.77	53
15	DE	384.30	0.94	53
16	ABC	113.50	0.98	52
17	ABD	269.08	0.96	52
18	ABE	493.69	0.92	52
19	ACD	194.97	0.97	52
20	ACE	162.30	0.97	52
21	ADE	383.79	0.94	52
22	BCD	221.27	0.97	52
23	BCE	717.87	0.89	52
24	BDE	302.59	0.95	52
25	CDE	203.79	0.97	52
26	ABCD	94.92	0.99	51
27	ABCE	103.92	0.98	51
28	ABDE	250.38	0.96	51
29	ACDE	142.38	0.98	51
30	BCDE	199.53	0.97	51
31	ABCDE	87.74	0.99	50

*Variables in the models and the model are significant at 0.050 probability level or less.

A = clay content, B = free Fe oxides, C = CEC–clay, D = OC and E = acid saturation.

2.4. Conclusions

A total of 56 soils representing 11 benchmark soil series of Lesotho were collected from a full spectrum of arable land of Lesotho which includes the lowlands and foothills, for this study of phosphorus retention. Soil properties covering the physical (sample density and particle size distribution), mineralogical (amorphous and free oxides of Fe and Al and aluminosilicate clay minerals) and chemical (pH, CEC, exchangeable bases, base saturation, acid saturation, OC and extractable phosphorus) aspects were determined on these soils. Wide variations in these soil properties, especially those that influence phosphorus retention, for example pH, clay mineralogy and content and OC were recorded, between the series. Extractable phosphorus was also widely variable among the study soils. This wide variation between the study soils, particularly in extractable P and in those soil properties that influence P retention brought about an interesting and hence a challenging question of how these soils would respond to P application in a P retention study.

In an attempt to categorize the soil series according to their natural fertility status, the series Fusi, Khabos and Thabana represented a high fertility group and the series Leribe, Rama, Sephula, Matela and Berea represented a low fertility group with the series Machache, Sefikeng and Tumo intermediate. The fertility status of these soils was indicated by the soil pH, acid saturation, OC, clay content, Fe and Al oxides and CEC–clay under the umbrella of the TEB, BS and CEC of the soil.

CHAPTER 3

INVESTIGATING AN OPTIMUM INCUBATION PERIOD FOR PHOSPHORUS RETENTION STUDIES ON THE BENCHMARK SOILS

3.1. Introduction

Studies investigating the mechanisms of P sorption reactions following the application of P to soils indicate that P sorption is a two–phase process, consisting of an initial rapid phase and a slow phase. The initial rapid phase involves adsorption and precipitation reactions of the applied P (Agbenin & Tiessen, 1995). Precipitation usually occurs near the fertilizer granule where concentrations of P and the precipitating cations, Al, Fe, Ca, Mg and Mn are high (Tisdale *et al.*, 1985; Wild, 1988). The concentration of these cations is increased as some soil minerals are dissolved by the concentrated P solutions formed from the dissolution of P fertilizers. The initial products of phosphate precipitation reactions are usually the Al containing mineral taranakite, some simple Al/Fe phosphate compounds and various Ca or Ca/Mg phosphate minerals (Taylor & Gurney, 1965; Mattingly, 1975; Tisdale *et al.*, 1985; Wild, 1988; Samadi & Gilkes, 1999). At some distance from the fertilizer granule the diffusing orthophosphate ions are trapped through adsorption by the oxides and hydroxides of Al and Fe, Al/Fe–OH groups associated with clay and OM as well as Ca/Mg carbonates if present (Russell *et al.*, 1974; Mattingly, 1975; Parfitt *et al.*, 1975; Williams *et al.*, 1980).

Some of the P precipitated or adsorbed during the initial reaction phase occurs in a plant available form which represents a labile pool that replenishes the soil solution P (Parfitt, 1989). This pool is generally characterized by sorption isotherms, viz. Q/I plots obtained by equilibrating the soil with P solutions for different durations using among others the method of Fox & Kamprath (1970). Fox & Kamprath (1970) observed for a typic clay loam hapludult from Georgeville, that the level of P in the soil solution reached an apparent equilibrium after six days of incubation. In another study on the oxisols from the Highland Sourveld of Natal (Reeve & Sumner, 1970), it was found that P sorption was complete within one hour and that no more P was sorbed in the next four days. Evidence from other

studies indicates that the rapid sorption reaction of P with aluminium oxide and kaolinite clays reaches a steady state equilibrium in one to three hours (Chen *et al.*, 1973) and that 75% of the added P can be sorbed in half an hour by the high sorbing and in about 12 hours by the low sorbing Cerrado soils of Brazil (Goncalves *et al.*, 1985; 1989). The general consensus is, therefore, that it takes from less than an hour to a maximum of six days for the initial phase to reach completion, depending on the soil type.

On the other hand, the slow P sorption phase involves the continuous migration of P adsorbed onto the surfaces of soil colloids and minerals, and its strong sorption into the internal surfaces between the plate–like crystal units of some silicate clay minerals, and into the defect sites of amorphous or poorly crystalline Al and Fe hydroxides or the microsites between aggregates of poorly crystalline Al and Fe compounds (Cabrera *et al.*, 1981; Barrow, 1985; Parfitt, 1989). It also includes the conversion of sparingly soluble phosphate precipitates into very less soluble phosphate minerals, for example, dicalcium phosphate into octacalcium phosphate and hydroxyapatite minerals (Eanes *et al.*, 1965; Barrow, 1980; Tisdale *et al.*, 1985; Wild, 1988). The slow P sorption reactions continue for a long time, at a decreasing rate but never appear to stop. It is this slow reaction phase that is responsible for the retention of fertilizer P, its effectiveness during the growing season of application and its residual effect thereafter.

Among all the studies that aimed to quantify the amount of applied P retained by the soil through the slow P sorption reactions, there is no agreement on the time that should be allowed for these reactions to become near complete. Johnston *et al.* (1991) and Indiati *et al.* (1995) incubated the soils in their P sorption studies for periods of 42 and 90 days, respectively, with repeated wetting to field capacity before they determined the proportion of applied P that was retained by the soils against the most common extractants of plant available P. Agbenin & Tiessen (1995) used an incubation period of 2 to 200 days in their P sorption studies. These researchers worked with soils from different parts of the world, viz. mollisols, alfisols, vertisols, ultisols and oxisols from Kwazulu–Natal Province in South Africa (Johnston *et al.*, 1991), non–calcic brown, planosol, cambisol, lithosol and alluvial from north–east Brazil (Agbenin & Tiessen, 1995) and entisols from Frosinone District in south–east Latium, Italy (Indiati *et al.*, 1995).

In their studies Agbenin & Tiessen (1995) found that P sorption approached a steady state equilibrium in all the soils on day 50. The results of this study indicated that between day 50 and day 200 the amount of sorbed P did not increase by more than 10%. Johnston *et al.* (1991) used a 42 days incubation period even though they conceded that it was still short compared to a single growing season for example, and therefore, an underestimation of P sorption was one possibility. They supported the idea of subjecting soils to cycles of wetting and drying and argued that the technique simulated real field conditions better than the method of Fox & Kamprath (1970) in which the P treated soils were subjected to continuous saturation conditions that are rare under actual field conditions.

The fact that these methods (Johnston *et al.*, 1991; Agbenin & Tiessen, 1995; Indiati *et al.*, 1995) utilize longer equilibration periods between P application and the assessment of sorbed P makes them very appropriate for studies dealing with slow P sorption reactions. Their merits are also that they can be used to estimate the amount of P required to raise the plant available P to a sufficiency level, known as the P requirement factor (PRF), directly from the plots of applied P against extractable P and that the PRF can also be used as an index of the P sorption properties of soils. Nevertheless, there is limited information on the optimum experimental conditions, particularly a standard incubation period for studying the slow P sorption reactions. Thus, in order to avoid running into problems of underestimating P sorption by allowing for a too short duration of incubation or wasting time by allowing for a too long duration of incubation, an experiment was conducted to establish a practical optimum incubation period that would be used for the P retention studies to be reported later.

3.2. Materials and Methods

3.2.1. Soils

Eleven of the 56 soils described in Chapter 2 were selected for this investigation. Each of these 11 soils, viz. Fs1, Khs1, Se1, Ta1, Le1, Ma1, Md1, Ba1, Rm1, Sg1 and Tm1 represented a benchmark soil series.

3.2.2. Experimental design and procedure

The layout was a factorial experiment with eleven soils, five P application rates and three replicates, arranged in a randomized complete block design. Application rates of P were 0, 50, 100, 200 and 400 kg P ha^{-1} hereafter referred to as P0, P50, P100, P200 and P400. The actual amounts of P applied to soils were calculated on the basis of the mass of a hectare to a depth of 300mm, using the sample densities reported in Chapter 2. A 10ml solution of KH_2PO_4 containing the relevant amount of P was sprayed on a soil spread on a plastic sheet. After spraying, each soil was mixed thoroughly and poured into a non–porous plastic container. Thereafter the treated soils were wetted with distilled water to 86% water filled pore space that was calculated from an assumed particle density of 2650 kg m^{-3} and the sample densities reported in Chapter 2. The total weight of the container, soil and water was recorded for every treatment sample immediately after the water had disappeared from the top of the soil. These treated samples were incubated at room temperature for nine weeks and rewetted to the initial soil water content every fortnight, using the recorded weights for reference.

3.2.3. Soil analysis

Small subsamples were taken from each treatment sample at 7, 14, 21, 28, 42 and 63 days after P application hereafter referred to as 7d, 14d, 21d, 28d, 42d and 63d, respectively. After every sampling, the subsamples were air–dried and pulverized to pass through a 2mm sieve. The P in each subsample was extracted by the Olsen procedure (Olsen *et al*, 1954) and determined by a colorimetric method using a slightly modified molybdenum blue colour complex according to Murphy & Riley (1962).

3.2.4. Data analysis

The retained P for each treatment sample was calculated as the difference between applied P and extracted P, corrected for P extracted from the control. This retained P for every

application level per soil was subjected to ANOVA and the mean difference of retained P between sampling times was tested by the Tukey–Kramer multiple comparison test, using the NCSS 2000. Only the variations at 0.050 probability level or less were considered statistically significant. The retained P for each application level was also fitted with a variety of models commonly used to describe the kinetics of P sorption, and multiple regression analysis was used to determine which model(s) best fitted the data. Linear (Ryden *et al.*, 1977b), parabolic diffusion (Evans & Jurinak, 1976), Elovich (Chien & Clayton, 1980), fractional power (Kuo & Lotse, 1974), apparent first order, zero order (Sparks & Jardine, 1984) and polynomial second degree (quadratic) models were used. The fit of each model to experimental data was evaluated by the size of the coefficient of determination (r^2) and the statistics of standard error of estimation (S_E = root of mean square error). Only when a model fitted the data at 0.050 probability level or less then the fit of that model was considered significant and hence the model was considered applicable for the data.

3.3. Results and discussion

The mean retained P and mean comparison between the six sampling times, viz. 7d, 14d, 21d, 28d, 42d and 63d for each soil at four different P application levels, viz. P50, P100, P200 and P400 are presented in Appendix 3.1. A summary highlighting significant variations in mean retained P between sampling times is given in Table 3.1. Regardless of the P application level, a significant difference in mean sorbed P between sampling times was found for the following six of the eleven soils: Khabos, Thabana, Machache, Matela, Rama and Tumo. In the case of the Fusi soil significant difference in mean sorbed P between sampling times was found at P100, P200 and P400 but not at P50. For the Sephula and Berea soils, mean sorbed P between sampling times varied significantly at P100 and P400 while for the Sefikeng soil it varied significantly at P200 only. For the remaining soil, viz. Leribe, there was no significant difference in mean sorbed P between sampling times throughout all application levels.

The values of the coefficient of determination (r^2) and the standard error of estimation (S_E) obtained with the models that were used to fit the retained P against sampling time are given

45

in Table 3.2. When a model fitted the data at probability level greater than 0.050 then the fit of that model and hence the actual r^2 value was regarded as non significant. Before discussing the results in Table 3.2 an attempt is made to check the consistency of these results with the results of the ANOVA given in Table 3.1. The aim is to see if there was at least one model that fitted retained P against sampling time for the soils and the P application levels for which there was a significant variation in mean sorbed P between the sampling times. Table 3.3 therefore, presents a schematic comparison between the information in Tables 3.1 and 3.2.

Table 3.1. The variations in mean retained phosphorus between sampling times and the degree of variation indicated by the level of significance according to the ANOVA.

Soils	Phosphorus application levels and number of observations							
	P50	n	P100	n	P200	n	P400	n
Fusi	NS	16	***	15	**	16	***	15
Khabos	***	15	***	17	***	17	***	17
Thabana	**	15	*	15	**	17	***	18
Leribe	NS	16	NS	13	NS	14	NS	15
Machache	***	16	**	14	***	16	**	15
Rama	***	15	**	15	**	16	*	16
Sefikeng	NS	16	NS	15	**	15	NS	15
Sephula	NS	16	***	18	NS	17	*	17
Tumo	***	18	**	14	*	14	**	16
Matela	***	14	***	16	*	17	***	15
Berea	NS	17	**	16	NS	15	***	14

NS = not significant, * = significant at $P \le 0.050$, ** = significant at $P \le 0.010$ and *** = significant at $P \le$ 0.001

According to this checklist, at least for the Fusi, Khabos and Machache soils the fitting of the models was fully consistent with the results of ANOVA (Table 3.3). That is, there was at least one model that fitted the mean sorbed P against sampling time significantly, for all four P levels in Khabos and Machache and for P100, P200 and P400 in Fusi. In the case of the other eight soils, viz. Thabana, Leribe, Rama, Sefikeng, Sephula, Tumo, Matela and Berea there was a lack of consistency here and there between the fitting of the models and the results of ANOVA. For instance, there was at least one model that significantly fitted the mean sorbed P against sampling time for three P levels in the case of the Thabana, Tumo and Matela soils and for only one P level in the case of the Rama soil even though the results of ANOVA indicated a significant difference in mean sorbed P between sampling

Table 3.2. The coefficient of determination (r^2) and standard error of estimation (S_E) obtained with the models that were used to fit the retained phosphorus against sampling time.

Soil series	P level	Linear		Zero order		Apparent first order		Parabolic diffusion		Elovich		Fractional power		Quadratic	
		r^2	S_E	r^2	S_E	r^2	S_E	r^2	S_E	r^2	S_E	r^2	S_E	r^2	S_E
Fusi	P50	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P100	0.47**	3.49	0.47**	0.13	NS	-	0.34*	0.14	NS	-	0.27*	0.22	0.90***	1.57
	P200	0.51**	1.79	0.51**	0.03	NS	-	0.53**	0.03	0.52**	1.78	0.54**	0.04	0.52**	1.84
	P400	0.46**	15.36	0.46**	0.15	NS	-	0.33*	0.16	NS	-	NS	-	0.91***	6.52
Khabos	P50	0.63***	14.25	0.64***	0.19	0.50**	0.15	0.52**	0.22	0.39*	18.43	0.60**	0.64	0.90***	7.60
	P100	0.82***	5.05	0.82***	0.12	0.62***	0.24	0.76***	0.14	0.68***	6.70	0.66***	0.44	0.86***	4.58
	P200	0.69***	12.08	0.69***	0.14	0.59***	0.13	0.62***	0.15	0.52**	15.14	0.59***	0.34	0.81***	9.73
	P400	0.69***	15.00	0.69***	0.12	0.49**	0.24	0.58***	0.14	0.46**	19.96	0.52**	0.26	0.89***	9.23
Thabana	P50	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	0.67**	0.85
	P100	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	0.53*	1.07
	P200	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P400	0.30*	3.23	0.31*	0.04	0.50**	0.30	0.37**	0.04	0.43**	2.91	0.43**	0.04	0.35*	3.21
Leribe	P50	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P100	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P200	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	0.59**	3.92
	P400	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
Machache	P50	NS	-	NS	-	NS	-	0.27*	0.09	0.41**	1.44	0.39**	0.10	0.75***	0.98
	P100	0.53**	1.89	0.53**	0.07	0.57**	0.16	0.57**	0.06	0.58**	1.79	0.52**	0.09	0.60**	1.81
	P200	0.38*	4.22	0.37*	0.07	NS	-	0.50**	0.06	0.64***	3.20	0.63***	0.06	0.76***	2.70
	P400	0.36*	9.09	0.36*	0.09	NS	-	0.39*	0.08	0.42**	8.63	0.39*	0.10	NS	-
Rama	P50	NS	-	NS	-	0.31*	0.25	NS	-	NS	-	0.58**	0.65	NS	-
	P100	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P200	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-

Table 3.2. (continues)

Soil series	P level	Linear		Zero order		Apparent first order		Parabolic diffusion		Elovich		Fractional power		Quadratic	
		r^2	S_E	r^2	S_E	r^2	S_E	r^2	S_E	r^2	S_E	r^2	S_E	r^2	S_E
	P400	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
Sefikeng	P50	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P100	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P200	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P400	NS	-	NS	-	NS	-	NS	-	0.26*	3.93	NS	-	NS	-
Sephula	P50	NS	-	NS	-	NS	-	NS	-	NS	-	0.64*	0.37	NS	-
	P100	0.44**	12.20	0.44**	1.02	0.25*	0.34	0.33*	1.11	NS	-	NS	-	0.80***	7.49
	P200	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P400	0.41**	8.63	0.41**	0.20	0.38*	0.16	0.42**	0.20	0.43**	8.50	0.35*	0.77	0.41*	8.93
Tumo	P50	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	0.34*	3.68
	P100	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P200	0.45**	8.03	0.45**	0.20	0.34*	0.32	0.49**	0.19	0.51**	7.58	0.47**	0.36	0.52*	7.83
	P400	0.25*	17.39	0.26*	0.25	NS	-	0.28*	0.25	0.28*	17.12	NS	-	NS	-
Matela	P50	0.58**	2.16	0.58**	0.16	0.48**	0.31	0.57**	0.16	0.52**	2.31	0.35*	0.35	0.58**	2.26
	P100	0.51**	2.73	NS		NS	-	NS	-	0.28*	3.31	NS	-	0.74***	2.06
	P200	NS	-	NS		NS	-	NS	-	NS	-	NS	-	NS	-
	P400	NS	-	NS	-	0.37*	0.24	NS	-	NS	-	NS	-	0.62**	14.79
Berea	P50	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	0.37*	2.57
	P100	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-
	P200	0.36*	8.80	0.36*	0.27	0.31*	0.19	0.29*	0.28	NS	-	NS	-	0.52*	7.89
	P400	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-	NS	-

NS = not significant, * = significant at P ≤ 0.050, ** = significant at P ≤ 0.010 and *** = significant at P ≤ 0.001

times for all four P application levels. In the case of the Leribe, Sefikeng and Sephula soils the fitting of models was consistent with ANOVA results for P50, P100 and P400 but not for P200, for P50 and P100 but not for P200 and P400 and for P100, P200 and P400 but not for P50, respectively. Furthermore, in the case of the Berea soil a significant fit was unexpectedly obtained for different P levels from those for which a significant variation in mean sorbed P between sampling times was found from the ANOVA. Noteworthy is that even though the variation in mean sorbed P between the sampling times in the case of the Leribe and Berea soils for P200 was not significant at 0.050 probability level, at least it was significant at probability level less than 0.100, which indicated a trend or a chance for a significant variation.

Table 3.3. Comparisons between the variations in mean retained phosphorus between the sampling times obtained with the ANOVA and the fitting of kinetic models to the data using multiple regression analysis, per soil per level of P application.

Soil	P50		P100		P200		P400	
	Anova	Model	Anova	Model	Anova	Model	Anova	Model
Fusi	NS	NO	S	YES	S	YES	S	YES
Khabos	S	YES	S	YES	S	YES	S	YES
Thabana	S	YES	S	YES	S	NO	S	YES
Leribe	NS	NO	NS	NO	NS	YES	NS	NO
Machache	S	YES	S	YES	S	YES	S	YES
Rama	S	YES	S	NO	S	NO	S	NO
Sefikeng	NS	NO	NS	NO	S	NO	NS	YES
Sephula	NS	YES	S	YES	NS	NO	S	YES
Tumo	S	YES	S	NO	S	YES	S	YES
Matela	S	YES	S	YES	S	NO	S	YES
Berea	NS	YES	S	NO	NS	YES	S	NO

NS/S ≡ variation not significant or significant at 0.050 probability level or less, respectively.

YES/NO ≡ at least one model or no model, respectively fitted the data at 0.050 probability level or less.

Returning to Table 3.2, there was generally a large tendency for more than just one model to fit the retained P against sampling time for the same P level per soil. For instance, all the models, regardless of the P application levels, significantly fitted the data for the Khabos soil. For the Thabana, Machache, Sephula, Tumo and Matela soils, all the models fitted mean sorbed P against sampling time significantly though not for each of the P levels. For the Fusi soil, all the models fitted retained P against sampling time significantly for at least

one P level with the exception of the apparent first order model which did not fit the data significantly for any P level. In the case of the Berea soil, all but two models, viz. Elovich and fractional power, significantly fitted the data for P200. On the contrary, for the Rama soil a significant fit was obtained with only two models, viz. the apparent first order and fractional power models for P50. The data for the soils Sefikeng and Leribe, and Berea at P50, were exceptional in that they were fitted by only one model per P level, viz. the Elovich model in the case of Sefikeng and the quadratic model in the case of Leribe and Berea.

When more than one model fitted the data, the statistic parameters r^2 and S_E were used to determine which model gave the best fit as designated in Table 3.2 by the r^2 values in bold font. In most cases, where applicable, the quadratic model gave the best fit. Where the quadratic model was not applicable, as occurred in the Sephula and Rama soils for P50 and in the Machache and Sefikeng soils for P400, either the Elovich or fractional power models gave the best fit. Sometimes even when the quadratic model was applicable the Elovich or fractional power model still gave the best fit, viz. in the Fusi and Sephula soils for P200 and P400, respectively. The other models, viz. the apparent first order, parabolic diffusion and linear models, respectively, gave the best fit for the Thabana soil at P400, the Tumo soil at P400 and Matela soil at P50. The linear model was considered the best model that fitted retained P against sampling time for the Matela soil at P50 since there was no improvement in r^2 with the other models like the quadratic and zero order, even though the latter had small S_E, and also because the linear model was the simplest of the three. Therefore, judged from statistic parameters, viz. r^2 and S_E, the retained P against sampling time was best fitted by the quadratic, fractional power, Elovich, apparent first order, parabolic diffusion or linear models, more or less in that order.

Although the F–statistics indicated that all these six models fitted retained P against sampling time significantly at a 0.050 significance level or less, the actual size of r^2 was very variable (Table 3.2). The size of r^2 gives an indication of the percentage of the total variation in the dependent variable (P sorbed) that is explained by the changes in independent variables (e.g. sampling time) included in the regression model, hence the importance of the regression model (Gomez & Gomez, 1984). The r^2 values obtained with

the Elovich, parabolic diffusion and apparent first order models, where the latter gave the best fit, were never greater than 0.5, implying that these models never explained more than 50% of the total variation in retained P between sampling times. The larger r^2 values, viz. > 0.5 were obtained with the linear, fractional power and quadratic models even though there were two exceptional cases of $r^2 = 0.34$ for the Tumo soil and $r^2 = 0.37$ for the Berea soil, both at P50, obtained with the latter model.

Therefore, it was conceded that only the linear, fractional power and quadratic models, significantly and satisfactorily fitted retained P against sampling time provided they gave the best fit compared to the other models as inferred from the r^2 and S_E statistic parameters, and also that they had r^2 values bigger than 0.50 that were at least significant at 0.050 probability level or less. The decision on considering $r^2 > 0.50$ as satisfactorily big was based on the facts that there was only one independent variable included in the regression models, viz. the time after the application of P to the soil. However, in reality, there are other factors besides the time (e.g. clay content, clay type, water content, pH and the P saturation of the adsorption matrix) that usually influence the retention of applied P by the soils. Such factors were purposely not considered in this study because the aim was not to determine their effects but the effect of time on P transformations.

Based on the above mentioned criteria, three models, viz. linear, quadratic and fractional power fitted retained P against sampling time significantly and satisfactorily in 10 of the 11 soils studied (Table 3.2). Those 10 soils and the respective P levels were Khabos for all four P levels, Machache for P50, P100 and P200, Fusi for P100, P200 and P400, Matela for P50, P100 and P400, Sephula and Thabana for P50 and P100, Leribe, Berea and Tumo for P200 and Rama for P50. These three models were, therefore, used to present the relationships between retained P and sampling time graphically for selected data in Figure 3.1. Only the means of the three replicates were used for the graphs.

The first relationship described by the fractional power model ($y = at^{1/b}$) shows that applied P was retained progressively throughout the entire incubation period, though at a decreasing rate (Figure 3.1a). Maximum retention was never attained nor the retention appeared to stop or reach a steady state equilibrium. According to Barrow (1974; 1980; 1987) this kind

51

of relationship is typical of the slow phase P retention. The same model was used by Goncalves *et al.* (1985; 1989) in their studies even though they did not test other kinetic models. In the study of Agbenin & Tiessen (1995) P retention against time was best fitted by the fractional power and Elovich models with similar r^2 and S_E values although after a thorough analysis to see which model applied best to the data, using the procedure proposed by Aharoni & Sparks (1991), the Elovich model proved to be more applicable than the fractional power model.

The second relationship described by the quadratic model ($y = -ct^2 + bt + a$) shows that the retained P increased with time at a decreasing rate to a point beyond which retained P started to decline with time (Figure 3.1b). Two explanations are possible for this type of relationship. One could be that a soil was given a small amount of P that was all sorbed after a few days of incubation, and thereafter desorbed. In this case, the left hand side of the curve (showing an increase in sorbed P with time) represented a shift towards the sorption phase in response to P application while the right hand side (showing a decrease in sorbed P with time) represented a shift towards the desorption phase after all the applied P had been sorbed. The peak of the curve should, therefore, represent the maximum retained P which according to the above mentioned explanation was not necessarily equivalent to the sorption capacity of the soil.

Another explanation could be that a soil was given a large amount of P that was sorbed until the sorption capacity of the soil for P was satisfied and some of the applied P remained in forms that were easily extractable. Thus, the left hand side of the curve still represented the sorption phase as in the first explanation above, but the right hand side represented an accumulation of applied P in easily extractable forms. The peak of the curve in this case should, therefore, represent the P sorption capacity of the soil even though there might be an underestimation of sorption capacity (Bache & Williams, 1971). The validity of these two explanations is supported by the fit of the quadratic model to retained P against sampling time for the Fusi soil at P100 and P400 (Figure 3.2), but with far different sorption maxima that were extrapolated from the two curves. Accumulation of applied P in easily extractable forms was possible in the present study because there was neither leaching of P from the soil nor uptake of P by plants.
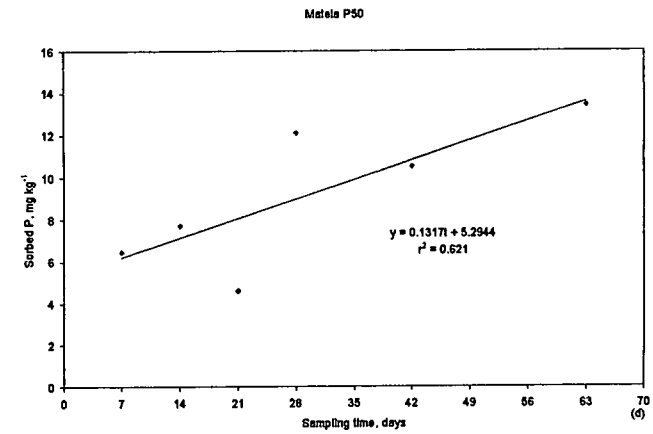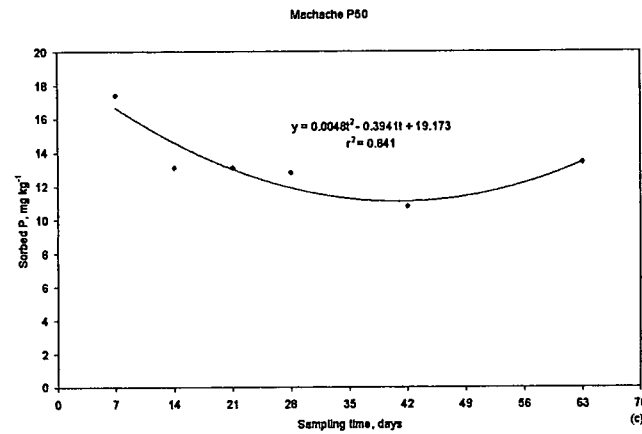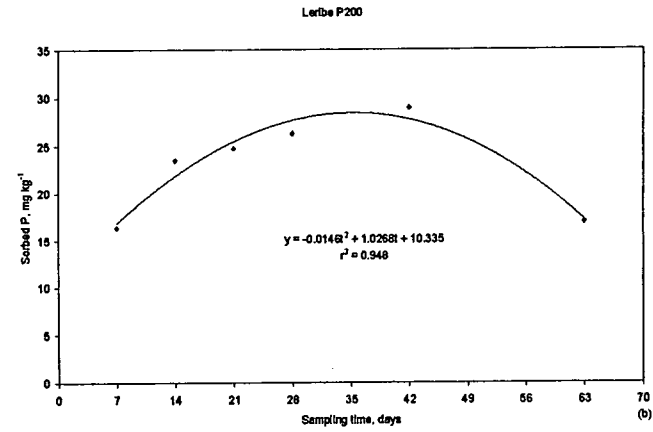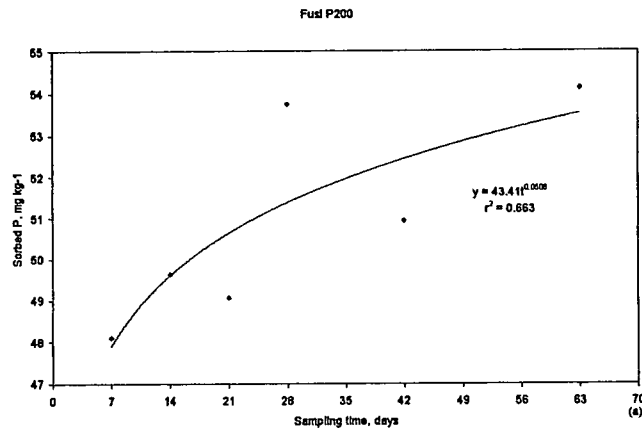
Figure 3.1. The relationships between retained phosphorus and sampling times as described by the fractional power (a), quadratic (b and c) and linear (d) models.
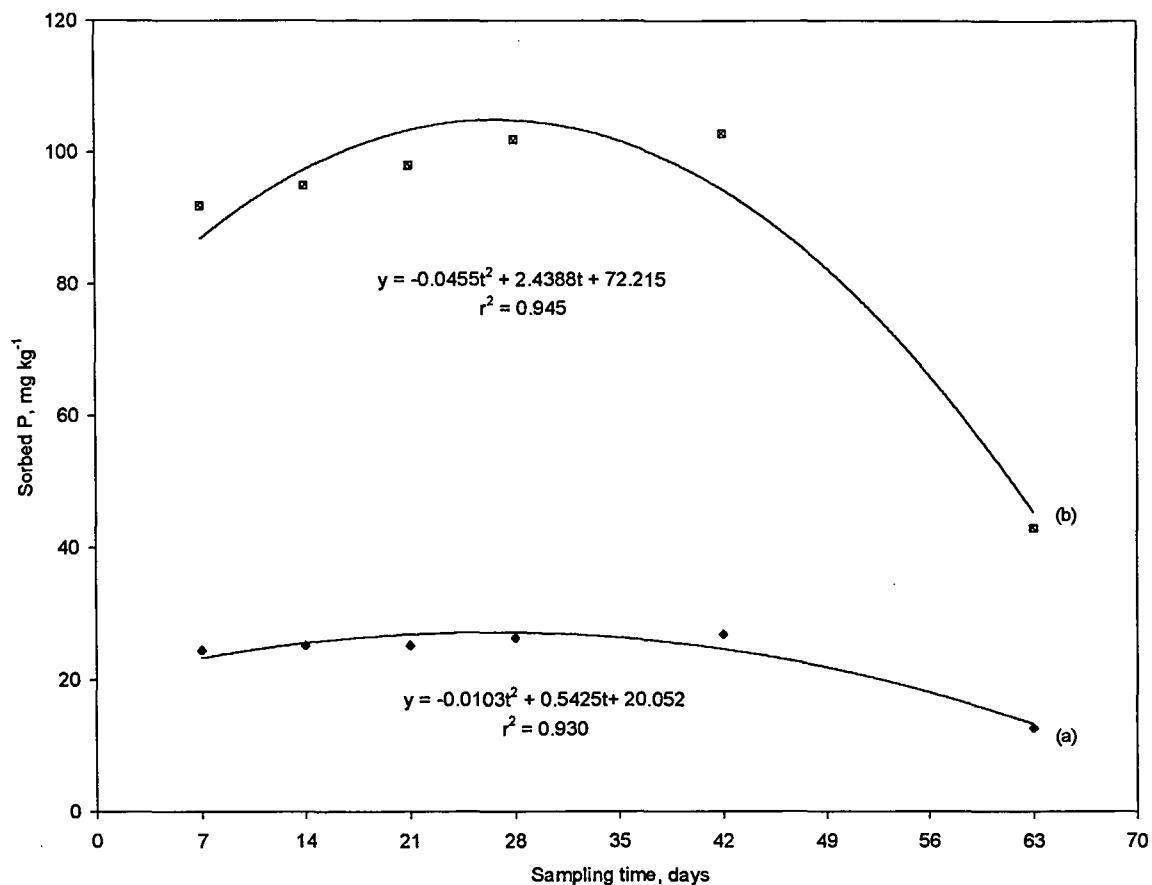
Figure 3.2. Comparison in phosphorus retention by the Fusi soil between P100 (a) and P400 (b) over a 63 days incubation period.

Alteration of sorption and desorption as indicated by the sides of the quadratic curve according to the first explanation, is a common phenomenon for P and it maintains an 'equilibrium' between the quantity and intensity factors. The 'equilibrium' between the quantity and intensity factors is disturbed by either the input or output of P from the soil. An input of P into the soil (e.g. fertilizer application) increases the intensity factor relative to the quantity factor and hence causes a shift towards P sorption reactions. If by any chance the quantity factor can be increased in excess of the intensity factor the sorbed P is desorbed as a way of adjusting the 'equilibrium' between the two factors. Likewise, if by chance the desorption of P following output of the latter from the soil (e.g. through plant uptake) can increase the intensity factor in excess of the quantity factor, the desorbed P is

readsorbed resulting in the two factors again being in 'equilibrium'.

The fact that retained P against sampling time for the intermediate P application level, viz. P200 for the Fusi soil, was best described by the fractional power model (Figure 3.1a) supported the assumptions that the quadratic model fitted retained P against sampling time when the P application level was too small (P100) or too large (P400) for the sorption capacity of the soil. The best fit obtained with the fractional power model at P50 and the quadratic model at P100 for the Sephula soil indicated that P50 was sufficient while P100 was too large for the sorption capacity of the respective soil. In the case of the Thabana soil both P50 and P100 were supposedly too small for its sorption capacity. In the case of the Leribe and Berea soils, for which a significant fit was obtained with the quadratic model albeit for only one P level per soil, it was not easy to interpret the results as to whether the amount of P applied was too small or too large.

Furthermore, the fact that both the fractional power and quadratic models fitted retained P against sampling time at different P levels for the same soil as occurred for Fusi and Sephula soils was evidence in support of the suggestions of Bache & Williams (1971) and Johnston *et al.* (1991) in relation to the amount of P used in P sorption studies. The former researchers showed that the use of too small additions of P usually results in a misinterpretation of the P sorption, as all the applied P will be sorbed. On the other hand, the latter researchers pointed out that if excessively large additions of P are used, they might saturate the P sorption of the soils to an artificial degree. Thus, the use of either too high or too low P application levels in P sorption studies always results in underestimation of P sorption properties of the soils.

The third relationship, described by the quadratic model ($y = ct^2 - bt + a$) shows that retained P initially decreased and then increased as incubation proceeded (Figure 3.1c). This relationship was observed in the Khabos, Machache and Tumo soils regardless of the P application levels and also in the Matela soil for P100 and P400. These soils differed in many aspects including parent materials, mineralogical composition, texture (Chapter 2) and their capacities for P sorption (Chapter 4). This relationship presumably indicated that a lot of the applied P was retained between the time that P was applied to soils (time zero)

55

and the first sampling time, viz. 7d, which was thereafter desorbed and readsorbed again according to the model. This implies that the phase of retention immediately after P application in the Khabos, Machache and Tumo soils for all four P levels and in the Matela soil for P100 and P400 lasted for less than seven days, hence was missed in this study and only the desorption and readsorption phases were determined.

This was possibly true for the high P sorbing soils according to explanations of Reeve & Sumner (1970) and Goncalves et al. (1985 & 1989). There are indications that Machache is a high P sorbing soil of Lesotho (Cauley, 1986; Arduino et al., 1993) but Khabos and Tumo also have considerably high P sorption as indicated in Chapter 4. For a low P sorbing soil like Matela, it is still possible that P retention following application of P to the soil can be completed in less than seven days, particularly with large P additions, viz. P400 compared to P50. This coincides with the best fit of the linear model ($y = bt + a$) to the data for the Matela soil at P50; the fourth type of relationship between retained P and sampling times presented in Figure 3.1d. This probably suggested that it would take longer time for a soil of low P sorption capacity to sorb applied P in forms that are not extractable, especially when only sufficient additions of P were used (P50 compared to P400).

From those four relationships between the retained P and sampling times three of them, that is, those presented in Figures 3.1a, 3.1c and 3.1d were unfortunately not useful for investigating the possible optimum incubation period because their plots did not have a plateau which represents an apparent steady state equilibrium between sorption and desorption reactions of P. The type of graphs presented in Figure 3.1b, which were described by the quadratic model $y = -ct^2 + bt + a$ became solely useful for this investigation. The soils and P application levels for which significant and satisfactory best fit was obtained with this model and which were, therefore, compatible with this investigation were Fusi (P100 and P400), Thabana (P50 and P100), Leribe (P200), Sephula (P100) and Berea (P200). The optimum incubation periods estimated from these soils and P application levels are presented in Table 3.4.

Regardless of soil type or P level, the estimated optimum incubation period varied from 21 to 38 days. The shortest period was for the Berea soil and the longest period was for the

Thabana (P100) and Leribe soils with intermediate periods for the Fusi (P100 and P400), Thabana (P50) and Sephula soils. As reported in Chapter 4, Fusi and Thabana represented the high P sorbing soils while Berea, Leribe and Sephula represented the low P sorbing soils but there was no distinctive demarcation for their estimated optimum incubation periods. Similarly, Barrow (1973) observed, for some noncalcareous soils from Western Australia, that the decrease in the effectiveness of applied P was not necessarily affected by the P sorption properties of the soils.

Table 3.4. The optimum incubation periods estimated from the graphs of retained P against sampling time described by the quadratic model $y = -ct^2 + bt + a$.

Soil	Application level	Optimum incubation period (days)
Fusi	P100	23 to 30
	P400	24 to 29
Thabana	P50	27 to 33
	P100	33 to 37
Leribe	P200	32 to 38
Sephula	P100	24 to 29
Berea	P200	21 to 26

Characteristics of the Fusi, Thabana, Leribe, Sephula and Berea soils used in this investigation of an optimum incubation period, especially those implicated in P sorption, viz. pH, clay, OC, amorphous and free oxides of Al and Fe and CEC–clay are given in Table 3.5. Accordingly, the Fusi and the Thabana soil had the highest clay content, OC, amorphous Al and Fe oxides, free Fe oxides and CEC–clay. Voluminous research shows that all these soil properties have a positive correlation with P retention.

The maximum incubation period found in this study was 38 days. This period compared with the 42 days used by Johnston et al. (1991) for mollisols, alfisols, vertisols, ultisols and oxisols from Kwazulu-Natal. The soils used in this investigation were mollisols (Fusi), vertisols (Thabana), alfisols (Leribe and Sephula) and inceptisols (Berea).

Table 3.5. Variation of some properties for the Fusi, Thabana, Leribe, Sephula and Berea soils normally implicated in phosphorus retention.

Soil properties	Fusi	Thabana	Leribe	Sephula	Berea
Clay (%)	45c	46c	24b	12a	16a
Amorphous oxides (%)					
Al	0.36e	0.32d	0.12c	0.04a	0.09b
Fe	0.62b	0.62b	0.08a	0.06a	0.06a
Free oxides (%)					
Al	0.00a	0.00a	0.05b	0.17c	0.19c
Fe	1.32ab	2.29b	1.13a	0.31a	0.72a
CEC–clay (cmol$_c$ kg^{-1})	65.14c	64.24c	19.69a	27.78b	23.91ab
OC (%)	2.58e	2.39d	0.46c	0.19a	0.34b
pH (H$_2$O)	6.47d	5.82bc	5.57ab	6.03cd	5.33a

Figures carrying the same letter in a row are not significantly different at 0.050 probability level or less according to Tukey–Kramer multiple comparison test.

3.4. Conclusions

Out of the 11 soils initially used in this study only five soils were eventually used to estimate an optimum incubation period for P retention studies. The other six soils fell out either because among the models tested no model fitted the retained P against sampling time significantly and satisfactorily as judged from the size of the r^2 statistic parameter (Sefikeng) or because the best fit for the retained P against sampling time was obtained with other models rather than the quadratic model $y = -ct^2 + bt + a$, which was the only model that was found appropriate for this investigation (Khabos, Machache, Rama, Sephula and Tumo). The five soils, which proved suitable for this study, were Fusi, Thabana, Leribe, Sephula and Berea. The optimum incubation period estimated using these soils and the different P application levels ranged between 21 and 38 days.

However, for the sake of investigating 'slow' reactions of applied P that continue for a long time and which determine the availability of P for the entire growing season, or even longer, it was decided that a longer incubation period should be allowed to ensure that measurements of P retention are made at least some time after an apparent steady state equilibrium in slow P sorption reactions has been reached. Therefore, a 42 day period that

included all the optimum incubation periods estimated was chosen as a general optimum incubation period for the P sorption studies conducted for this thesis. In choosing this period consideration was given to the period chosen to be both practically demonstrable for a short–term laboratory experiment and yet not too short for the length of at least one growing season for annual crops.

CHAPTER 4

PHOSPHORUS RETENTION PROPERTIES OF THE BENCHMARK SOILS

4.1 Introduction

The capacity of a soil to retain and release applied P is a property that varies amongst soils with different characteristics. Soil characteristics that determine this capacity include, *inter alia*, clay mineralogy and content, organic matter content, soil water content and soil solution pH (Weir & Soper, 1963; Ahenkorah, 1968; Holford & Mattingly, 1975c; Juo & Fox, 1977; Sample *et al.*, 1980; Sanchez & Uehara, 1980; Le Mare, 1982; Norrish & Rosser, 1983; Mengel & Kirkby, 1987; McIntoch & Whitton, 1988; Arduino *et al.*, 1993; Bainbridge *et al.*, 1995). The influence of these characteristics on fertilizer phosphorus reactions in soils is discussed thoroughly in Section 1.3.

The availability of applied P for plant uptake in any soil depends largely on the P retention capacity of the soil. In soils with high P retention capacities like clayey and loamy soils, the largest part of applied P is sorbed in less available forms and hence only a small portion is available for plant uptake. On the other hand, in soils with low P retention capacities such as sandy soils, a small part of applied P is sorbed, leaving the largest portion available for plant uptake. The sorbed P serves as a labile pool that replenishes the pool of available P during plant uptake and it is larger in clayey and loamy soils than in sandy soils. Thus, though the availability of applied P might be lower in clayey and loamy soils than in sandy soils immediately after application, in the long–run clayey and loamy soils have an advantage to sustain a higher and longer lasting P availability as compared to sandy soils. While P is recognizably an immobile nutrient in soils, the availability of applied P in sandy soils might be reduced by leaching, particularly when the plant uptake is low (Neller *et al.*, 1951; Ozanne & Shaw, 1961; Mattingly, 1970; Ritchie & Weaver, 1993).

Replenishment of soil solution P from adsorbed or sorbed P is determined by the P buffering capacity of a soil which is in turn governed by the capacity of that soil for P retention. Although in general, the reactions between applied P and soil components continue for a long period albeit at a decreasing rate, the reaction period is longer in soils

60

with a high P retention capacity (Ritchie & Weaver, 1993). This results in more total P in soils with high, compared to those with low, P retention capacities after a long P fertilizer application history, even if both soil types have been under the same cropping system (Indiati, 1998). Therefore, the high sorbing soils consequently have high total P, hence strong P buffering capacity and therefore, better chances to maintain strong soil solution P concentrations over longer periods compared to the low sorbing soils with low total P content. Thus, effectiveness of P fertilizer and its residual effect are usually controlled by P retention properties of soils (Barrow, 1980; Ritchie & Weaver, 1993; Dalal, 1997).

In order to correct P deficiencies in soils, adequate P fertilizer applications are required to satisfy the capacity of soils for P sorption and also to increase plant available P to sufficiency level. The use of the soil P test values and critical tissue P concentrations for particular crops alone without consideration of the P sorption properties of the soils could sometimes result in lack of response to fertilizer applications because most of applied P is sorbed. The importance of measurements of the P retention properties of soils for predicting amounts of P fertilizers required to correct P deficiency in soils is well established (Juo & Fox, 1977; Farina & Channon, 1987; Guertal et al., 1991; Johnston et al., 1991; Agbenin & Tiessen, 1995; Bainbridge et al., 1995).

Different approaches are used to quantify the P retention capacities of soils, which include long–term and short–term studies. In long–term studies, different levels of P fertilizer are applied repeatedly to the soils in the field, for many years during which constant measurements of the fractions of applied P released and retained are made. The measurements are also made years after cessation of applications to determine recovery of residual P. In short–term studies usually conducted under laboratory conditions, soils are incubated with varying amounts of P, allowed to equilibrate for some time and then analyzed for the fractions of applied P released and retained.

The laboratory studies are indeed very quick but their applicability depends on their success in predicting the amount of P fertilizer required on a specific soil by a particular crop as measured by field experimentation. This in turn depends on the method used and on its proximity to mimic field conditions affecting P sorption reactions. Different incubation

methods are used by different researchers in different laboratories and for different soils (Reeve & Sumner, 1970; Guertal *et al.*, 1991; Agbenin & Tiessen, 1995; Indiati *et al.*, 1995). The most varying factors in laboratory incubation methods are the levels of applied P used, period of incubation, moisture content during incubation, treatment of samples after incubation and prior to analysis of sorbed P and the expression of P retention properties of the soils. For instance, Reeve & Sumner (1970) and Guertal *et al.* (1991) employed very short equilibration periods of 16 and 2 hours, respectively and subjected their soil samples to a single moisture condition. Others employ longer equilibration periods of 90 – 200 days under alternating drying and wetting to mimic field conditions (Agbenin & Tiessen, 1995; Indiati *et al.*, 1995).

In their study on P sorption with regard to the kinetics and transformations of P in some benchmark soils of Brazil, Agbenin & Tiessen (1995) observed that the rate of P sorption reactions had reached a steady state at about day 50. In other studies to quantify the P requirement factors for Kwazulu–Natal soils (Johnston *et al.*, 1991), a similar method was used but with 42 days incubation period. In the preliminary study to establish an appropriate incubation period for the benchmark soils of Lesotho (Chapter 3) 42 days was found to be optimum and the most practical period. The variation in time of incubation in these studies is probably a function of soil type, amount of P already present in the soil and the amount of P added to the soil. The amount of P to be used in P sorption studies is in turn determined by the capacity of the soil for P sorption and the amount of P already present in the soil. According to Bache & Williams (1971) P application should be large enough to satisfy the P retention capacity of the soil and optimize its labile pool of P. However, according to Johnston *et al.* (1991) P additions should not be too large that the sorption capacities of the soils are oversaturated. Thus, incubation methods used in P sorption studies should be standardized for different soils.

Besides all the differences in the incubation methods used by Reeve & Sumner (1970), Guertal *et al.* (1991), Agbenin & Tiessen (1995) and Indiati *et al.* (1995) P retention properties of the soils were commonly estimated from the fraction of applied P retained against the most common extractants for plant available P. When retained P is plotted against either applied or extracted P, the parameters of such plots can be used to

characterize the P retention properties of the soils. Depending on the type of graphs obtained, different terminology can be employed but in the end all that is important is how much of the applied P a particular soil sorbs before available P in that soil is raised to sufficiency level and what is the ease of release of sorbed P to increase the plant available P. The commonly used terms in describing the soil P sorption properties are P retention capacity, P sorption maxima, P sorption (retention) index and P buffering capacity. The objectives of this study were to investigate the P retention and buffering capacities of the benchmark soils of Lesotho and to identify the principal soil factors that can be used to predict those P retention and buffering capacities.

4.2. Materials and methods

4.2.1. Soils and experimental procedure

All 56 soils described in Chapter 2 were used in this study. The layout was a factorial experiment with 11 soil series, five levels of P application, five soil phases (six for Rama series) and three replications arranged in a split–split plot design. Application levels of P were 0, 50, 100, 200 and 400 kg P ha^{-1}, hereafter referred to as P0, P50, P100, P200 and P400. The actual amounts of P applied to soils were calculated on the basis of the mass of a soil per 300mm hectare–furrow–slice, using the sample densities reported in Chapter 2.

Air–dried samples of the soils (< 2mm) were spread on plastic sheets, and 10ml solution of KH$_2$PO$_4$ containing the relevant amount of P was sprayed on them. After spraying, the soils were mixed thoroughly, poured into non–porous plastic containers and then wetted with distilled water to 85% water filled pore space that was calculated from an assumed particle density of 2650 kg m^{-3} and sample densities reported in Chapter 2. The total weight of the containers with the soils and water was recorded for each treatment sample, immediately after the water had disappeared from the top of the soils. Soils were then incubated for 42 days at room temperature, in the laboratory. During incubation, soils were subjected to three drying cycles by rewetting to the initial water content every fortnight, using the recorded weights for reference.

At the end of incubation each of the samples was mixed, air–dried and pulverized to pass a 2mm sieve. The P was extracted by the Bray procedure (Bray & Kurtz, 1945) and the Olsen procedure (Olsen *et al.*, 1954) and determined by the colorimetric method using the modified molybdenum blue colour complex of Murphy & Riley (1962). The two extraction procedures were chosen on the basis that they are very commonly used and are suitable for a wide range of soils, viz. Bray for acid and neutral soils and Olsen for acid to alkaline and calcareous soils (Olsen & Sommers, 1982).

4.2.2. Data analysis

The retained P for each treatment sample was calculated as the difference between an applied P and an extracted P that was corrected for P extracted from the control. Thereafter, the relative amount of P retained by each soil was calculated as a percentage of applied P. To investigate the phosphorus retention capacities of the soils retained P was plotted against applied P for every soil. All the plots showed linear increase in retained P as the level of applied P increased, with constant slopes that were used as the P retention index (PRI) of the soils. The linear relationships between retained and applied P means that maximum retention was never attained, therefore, the phosphorus retention capacities (PRC) of the soils were rather estimated from a single level of applied P, viz. P400. The retained P was also plotted against extracted P and logarithmic curves were obtained. The slopes of their linearized curves were used as the P buffering index (PBI) of the soils.

Variations in means of PRI, PRC at P400 and PBI between the series were tested with ANOVA, viz. general linear models and Tukey–Kramer multiple comparison test, using the NCSS 2000. Correlations between PRI, PRC at P400 and PBI were investigated using the correlation/regression analysis in Microsoft Excel. In addition, correlations and regressions were conducted between those three parameters and some soil properties reported in Chapter 2, which were known for their implication in P retention, using the simple linear, simple non–linear and multiple linear regression analyses with Microsoft Excel and NCSS 2000.

4.3. Results and discussions

4.3.1. General

This study revealed a very wide range of P retention by the benchmark soils of Lesotho, which is consistent with the wide variation in characteristics of these soils, as reported in Chapter 2. The proportions of applied P retained from each P application level by each of the 56 soils studied are given in Appendices 4.1 and 4.2 while other P retention parameters, viz. PRI, PRC at P400 and PBI as defined in Section 4.2.2, for all 56 soils are presented in Appendices 4.3 and 4.4.

In general, less applied P was retained against the Bray compared with the Olsen extractant in samples of most soil series except for the Fusi and Thabana series and a few samples of the Machache series. This implied that the Bray method had a higher reproducibility than the Olsen method in most of the soils. It therefore, supports the high preference for Bray to Olsen method in Lesotho (Badamchian *et al.*, 1991). The Bray method is principally suitable for acid and neutral soils while the Olsen method is suitable for acid to alkaline and calcareous soils (Olsen and Sommers, 1982). All soils in this study fell under acid to neutral soil pH (Chapter 2), hence are more suitable for Bray than Olsen.

In the case of the Bray method, 13 of the 56 soils were not responsive in terms of P retention to the P application regardless of the application level. In addition, four more soils were not responsive to the P application at P400, bringing the total number of soils not responsive to this level to 17. The 13 soils were Se1, Le2, Le3, Le4, Md2, Md3, Ba1, Ba2, Ba3, Ba4, Rm1, Rm3 and Rm6 and the other four were Le1, Rm2, Rm4 and Rm5. In the case of the Olsen method, however, all the soils were responsive to the P application at all application levels. Therefore, the results presented below are based on the analyses of only 43 or 39 soils respectively in the case of the Bray method and of all 56 soils in the case of the Olsen method.

4.3.2. Percentage of applied phosphorus retained against Bray and Olsen extractants

The distribution of the soils according to the percentage of retained P per level of application and on average is shown in Table 4.1 while the ranges and means of percentage of retained P across all the application levels for each benchmark soil series as well as the mean comparison between the series are summarized in Table 4.2.

Table 4.1. Distribution of the soils based on the percentage of retained P per level of application and on average.

| Retained P | Occurrence of the soils | | | | | | | | | |
| (%) | P50 | | P100 | | P200 | | P400 | | Mean | |
	Bray	Olsen	Bray	Olsen	Bray	Olsen	Bray	Olsen	Bray	Olsen
90 - 100	9	2	8	1	7	0	2	0	6	0
80 - 90	6	12	6	12	7	12	8	6	8	11
70 - 80	4	11	3	9	2	12	4	12	2	11
60 - 70	3	17	5	16	5	9	3	10	4	11
50 - 60	5	10	3	10	2	12	5	14	4	19
40 - 50	3	1	2	8	4	9	1	12	3	3
30 - 40	2	2	4	0	1	2	4	2	2	1
20 - 30	6	1	6	0	4	0	5	0	4	0
10 - 20	3	0	4	0	7	0	3	0	9	0
0 - 10	2	0	2	0	4	0	4	0	1	0
n	43	56	43	56	43	56	39	56	43	56

Across all the soils and application levels 6 to 97 and 21 to 91% of the applied P was retained against Bray and Olsen extractants, respectively. The amount of applied P retained against both extractants increased with the level of P application but the percentage retained P decreased with an increase in P application level. In the case of the Bray method it is interesting to note that except at P400, about one third of the soils retained 80% and more of the applied P, approximately another one third of the soils retained 40% and less and the remaining one third of the soils retained between 40 to 80%. In the case of the Olsen method the majority of the soils retained 40 to 90% of the applied P (Table 4.1).

According to the Tukey–Kramer mean comparison for percentage of retained P across the application levels there were significant differences between the benchmark soil series (Table 4.2). The Fusi, Thabana, Machache and Sefikeng series retained on average more

than 70% of the applied P against both extraction procedures. The Tumo series also retained, on average, more than 70% of the applied P against the Olsen extractant but less than 30% of the applied P against the Bray extractant. All six other soil series, viz. Khabos, Sephula, Berea, Matela, Rama and Leribe retained less than 50% of the applied P against the Bray extractant. The Sephula and Khabos series retained 41 and 48%, respectively whereas the rest of the soil series retained only 15 to 20%. In contrast, these soil series retained, on average, 52 to 63% of the applied P against the Olsen extractant. It was decided therefore, to regard the Fusi, Thabana, Machache, Sefikeng and Tumo series as the higher P retaining soil series and the Khabos, Sephula, Berea, Matela, Rama and Leribe series as the lower P retaining soil series for further discussion in this section.

Table 4.2. The ranges and means of the percentage of retained phosphorus across all the application levels for each benchmark soil series, and the mean comparisons between the series according to Tukey–Kramer.

Extraction Method	Soil series	Range	Mean
Bray	Thabana	62.45 - 96.64	87.16 d
	Fusi	56.98 - 95.36	84.18 d
	Machache	59.03 - 91.46	81.15 d
	Sefikeng	56.01 - 95.92	77.02 d
	Khabos	23.69 - 71.27	47.60 c
	Sephula	17.28 - 63.42	41.09bc
	Tumo	9.21 - 76.15	28.87ab
	Berea	9.14 - 27.79	19.54ab
	Matela	6.08 - 30.00	19.11 a
	Rama	6.12 - 43.98	17.62 a
	Leribe	7.60 - 30.83	14.67 a
Olsen	Sefikeng	65.94 - 89.93	83.37 e
	Machache	72.63 - 91.52	83.00 e
	Thabana	66.17 - 90.83	82.26 e
	Fusi	21.34 - 85.26	72.71 d
	Tumo	55.92 - 85.66	70.51cd
	Matela	54.08 - 80.16	62.75bc
	Khabos	34.22 - 70.41	57.94ab
	Berea	43.49 - 69.91	57.05ab
	Leribe	42.88 - 72.66	55.55ab
	Rama	38.61 - 69.31	54.11 a
	Sephula	31.87 - 66.70	52.01 a

Figures carrying the same letter in a column are not significantly different at 0.050 probability level or less.

The higher P retaining soil series, viz. Fusi, Machache, Sefikeng, Thabana and Tumo occupy the highest positions in the country, normally on the lower mountains and foothills, at an elevation above 1800m. These soil series receive the highest mean annual precipitation of about 800mm or more, are formed from basaltic colluvium and residuum and had higher contents of clay and organic carbon than the rest of the soils (Chapter 2). However, they had variable mineralogical properties. The black soil series, Fusi and Thabana, contain moderate to abundant montmorillonitic and small quantities of kaolinitic clays whereas the reddish brown soil series, Machache, Sefikeng and Tumo, contain kaolinitic clays in moderate to abundant amounts (Cauley, 1986). It was, therefore, obvious that P retention in these series was more attributed to clay content and perhaps organic carbon content than clay type. Noteworthy is a strange behaviour of the series Khabos, which has more clay and OC than the Tumo series (Chapter 2) but a lower P retention. The explanation if this behaviour of the Khabos series is, however, beyond the scope if this study.

Furthermore, it was very likely that rainfall had had some considerable influence on P retention in these soils. Under alternate wetting and drying caused by occasions of high rainfall, fresh Fe hydrous oxides are repeatedly formed through redox reactions. The free Fe oxides, which are formed on drying of previously wetted soils, have a large fresh surface area and thus a high affinity for P sorption (Fordham & Norrish, 1974; 1979; Phillips, 1998). It is, therefore, suggested that high rainfall was accountable for a high content of amorphous and free Fe oxides in Fusi, Machache, Sefikeng, Thabana and Tumo (Chapter 2) and hence strong P retention properties of these soil series. McIntoch & Whitton (1988) and Bainbridge et al. (1995) had reported a high P retention associated with high rainfall.

On the other hand, all the lower P retaining series, viz. Khabos, Sephula, Berea, Matela, Rama and Leribe occur in the western lowlands where the mean annual precipitation never exceeds 800mm. As reported in Chapter 2, they all had lower contents of clay, organic carbon and of amorphous and free Fe and Al oxides than the higher P sorbing series which should explain their relatively low P retention. These soil series were derived from different parent rock materials and their mineralogical composition is very variable. The Khabos and

Sephula series contain montmorillonite and a mixture of montmorillonite, kaolinite and quartz, respectively while the rest of the soil series contained mainly kaolinite (Cauley, 1986). It can, therefore, be deduced that even in these low P sorbing soil series clay type was not the main factor influencing P retention.

Furthermore, there was evidence of a high P retention in soils dominated by 2:1 silicate clay minerals as in those dominated by 1:1 silicate clay minerals in this study. In another study on some soils of Kwazulu-Natal, Johnston et al. (1991) noticed that P retention was higher in soils rich in 2:1 than in those rich in 1:1 silicate clay minerals. Both in this study and in the study of Johnston et al. (1991) the soils rich in 2:1 silicate clay minerals were not as widely represented as were the soils predominated by the 1:1 silicate clay minerals. Therefore no argument can be made regarding this situation. Nevertheless, it is concluded that, for the present study, P retention was mainly a function of clay content because, despite their difference in mineralogy, the high P retaining soils have fairly equal clay contents.

4.3.3. Relations between retained and applied phosphorus

When retained P was plotted against applied P linear relationships were observed for all the soils and for both the Bray and Olsen methods so that all the data were fitted with simple linear regression models. Their coefficients of determination, viz. r^2 values were in the order of 0.40 to 1.00 for the Bray method and 0.96 to 1.00 for the Olsen method, all significant at 0.050 probability level or less. Some selected plots showing the retention of P as an effect of P application are shown in Figures 4.1 and 4.2. As already mentioned, the slopes of the simple linear regression equations that described these relationships were used to express the potential of the soils to retain P, viz. PRI. The intercepts of the linear regression equations were interpreted as the amount of P already present in the soils as sorbed P before treatment, viz. initially sorbed P.

According to Bache & Williams (1971) the soil type and amount of initially sorbed P determine the retention of applied P by soils. In the present study, the amount of initially sorbed P had no effect on P retained against the Bray extractant, which was not the case for

the Olsen extractant at P50. The retention of P at this application level increased exponentially with the amount of initially sorbed P and the relationship was described by the equation $y = 8.17e^{0.035x}$ ($r^2 = 0.15$; P $\leq$ 0.01 and n = 56). The lack of correlation between initially sorbed P and P retained against the Olsen extractant at higher application levels supports the notion that the effect of initially sorbed P on total retained P could be overcome by using sufficiently large levels of P (Williams et al., 1958; Bache & Williams, 1971). If a small amount of P is added to soils, the proportion of initially sorbed P to the P finally sorbed becomes relatively larger than the proportion of added P that is sorbed. Subsequently, if the amount of initially sorbed P is not taken into consideration in the computation of the sorbed P the ultimate results of P sorption would be biased.

The initially sorbed P was also correlated linearly with PRI ($r^2 = 0.14$; P $\leq$ 0.001) in the case of the Olsen method. The inverse relationship between the initially sorbed P and the PRI indicated that soils with a large amount of P in their sorption matrix sorb applied P at a slower rate than soils with less P in their sorption matrix. There was no significant correlation between the initially sorbed P and the PRI in the case of the Bray method, which was consistent with lack of correlation between the initially sorbed P and P retained against the Bray extractant.
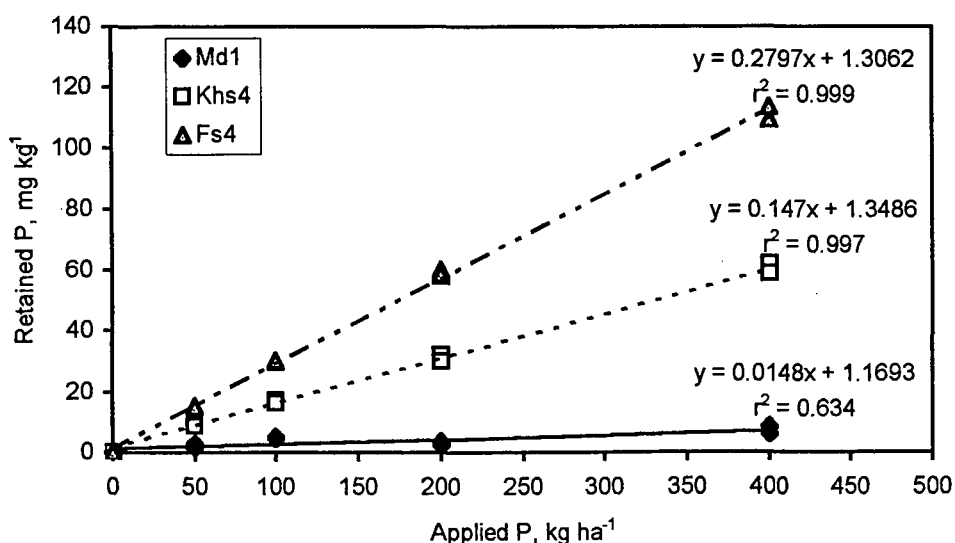
Figure 4.1. Selected plots of P retention in response to P application, each plot representing soils with large (Fs4), intermediate (Khs4) and small (Md1) slopes (Bray method).
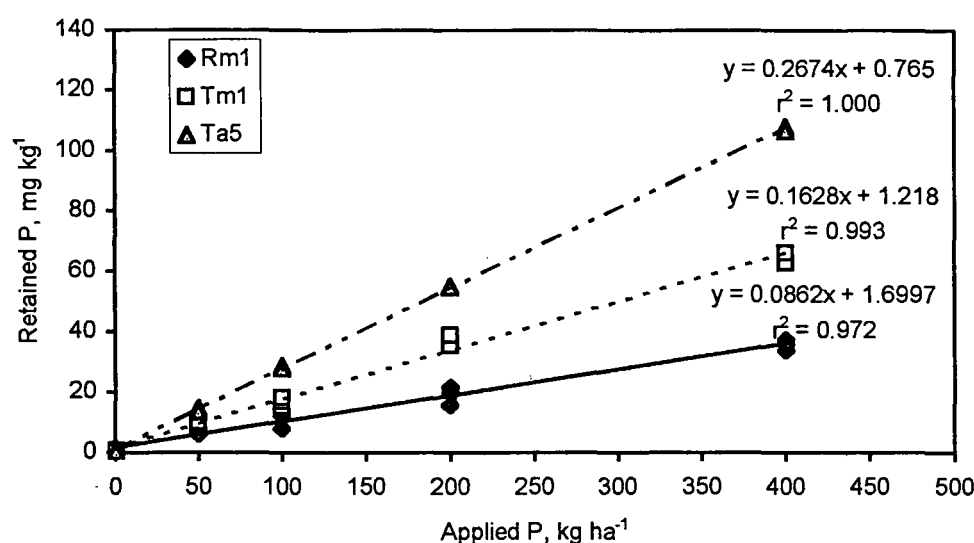
Figure 4.2. Selected plots of P retention in response to P application, each plot representing soils with large (Ta5), intermediate (Tm1) and small (Rm1) slopes (Olsen method).

Although the response of all the soils with regard to P retention was uniformly linear, the slopes of those linear plots for the different soils were extremely variable. A wide range of PRI's was, therefore recorded: $-0.04 - 0.28$ for the Bray method and $0.07 - 0.27$ for the Olsen method. That was an indication of a wide variation in the benchmark soils with respect to P retention, hence a problem on the management of P fertility in these soils. The PRI's determined by the Bray and Olsen methods were, however, strongly correlated ($r = 0.89$; $P < 0.0001$ for $n = 43$).

Soils with absolute Bray PRI's of zero to 0.01 had insignificant P retention at 0.050 probability level or less and therefore, together with those with negative PRI's even if they were statistically significant at 0.050 probability level or less were considered as non–sorbing soils and hence were not subjected to ANOVA. In total it was 13 of the 56 soils, viz. the same soils, which in terms of P retention did not respond to the P application regardless of the application level (see Section 4.3.1). In the case of the Olsen method all the soils had positive and significant PRI's and were, therefore, all subjected to ANOVA.

The distribution of the soils according to PRI is given in Table 4.3 while the ranges and means of PRI for each benchmark soil series as well as the mean comparison between the

71

series are presented in Table 4.4. Across all the soils the PRI's ranged from 0.013 to 0.280 for the Bray method and from 0.071 to 0.267 for the Olsen method. The distribution of the soils according to PRI (Table 4.3) was closely comparable to that according to percentage of retained P (Table 4.1). For instance, in the case of the Bray method, the PRI's of the soils are far more evenly distributed than in the case of the Olsen method. In the latter case 47 of the 56 soils have a PRI in the range of 0.10 to 0.25.

Table 4.3. Distribution of the soils according to their phosphorus retention index (PRI).

	Occurrence of the soils	
PRI	Bray method	Olsen method
0.25 - 0.30	5	2
0.20 - 0.25	9	13
0.15 - 0.20	4	14
0.10 - 0.15	5	20
0.05 - 0.10	9	7
0.01 - 0.05	11	0
n	*43*	*56*

The ranking of the soil series according to the PRI (Table 4.4) was also to a large extent very much the same as according to the percentage of retained P (Tables 4.2), particularly at the high ranks. Based on the Tukey–Kramer mean comparison for PRI, the benchmark soil series were grouped into two distinct classes in the case of the Bray method, viz. a fast and slow retaining class and into three distinct classes in the case of the Olsen method, viz. a fast, moderate and slow retaining class. The fast retaining classes consisted of the series Fusi, Thabana, Machache and Sefikeng for both extraction methods and the remaining series comprised the slow retaining class in the case of the Bray method. In the case of the Olsen method, the Tumo and Khabos series represented the moderate retaining class and the Rama and Sephula series represented the slow retaining class, with the Matela, Berea and Leribe series intermediate between these two classes. Thus, the higher P retaining Fusi, Thabana, Machache, Sefikeng and Tumo series consequently retained P faster than the lower P retaining Khabos, Sephula, Berea, Matela, Rama and Leribe series.

Table 4.4. The ranges and means of phosphorus retention index for each benchmark soil series and the mean comparisons between the series according to Tukey–Kramer.

Extraction method	Soil series	Range	Mean
Bray	Thabana	0.165 - 0.275	0.237b
	Fusi	0.153 - 0.280	0.230b
	Machache	0.160 - 0.258	0.221b
	Sefikeng	0.151 - 0.236	0.199b
	Khabos	0.062 - 0.147	0.104a
	Sephula	0.038 - 0.086	0.070a
	Tumo	0.020 - 0.140	0.055a
	Matela	0.015 - 0.059	0.044a
	Rama	0.013 - 0.037	0.027a
	Berea	*0.021	0.021a
	Leribe	0.019 - 0.019	0.019a
Olsen	Sefikeng	0.177 - 0.258	0.232 c
	Machache	0.199 - 0.246	0.227 c
	Thabana	0.191 - 0.267	0.225 c
	Fusi	0.184 - 0.243	0.215 c
	Tumo	0.141 - 0.172	0.164 b
	Khabos	0.149 - 0.173	0.163 b
	Matela	0.120 - 0.180	0.142ab
	Berea	0.093 - 0.140	0.118ab
	Leribe	0.105 - 0.125	0.117ab
	Rama	0.086 - 0.144	0.109 a
	Sephula	0.071 - 0.129	0.108 a

Figures carrying the same letter in a column are not significantly different at 0.050 probability level or less;
* ≡ only one soil sample for the series was significantly responsive.

4.3.4. Phosphorus retention capacity from a constant application level.

Since the plots of retained P against applied P were linear, it was impossible to determine the PRC of the soils from the graphs. The linear increase in retained P with applied P indicated that the levels of P added to the soils were not large enough to satisfy the PRC of the soils studied. Perhaps a wider range, including levels greater than the 400 kg P ha^{-1} would be necessary to attain graphs with a plateau. With such graphs, maximum retained P could be read straight from the regression lines, as the value on the y–axis perpendicular to the tangent of the plateau. The maximum retained P would, therefore represent the PRC of the soils, and the level of P application from which it would be obtained could also be

extrapolated from the graphs.

Under the circumstances, PRC was estimated with a method that does not use the P sorption curves. The method chosen was the simple single–point method (Bache & Williams, 1971) which uses the principle of estimating and comparing the P retention capacities of soils from a constant level of P application. This method is very simple as opposed to the laborious traditional P sorption method that requires several points for P sorption isotherms. A few points are important to remember when using this method to compare the soils for their PRC's, however. One is that a sufficiently large addition of P is necessary or otherwise, if a small amount is used all the soils will sorb most of the added P and eventually it will not be easy to distinguish between the low and the high P sorbing soils (Williams *et al.*, 1958; Bache & Williams, 1971). Another point is that an addition of an excessively large amount of P should be avoided as this could lead to the sorption capacity of the soils being saturated to an artificial level and hence the sorption results being inaccurate (Johnston *et al.*, 1991).

Table 4.5. Correlation coefficients between phosphorus retention index and phosphorus retained against Bray and Olsen extractants at different phosphorus application levels.

Application level	Correlation coefficients			
	Bray method		Olsen method	
P50	0.962	(n = 43)	0.768	(n = 56)
P100	0.973	(n = 43)	0.925	(n = 56)
P200	0.994	(n = 43)	0.979	(n = 56)
P400	1.000	(n = 39)	0.998	(n = 56)

All the correlation coefficients were significant at $P \leq 0.0001$.

An application level from which the PRC of the soils was estimated was sought by running correlations between the PRI and retained P at different P application levels to find the application level that gave the highest correlation coefficients (Table 4.5). As illustrated in Table 4.5, PRI was highly and strongly correlated with the actual P retained against both the Bray and Olsen extractants and the correlation improved as the level of added P increased. At lower application levels, correlations were variable between the two extraction methods but at the highest application level they were almost the same for both extraction methods. Therefore, PRC of the soils was estimated and compared at P400. Noteworthy is that due to

the linearity of the relationships between the retained and applied P up to the highest P application level (Figures 4.1 and 4.2) the P400 was not necessarily excessively too large. Thus, this level was chosen with an understanding that it would not artificially saturate the sorption capacity of the soils.

The percentage of retained P rather than the actual amounts of retained P, viz. mg P kg^{-1} of soil, was used to express the PRC at P400 because the actual amount of retained P was determined by the actual amount of P initially added to each soil which varied depending on the sample density of each soil. Again, since 17 of the 56 soils did not respond to the P application at P400 in the case of the Bray method (Section 4.3.1) only 39 soils were considered in the estimation of the PRC at P400 using the Bray method. In the case of the Olsen method, however, PRC at P400 was estimated for all 56 soils.

The distribution of the soils according to PRC at P400 is shown in Table 4.1 while the ranges and means of PRC at P400 as well as the mean comparison between the series are presented in Table 4.6. A much wider range of PRC at P400 was recorded for the Bray method, viz. from 8 to 92% than for the Olsen method, viz. 32 to 89% (Appendices 4.3 and 4.4). Again, in the case of the Bray method the soils' PRC at P400 are far more evenly distributed than in the case of the Olsen method (Table 4.1). This was consistent with the percentage of retained P across the application levels and PRI previously discussed in Sections 4.3.2 and 4.3.3, respectively. There was, however, a strongly correlation between the Bray and Olsen methods with respect to PRC's at P400 with r = 0.81; P < 0.0001 and n = 39.

The order of the benchmark soil series according to PRC at P400 (Tables 4.6) was very much the same as according to PRI (Tables 4.4) and even to percentage retained P (Tables 4.2). In the case of the Bray method three distinct groups were indicated, viz. the Thabana, Fusi, Machache and Sefikeng series with a high PRC at P400, the Khabos, Sephula, Tumo, Matela, Berea and Leribe series with a low PRC at P400 and the Rama series with no PRC at P400. In the case of the Olsen method three groups were also indicated, viz. the Machache, Sefikeng and Thabana series with a high PRC at P400, the Fusi, Tumo, Khabos, Matela, Berea and Leribe series with varying intermediate PRC at P400 and the Rama and

75

Sephula series with a low PRC at P400.

Table 4.6. The ranges and means of PRC at P400 in percent, for each benchmark soil series and the mean comparisons between the series according to Tukey–Kramer.

Extraction method	Soil series	Range	Mean
Bray	Thabana	62.45 – 90.36	83.23b
	Fusi	56.98 – 91.61	80.83b
	Machache	59.03 – 92.31	78.59b
	Sefikeng	56.01 – 81.57	69.07b
	Khabos	23.69 – 56.67	39.14a
	Sephula	17.28 – 39.34	30.56a
	Tumo	7.93 - 56.32	22.31a
	Matela	7.98 - 23.62	18.02a
	Berea	* 9.14 -	9.14a
	Leribe	* 8.18 -	8.18a
	Rama	–	–
Olsen	Machache	77.93 - 84.05	80.96 e
	Sefikeng	65.94 - 88.86	79.71 e
	Thabana	71.52 - 85.72	79.20 e
	Fusi	67.61 - 80.44	74.81 de
	Tumo	59.62 - 70.19	65.94 cd
	Khabos	57.54 - 64.28	60.25 bc
	Matela	53.33 - 69.14	58.26abc
	Berea	43.49 - 60.50	50.18 ab
	Leribe	42.88 - 50.75	48.13 ab
	Rama	38.61 - 58.08	46.80 a
	Sephula	31.87 - 55.69	46.57 a

Figures carrying the same letter in a column are not significantly different at 0.050 probability level or less;

– ≡ not subjected to ANOVA because the whole series was not responsive to P the application at P400;

* ≡ one soil sample only for the series was significantly responsive to the P application at P400.

This principle of estimating PRC from a constant application level confirmed the previous results on PRI that the Fusi, Thabana, Machache and Sefikeng series have a significantly similar and stronger P retention than the other series, particularly in the case of the Bray method. The Fusi, Thabana, Machache and Sefikeng series have the highest P retention in the case of the Olsen method even though P retention for the Fusi series was not significantly different from the P retention for the Tumo series. The series Rama and Sephula had the least P retention while Khabos, Leribe, Matela and Berea had intermediate

76

P retention in the case of the Olsen method. The correlation between PRC at P400 and PRI was very high (r = 1.00 for both Bray and Olsen) which was a good suggestion for an appropriate use of PRI for characterizing P retention by the benchmark soils of Lesotho. This PRI is practically identical to, though the opposite of, the phosphorus desorption index (PDI) of Reeve & Sumner (1970). In their studies, Johnston *et al* (1991) found that among all the other factors the PDI was best correlated with the amount of P required to raise the level of soil P by unity, which was also used as an index of P sorption. Thus, as Wild (1988) indicated, the PRI and PDI detected by sorption/desorption studies could become a very handy tool when advising on the use of P fertilizer, particularly on soils which vary greatly in P sorption.

Another alternative method for determining and/or comparing P retention of soils, which does not involve the use of sorption isotherms, is to use the principle of estimating and comparing the amount of P retained (x) at the same P equilibrium concentration of P (c) remaining in solution after a single addition of P and shaking for some time (Bache & Williams, 1971). This principle is, however, violated by the fact that when large amounts of P are added to soils both the solid and liquid phases of the soil P are affected variably depending on the type of the soil. This is why normally the quotient x/c or $x/logc$ is used instead of x to indicate the sorption (Bache & Williams, 1971; Johnston *et al.*, 1991; Guertal *et al.*, 1991; Agbenin & Tiessen, 1995; Indiati *et al.*, 1995). In fact, $x/logc$ is preferred to x/c because in order to convert the normal curvilinear P sorption isotherms to straight line graphs with constant slopes, either the P concentration is plotted on a logarithmic scale (Fox & Kamprath, 1970; Bache & Williams, 1971; Bainbridge *et al.*, 1995) or the $logc$ is used instead of c in equations describing the curved P sorption isotherms (White & Beckett, 1964; Barrow *et al.*, 1965). In the present study, however, this principle was not used because it requires a method different from the one used for this study.

4.3.5. Relations between retained and extracted phosphorus

When the retained P was plotted against the extracted P curvilinear relationships were obtained for all the soils and for both extraction methods. Those relationships were best described by a logarithmic regression equation of the Tempkin format (Hayward &

Trapnell, 1964), viz. $y = a + b lnx$: where y was the retained P and x was the extracted P, both in mg P kg^{-1} of soil. The constants a and b are the intercept and slope, respectively and lnx is the affinity term. The coefficients of determination (r^2) for the logarithmic models ranged from 0.30 to 0.99 for the Bray method and from 0.43 to 0.98 for the Olsen method, and all were significant at 0.050 probability level or less. Plots of some selected soils are shown in Figures 4.3 and 4.4.

According to this model, P retention increased with the increase in the pool of labile P but decreased as the affinity for P and the sorption capacity diminished. This is a typical characteristic of adsorption in which as more P becomes adsorbed the sorption capacity for P diminishes as is the affinity of the adsorbing surface for additional P (Hayward & Trapnell, 1964; Barrow, 1978). These two terms, viz. affinity and sorption capacity, decrease with every additional increment of P that is retained, which is in turn subject to an increase in adsorbed and/or precipitated P, which is, again, in turn affected by the increase in the soil solution P. Noteworthy is that in this study, x represented extractable P, which consisted of the soil solution P, adsorbed P and P in the readily soluble phosphate precipitates, all of which constitute labile P.

When the extracted P was plotted on a log scale, straight line graphs with constant slopes were obtained (Figures 4.5 and 4.6). The slopes of those graphs indicated the P buffering indices (PBI's) of the soils. In many P sorption studies, the slope of P sorption isotherms expresses phosphorus buffering capacity (PBC) of the soils (Barrow, 1967; Fox & Kamprath, 1970; Bache & Williams, 1971; Bainbridge et al., 1995). Since the method used to assess P retention in the present study differed from that normally used whereby soil samples are shaken in P solutions of varying strength, it was decided that the slope of retained P against extracted P be termed PBI rather than PBC. From an agronomic point of view, PBC or PBI is an important factor indicating the capacity of the soil to replenish the soil solution P during plant growth.

The 13 soils which, in the case of the Bray method were not responsive to the P application regardless of the application levels (Section 4.3.1) and also had negative or PRI's of less than 0.01 (Section 4.3.3), again had Bray PBI's below zero, most of which were not
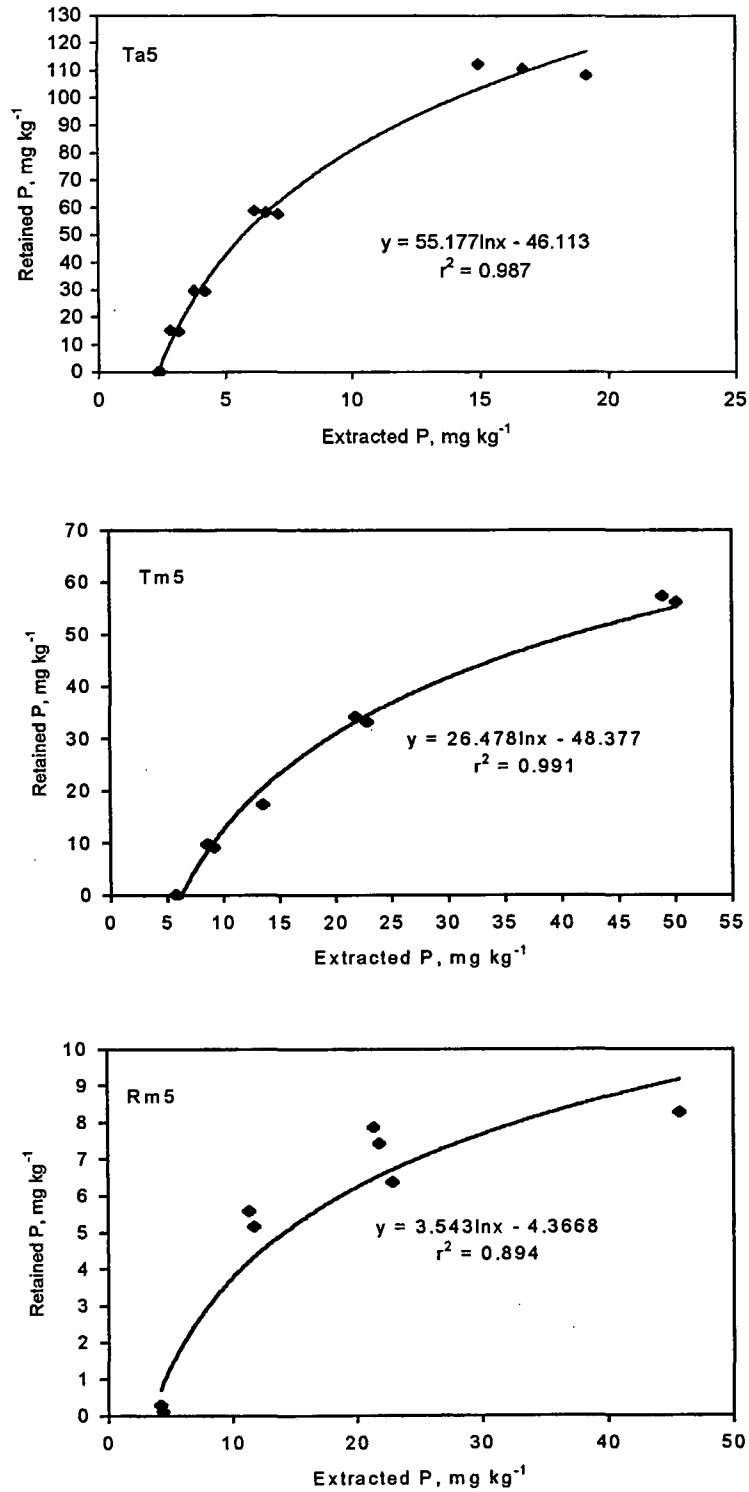
Figure 4.3. Selected plots of retained P against extractable P, each plot representing soils with large (Ta5), intermediate (Tm5) and small (Rm5) slopes (Bray method).
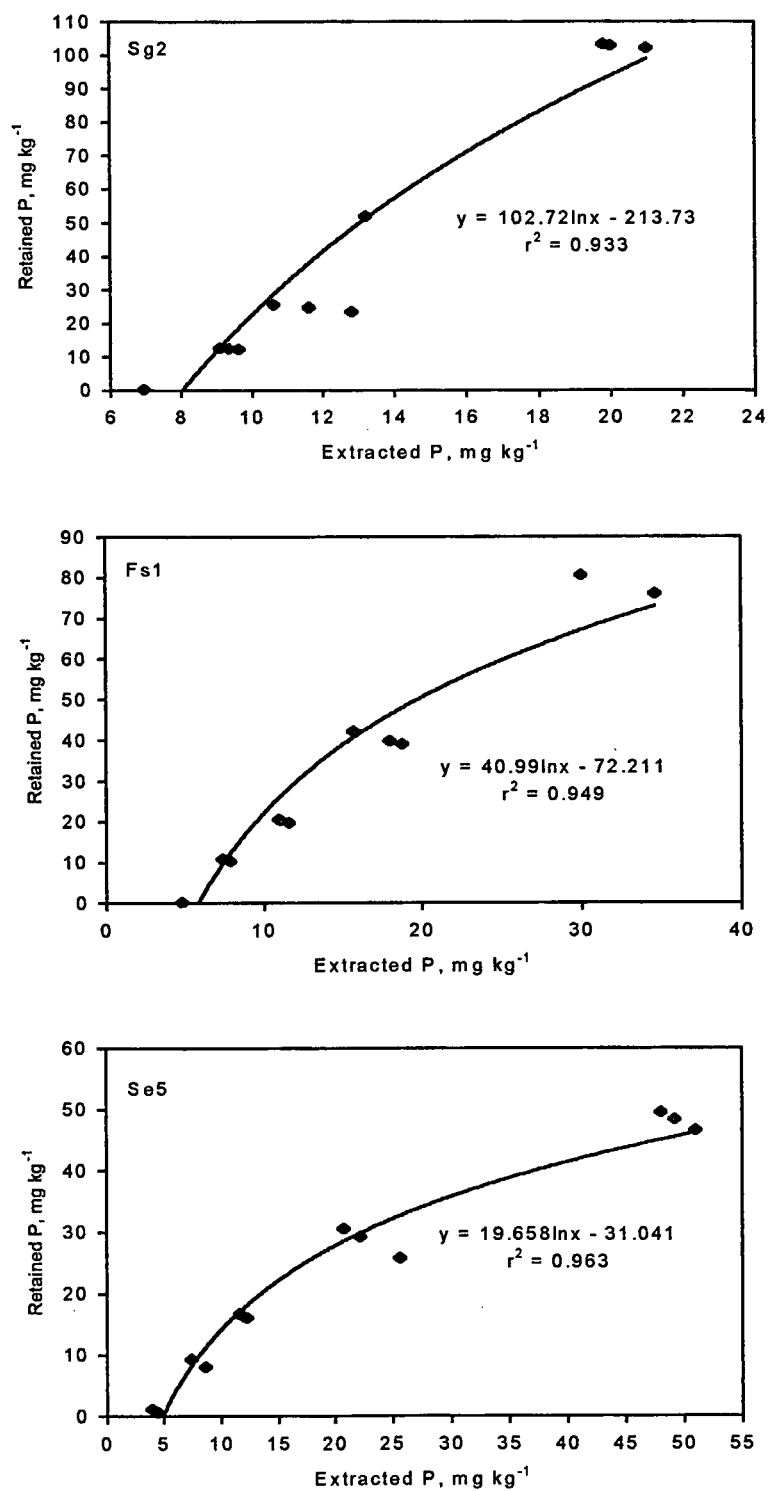
Figure 4.4. Selected plots of retained P against extractable P, each plot representing soils with large (Sg2), intermediate (Fs1) and small (Se5) slopes (Olsen method).
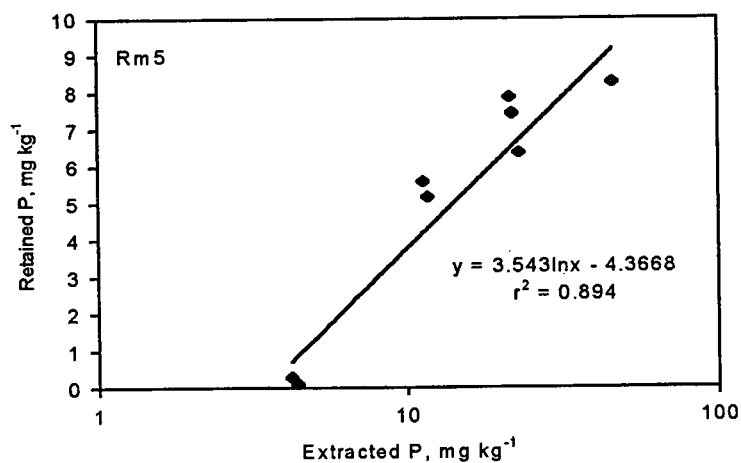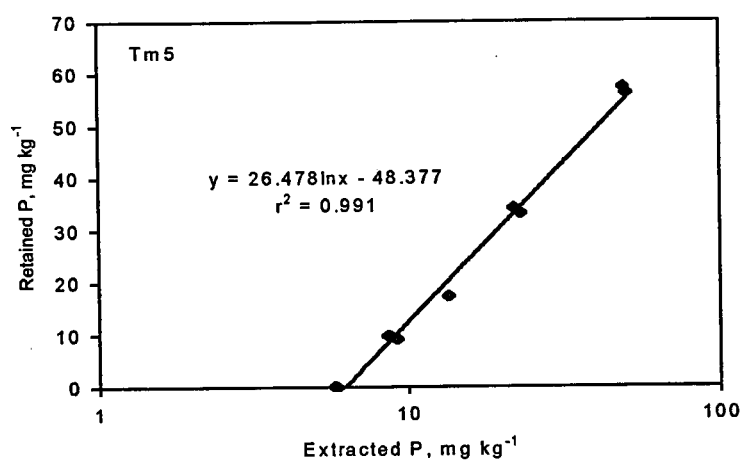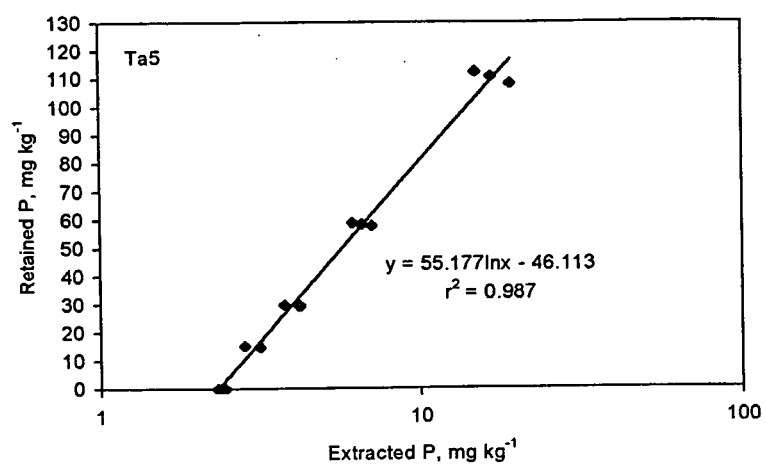
Figure 4.5. Selected linearized plots of retained P against extractable P (Bray method).
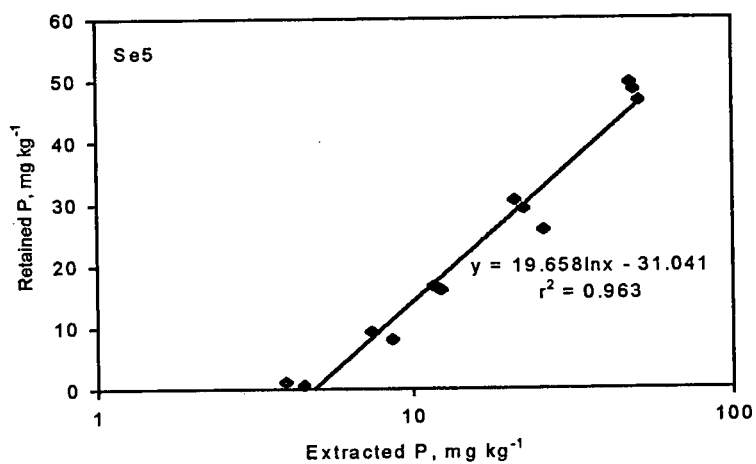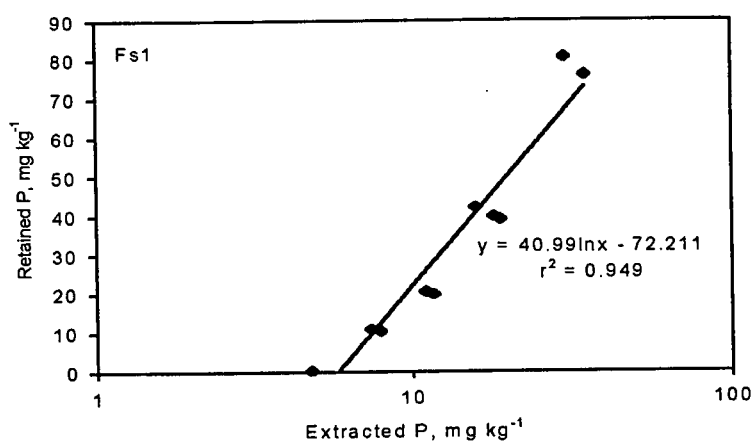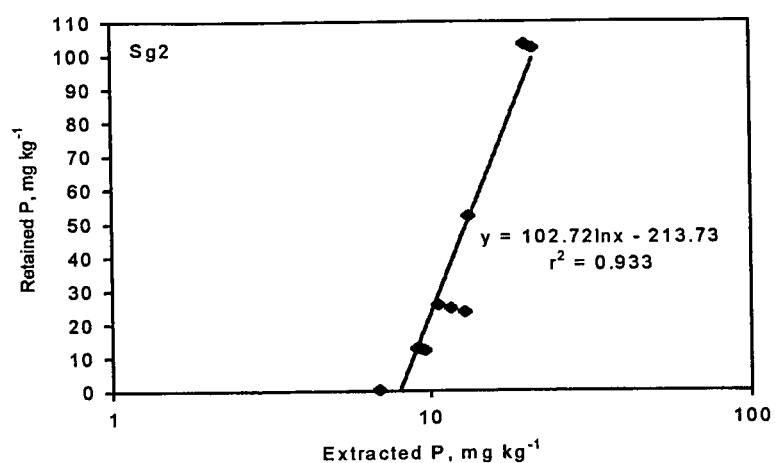
Figure 4.6. Selected linearized plots of retained P against extractable P (Olsen method).

significant at 0.050 probability level or less. Therefore, they were excluded from the soils that were used to estimate the P buffering properties using the Bray extraction method. In the case of the Olsen method, however, all the soils had positive and significant PBI's. Table 4.7 presents the distribution of the soils according to PBI while Table 4.8 presents the ranges and means of PBI for each benchmark soil series as well as the mean comparison between the series.

Table 4.7. Distribution of the soils according to the phosphorus buffering indices (PBI's).

| PBI | Occurrence of the soils | |
	Bray method	Olsen method
100 – 110	0	1
90 – 100	0	0
80 – 90	0	1
70 – 80	0	0
60 – 70	0	2
50 – 60	2	7
40 – 50	5	15
30 – 40	13	9
20 – 30	5	14
10 – 20	4	7
0 – 10	14	0
n	*43*	*56*

The distribution of the soils according to the PBI was still consistent with the distributions according to the other P retention parameters, viz. percentage of retained P across the application levels, PRI and PRC at P400. A large number of soils occurred at the lower end of the range in the case of the Bray method, which was not the case for the Olsen method (Tables 4.1, 4.3 and 4.7). This was quite acceptable because the higher the P retention capacity of a soil the stronger the P buffering capacity of that soil.

The range of the PBI was, however, narrower in the case of the Bray method than in the case of the Olsen method unlike the ranges of the percentage of retained P across the application levels, PRI and PRC at P400, which were narrower in the case of the Olsen method than in the case of the Bray method (compare Tables 4.2, 4.4, 4.6 and 4.8). The PBI's of 2 to 55 were recorded for the Bray method whereas for the Olsen method the PBI's of 12 to 103 were recorded. In the case of the Bray method about 33% of the soils had

PBI's of less than 10 and the remaining 67% of the soils had PBI's of 10 to 60. On the contrary, in the case of the Olsen method about 90% of the soils had PBI's of 10 to 60 and the remaining 10% of the soils had PBI's of more than 60. The correlation between the Bray and Olsen methods with respect to the PBI's was still strong (r = 0.72; P < 0.0001 for n = 43).

Table 4.8. The ranges and means of the phosphorus buffering index for each benchmark soil series and the mean comparisons between the series according to Tukey–Kramer.

Extraction method	Soil series	Range	Mean
Bray	Thabana	33.98 - 55.18	43.32 d
	Machache	32.96 - 45.67	39.21cd
	Fusi	31.63 - 46.23	37.76cd
	Sefikeng	21.65 - 50.54	35.14cd
	Khabos	17.52 - 31.25	25.16bc
	Tumo	5.14 - 26.48	12.73ab
	Sephula	4.75 - 18.36	8.02ab
	Matela	2.49 - 10.33	7.08 a
	Berea	* 5.65 -	5.65 a
	Rama	2.07 - 6.08	3.90 a
	Leribe	2.65 - 4.99	3.82 a
Olsen	Sefikeng	46.29 - 102.72	62.62 d
	Thabana	37.16 - 84.61	56.40 d
	Machache	45.46 - 63.16	52.39 d
	Tumo	35.51 - 54.97	45.21 cd
	Khabos	35.08 - 47.89	43.84bcd
	Fusi	34.74 - 49.36	42.47bcd
	Matela	20.02 - 37.82	28.35 bc
	Berea	20.08 - 32.04	28.26abc
	Leribe	22.78 - 30.94	27.47abc
	Rama	12.35 - 29.82	23.10 ab
	Sephula	12.55 - 26.39	19.34 a

Figures carrying the same letter in a column are not significantly different at 0.050 probability level or less; * ≡ only one soil sample for the series was significantly responsive.

In contrast to the percentage of retained P across the application levels, PRI and PRC at P400, the Tukey–Kramer mean comparison for the PBI indicated considerable integration of the series which made it difficult to separate them into distinct groups in both extraction methods (Table 4.8). Nevertheless, the order of the soil series according to the PBI was

relatively similar to that according to the percentage of retained P, PRI and PRC at P400 in Tables 4.2, 4.4 and 4.6, respectively. In the case of the Bray method, the fast and higher P retaining Fusi, Thabana, Machache and Sefikeng series had PBI's of 35 to 43 and the rest of the series which were slow and low in P retaining, had PBI's of 4 to 25. In the case of the Olsen method the moderate to fast and intermediate to higher P retaining Fusi, Khabos, Thabana, Machache, Sefikeng and Tumo series had PBI's of 42 to 63 whereas the slow and lower P retaining Matela, Berea, Leribe, Rama and Sephula series had PBI's of 19 to 28.

Considering that PRI defined the capacity of the soils for P retention and PBI defined the capacity of the soils to maintain an equilibrium between quantity and intensity factors, it was found that soils that exhibited high PBI were more or less those that had high PRI and vice versa. The correlation coefficients between the PBI and PRI were 0.94 for the Bray method and 0.81 for the Olsen method (both significant at $P < 0.0001$). The PBI was also closely related to the PRC at P400 (Figures 4.7 and 4.8). All these correlations confirm that soils with high P retention capacity have high P buffering capacity and better chances to support a stronger concentration of plant available P for a longer period than the soils with low P retention and buffering capacities. Therefore, PRI, PRC at P400 and PBI were considered as the three main interrelated P retention properties and any one of them can be used to express and/or compare P retention of the soils.

While most of the work on the soils of Lesotho (Cauley, 1986; Schmitz and Rooyani, 1987; Arduino et al., 1993) shows that only the Machache and Sefikeng series have a high P retention capacity, the present study revealed high P retention in the Thabana, Fusi and Tumo series as well. Since Tumo and Sefikeng are both variants of Machache, it would be expected that the Tumo series also have a high P retention but this has never previously been established. Another possibility was that it was very likely that the high preference for use of the Bray extractant only in Lesotho had masked the high P retention capacity of this soil series, as it had indeed in the present study. In this study only the Olsen method indicated high P retention in the Tumo series. In case of Fusi and Thabana series, it should be borne in mind that Arduino et al. (1993) worked with the alfisols and inceptisols only, but not the vertisols (Thabana) or mollisols (Fusi), which is probably why they never reported the high P retention in these two series.

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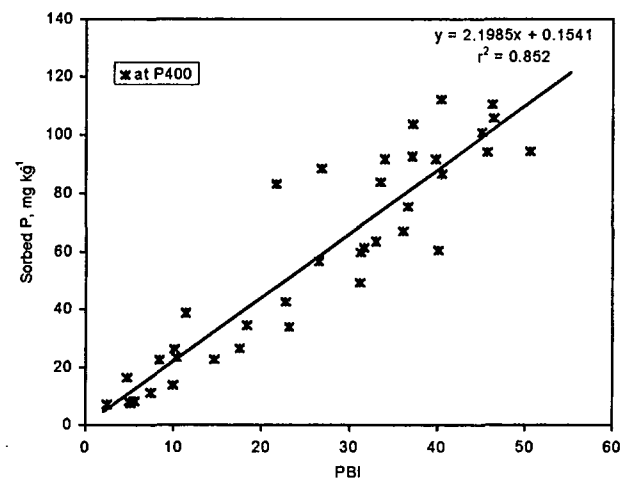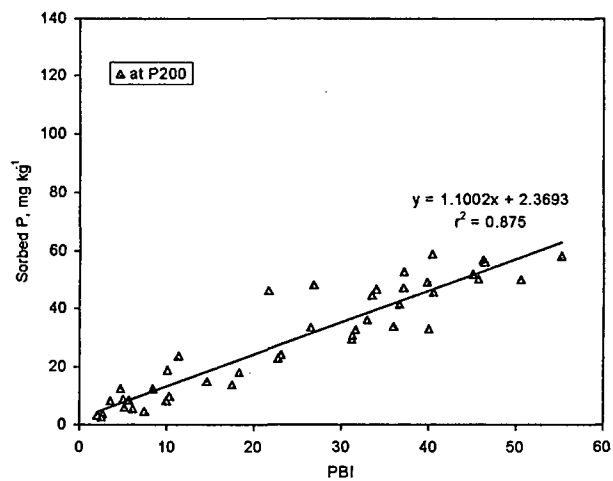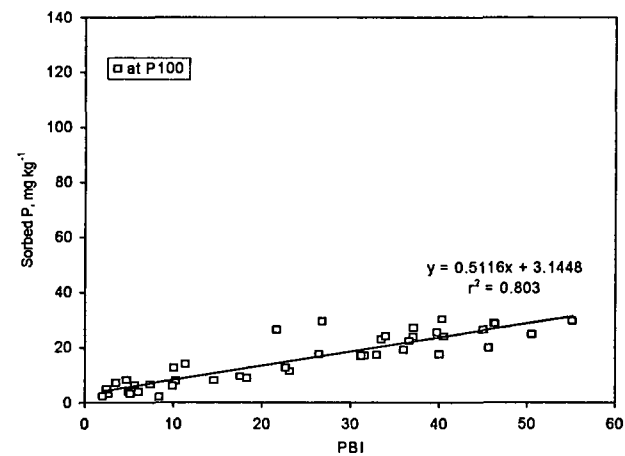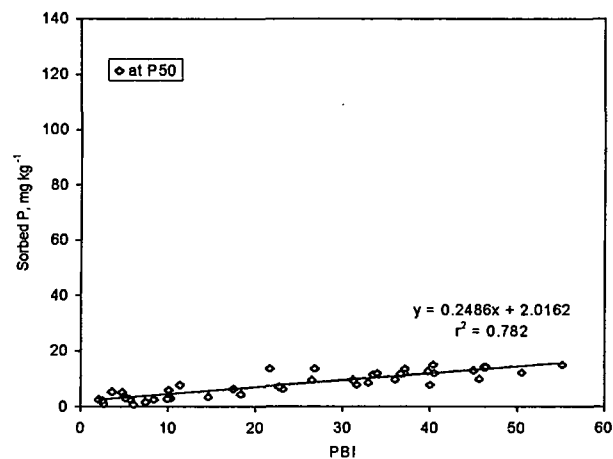
Figure 4.7. Relationships between PBI and P sorbed at different application levels (Bray method).
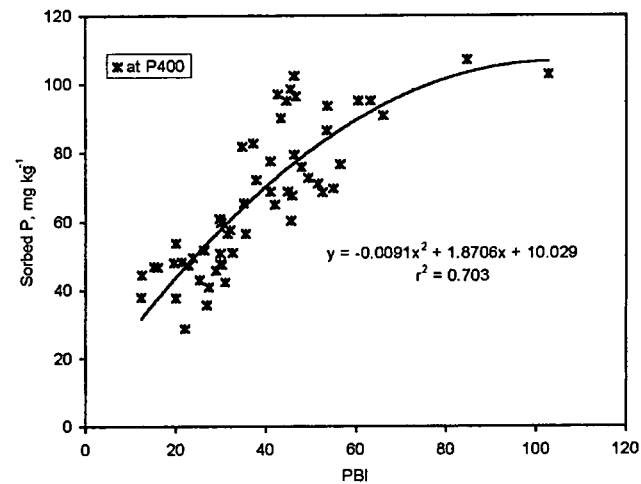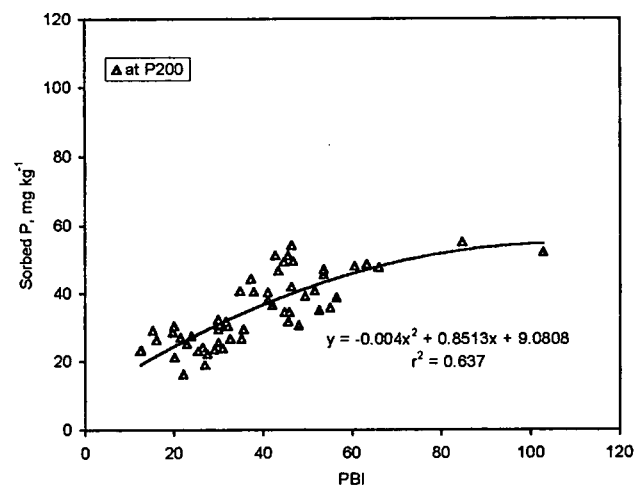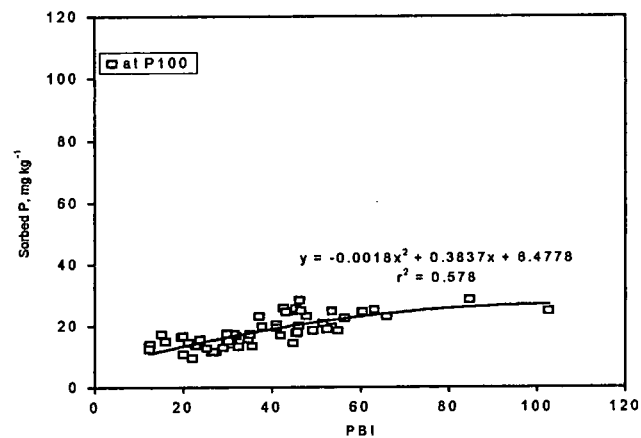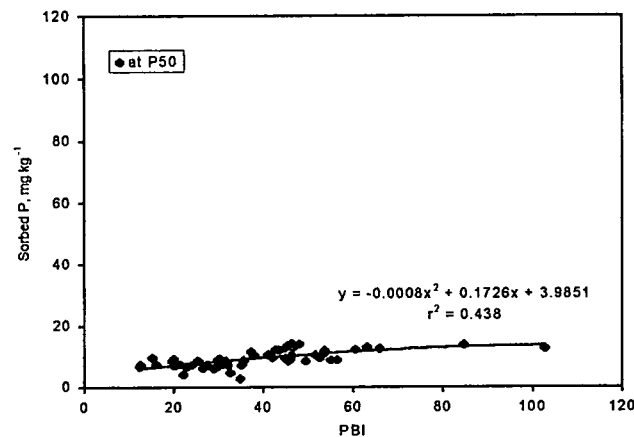
Figure 4.8. Relationships between PBI and P sorbed at different application levels (Olsen method).

4.3.6. Relationships between phosphorus retention properties and other properties of the soils

The relationships between the P retention properties, viz. PRI, PRC at P400 and PBI and other soil properties like sample density (ρ_s), pH, the contents of sand, silt, clay, OC, amorphous Fe and Al (determined by acid oxalate method, Fe_o and Al_o), free Fe and Al oxides (determined by citrate bicarbonate dithionite method, Fe_d and Al_d), CEC–clay (CEC^c), CEC of the soil hereafter referred to as CEC, exchangeable bases (Ca, Mg, K, Na), total exchangeable bases (TEB), base saturation (BS), acid saturation (AS) and the extractable P prior to treatment hereafter referred to as extractable P, were investigated. Except for pH and Al_d, all the other properties were significantly correlated with the three P retention properties. Table 4.9 shows the coefficients of determination (r^2 values) obtained with different simple regression models that were used to describe the effects of some soil properties on the PRI, PRC at P400 and PBI determined by the Bray and Olsen methods, ranked in their decreasing order.

More than 60% of the variation in PRI, PRC at P400 and PBI determined by the Bray method could be attributed to the contents of sand, clay, OC, CEC, Fe_o and Al_o, and to ρ_s (except for PBI). Similarly, those seven soil properties as well as Fe_d also explained more than 60% of the variation in PRI and PRC at P400 in the case of the Olsen method. However, only the contents of clay, Al_o and Fe_d explained more than 60% of the variation in PBI determined by the Olsen method. These results agreed with the results from other studies where P retention was mainly correlated to clay content, OM, amorphous and free oxides of Fe and Al and sample density (Ahenkorah, 1968; Syers *et al.*, 1971; Juo & Fox, 1977; Lopez–Hernandez & Burnham, 1974a; Fordham & Norrish, 1974; 1979; Wada & Gunjigake, 1979; Haynes, 1984; Hughes & Hornung, 1987; Loganathan *et al.*, 1987; Johnston *et al.*, 1991; Soon, 1991; Arduino *et al.*, 1993; Brennan *et al.*, 1994; Bainbridge *et al.*, 1995). Significant correlation between P retention and soil pH is not always found particularly for soils varying in many aspects (Lopez–Hernandez & Burnham, 1974b) but pH has a profound influence on P retention through its effects on the solubility of Fe, Al, Ca and Mg which react with P in soils. The lack of influence by Al_d on P retention in this study is ascribed to the low Al_d contents of the soils.

Table 4.9. The order of contribution from some soil properties to the variation in PRI, PRC at P400 and PBI as indicated by r^2 values which were all significant at $P \le 0.001$.

Extraction method	Rank	PRI	Model	PRC at P400	Model	PBI	Model
Bray	1	Sand = 0.75	linear	Sand = 0.76	linear	OC = 0.80	power
	2	Clay = 0.73	linear	Clay = 0.74	linear	Sand = 0.79	linear
	3	OC = 0.72	power	OC = 0.74	log	CEC = 0.77	power
	4	CEC = 0.72	power	Fe_o = 0.69	log	Clay = 0.77	linear
	5	Al_o = 0.68	linear	Al_o = 0.68	linear	Fe_o = 0.76	power
	6	Fe_o = 0.67	power	CEC = 0.68	log	Al_o = 0.67	linear
	7	ρ_s = 0.61	linear	ρ_s = 0.61	linear	ρ_s = 0.55	linear
	8	P = 0.50	log	P = 0.49	log	Ca = 0.44	log
	9	CEC^c = 0.40	power	TEB = 0.40	log	TEB = 0.43	log
	10	Mg = 0.40	power	Ca = 0.39	log	Mg = 0.42	log
	11	TEB = 0.40	power	Mg = 0.39	log	CEC^c = 0.38	power
	12	Ca = 0.39	power	Fe_d = 0.34	linear	Fe_d = 0.34	linear
	13	Fe_d = 0.34	linear	CEC^c = 0.29	log	Silt = 0.31	linear
	14	Silt = 0.31	exp	Silt = 0.29	linear	K = 0.28	power
	15	K = 0.21	power	AS = 0.13	linear	P = 0.25	log
	16	BS = 0.13	linear	BS = 0.13	linear	BS = 0.17	linear
	17	AS = 0.13	linear			AS = 0.16	linear
	n	43		39		43	
Olsen	1	Clay = 0.84	power	Clay = 0.82	linear	Clay = 0.72	power
	2	OC = 0.80	power	OC = 0.80	power	Al_o = 0.68	power
	3	Al_o = 0.76	linear	ρ_s = 0.77	linear	Fe_d = 0.65	power
	4	ρ_s = 0.76	linear	Al_o = 0.75	linear	OC = 0.58	power
	5	Sand = 0.70	linear	Fe_d = 0.69	power	Fe_o = 0.50	power
	6	Fe_d = 0.69	power	CEC = 0.69	power	ρ_s = 0.49	exp
	7	CEC = 0.68	power	Sand = 0.69	linear	Sand = 0.49	linear
	8	Fe_o = 0.63	power	Fe_o = 0.63	power	CEC = 0.45	power
	9	TEB = 0.33	power	TEB = 0.34	power	K = 0.26	power
	10	Mg = 0.33	log	Mg = 0.33	log	TEB = 0.22	power
	11	Ca = 0.32	power	Ca = 0.33	power	Ca = 0.22	power
	12	Silt = 0.28	linear	K = 0.28	power	Silt = 0.20	linear
	13	K = 0.27	power	Silt = 0.27	linear	Mg = 0.20	power
	14	CEC^c = 0.20	power	CEC^c = 0.22	power		
	15	P = 0.20	exp	P = 0.19	exp		
	n	56		56		56	

linear: $y = a + bx$, log: $y = a + b\ln x$, power: $y = ax^b$ and exp: $y = ae^{bx}$.

The contributions of all those soil properties that singly had a significant influence on the P retention properties were detected simultaneously using a stepwise multiple regression analysis. TEB was excluded from this analysis because it is the sum of other properties. Multiple linear regression models obtained and their r^2 values are shown in Table 4.10. According to this analysis, the order of importance of those soil properties in P retention, particularly for CEC, OC, Fe and Al compounds, K and extractable P changed when the soil properties were considered simultaneously. The contributions from OC and CEC to the variation in all three P retention parameters determined by either extraction method became insignificant. In contrast, the contributions from extractable P, especially in the case of the Bray method and from K but only in the case of the Olsen method, became more significant. Apparently, the soil properties which both singly and collectively had a significant influence on P retention were in decreasing order sand, extractable P, sample density (except for PBI) and Al_o for the Bray procedure and sample density, clay, Fe_d, extractable P, Fe_o and K for the Olsen procedure. Only clay and Fe_d collectively influenced PBI determined by the Olsen procedure. A detailed discussion on how these soil properties influence P retention is given in Chapter 1.

The multiple linear regression models given in Table 4.10 are proposed for future use to predict P retention based on either the Bray or Olsen extraction method from routine laboratory soil analyses. With the exception of Fe and Al oxides all the properties included in these models are determined in routine laboratory soil analysis. Besides, it is very interesting to note that sample density, a soil property determined by a very simple method (Johnston *et al.*, 1987) is also included in the regression models used to predict PRI and PRC at P400. The implication of sample density on P retention was established by Johnston *et al.* (1991) using similar soils to those used in this study. Although the procedures for determining Fe and Al oxides (Jackson *et al.*, 1986) are very laborious, at least they are not as long and laborious as the procedures for a P incubation experiment. Therefore, since the reason for establishing the soil properties that can be used to predict the P retention characteristics is to avoid those laborious and time consuming determinations (White, 1980; Johnston *et al.*, 1991; Agbenin & Tiessen, 1994), the establishment of soil properties and hence the models (Table 4.10) that can be used to predict P retention is considered a great

success for this study.

In order to cater for situations where it may not possible to determine the Fe and Al oxides, some partial models (without Fe or Al) were also obtained (Table 4.10). Their r^2 values were, in the case of the Bray and Olsen methods respectively, 0.01 to 0.02 and 0.04 to 0.10 units smaller than the r^2 values for the full models. It was, therefore, obvious that P retention properties based on the Bray procedure could still be predicted with a large degree of confidence from the soil properties other than Al_o. However, if P retention were based on the Olsen procedure, exclusion of Fe oxides from the regression models, particularly for predicting PBI could significantly reduce the precision of the results. The suggestion was, therefore, that it might not be necessary to go to the expense of determining Fe and Al oxides of soils in order to predict their P retention based on the Bray procedure. Even when P retention was based on the Olsen procedure, Fe and Al oxides might not be necessary unless the aim is specifically to predict P buffering properties of the soils. The soil properties that collectively describe the variation in P retention according to either the Bray or Olsen method when Fe and Al oxides were ignored were basically the same, viz. sand (Bray) and clay (Olsen) obtained from particle size analysis, sample density and extractable P. The only difference is that K was important if P retention was based on the Olsen procedure but, in terms of determination, this would not be a problem since exchangeable bases are always determined in routine laboratory soil analysis.

A note was made on the difference between the Bray and Olsen method on account of the soil properties implicated in the three P retention properties (that is, considering the full regression models) and because the Bray method is considered more appropriate than the Olsen method for the soils studied, the P retention results according to the Bray method rather than the Olsen method were more acceptable. Nevertheless, the P retention result according to the Olsen method could not be completely disregarded because there were some soils (e.g. those of Fusi and Thabana series and some of the Machache series) for which the Olsen extractant had a higher reproducibility than the Bray extractant. Based on the soil properties implicated in PRI and PRC at P400 determined by the Olsen procedure free Fe oxides have more influence than amorphous Fe oxides on P retention by the benchmark soil series of Lesotho as reported by Arduino *et al.* (1993).

Table 4.10. Multiple linear regression models for estimating the PRI, PRC at P400 and PBI of the benchmark soil series.

Model	Regression models and their r^2 values		Order of soil properties included in the models
	Bray method[2]		
Full	PRI = 0.4676 - 0.002499 sand - 0.003241 Bray P - 0.1798 ρ_s + 0.1770 Al_o;	$r^2 = 0.926$	Sand>P> ρ_s>Al_o
Partial	PRI = 0.5757 - 0.003121 sand - 0.003373 Bray P - 0.2200 ρ_s;	$r^2 = 0.916$	Sand>P> ρ_s
Full	PRC = 202.7 - 0.9835 sand - 1.307 Bray P - 81.65 ρ_s + 55.80 Al_o;	$r^2 = 0.940$	Sand>P> ρ_s>Al_o
Partial	PRC = 237.3 - 1.174 sand - 1.338 Bray P - 94.93 ρ_s;	$r^2 = 0.933$	Sand>P> ρ_s
Full	PBI = 47.03 - 0.6620 sand - 0.2567 Bray P + 40.56 Al_o;	$r^2 = 0.843$	Sand>P>Al_o
Partial	PBI = 62.22 - 0.8535 sand - 0.2943 Bray P;	$r^2 = 0.824$	Sand>P
	Olsen method[2]		
Full	PRI = 0.2840 - 0.1280 ρ_s + 0.001168 clay + 0.01259 Fe_d - 0.001283 Olsen P+ 0.05153 Fe_o - 0.004842 K;	$r^2 = 0.960$	ρ_s>Clay>Fe_d>P>Fe_o>K
Partial	PRI = 0.3235 - 0.1571 ρ_s + 0.003496 clay - 0.001800 Olsen P - 0.02388 K;	$r^2 = 0.918$	ρ_s>Clay>P>K
Full	PRC = 122.4 - 56. 68 ρ_s + 0.4146 clay + 4.872 Fe_d - 0.4558 Olsen P + 19.9988 Fe_o - 18.06 K;	$r^2 = 0.957$	ρ_s>Clay>Fe_d>P>Fe_o>K
Partial	PRC = 137.7 - 67.95 ρ_s + 0.8878 clay - 0.6559 Olsen P - 12.86 K;	$r^2 = 0.916$	ρ_s>Clay>P>K
Full	PBI = 10.62 + 0.6538 clay + 5.166 Fe_d;	$r^2 = 0.721$	Clay>Fe_d
Partial	PBI = 9.174 + 1.036 clay;	$r^2 = 0.624$	Clay

[1]The models are significant at P < 0.0001 and variables in the models are significant at P = 0.1500

[2]Models obtained for 39 (PRC) and 43 (PRI and PBI) soils in the case of the Bray method and 56 (PRI, PRC and PBI) soils in the case of the Olsen method

4.4. Conclusions

In all the benchmark soil series of Lesotho P retention increased with the application of P. However, with the range of P application levels used in this study, viz. 0 to 400 kg P ha^{-1} maximum P retention was not reached. Phosphorus retention capacity was, therefore, estimated from a constant application level, viz. P400. Using this principle, three groups of soil series were identified, especially in the case of the Bray method, Fusi, Thabana, Machache and Sefikeng comprised one group of high PRC at P400, Khabos, Leribe, Matela, Berea, Sephula and Tumo comprised another group of low PRC at P400 and Rama represented a group of no PRC at P400. The other two P retention properties established in this study, viz. PRI and PBI were closely related to the PRC at P400. As a result, it was suggested that any one of these parameters could be used to indicate P retention. The order of P retention according to the Olsen method was almost the same as according to the Bray method except that the range of P retention in terms of PRI and PRC at P400 was wider in the case of the Bray method than in the case of the Olsen method and the reverse was true for the range of P retention in terms of PBI.

Finally, multiple linear regression models were established with which P retention based on Bray or Olsen extraction procedure could be predicted from results of routine laboratory soil analysis. Soil properties used to develop those models were sand fraction, extractable P, sample density and amorphous Al for P retention based on Bray procedure and sample density, clay fraction, amorphous and free Fe oxides, extractable P and exchangeable K for P retention based on Olsen procedure. Two alternative models were developed for each P retention parameter, one model with all soil properties listed above and another model in which Al_o or Fe_o and Fe_d were excluded, depending on the phosphorus extraction method on which P retention was based. The reasoning behind this was that procedures for determining Fe and Al oxides are too laborious and therefore Fe and Al oxides are not determined as a routine laboratory soil analysis. Other soil properties such as OC and CEC had strong correlations with P retention but their inputs in the regression models were not significant.

CHAPTER 5

PHOSPHORUS REQUIREMENT FACTORS OF THE BENCHMARK SOILS

5.1. Introduction

Phosphorus deficiency is a major constraint in agricultural production worldwide due to generally low availability of soil P. This low availability of soil P is an inherent property of parent materials genetically low in P or that had undergone intense weathering, and/or also a result of a prolonged cropping history. Consequently, the use of P fertilizers is a prerequisite to improve the P fertility status of agricultural soils and hence increase agricultural production throughout the world. However, the high costs of P fertilizers and increasing need to improve agricultural production to meet the needs of the alarmingly growing world population, which is unfortunately accompanied by decreasing arable land, demand efficient use of such fertilizers, which is of coarse, a major concern in crop production. Therefore, in order to ensure efficient and economic use of P fertilizers for sustainable agriculture, proper fertilizer recommendations must be established for various crops on specific soils.

Proper fertilizer application rates are established from soil fertility studies consisting of greenhouse and field trials, laboratory analyses of soil P and plant tissue P and calibration and correlation between soil P, application levels of P, crop yield, P uptake by plants and plant tissue P. In order to establish a proper P fertilizer application rate for a particular crop on a specific soil the following factors are required: the P requirement of the crop, an optimum soil P content for the crop, a soil P test value and the amount of P required to raise the level of plant available P by unity in the soil, termed the P requirement factor. By multiplying the P requirement factor (PRF) with the optimum soil P content for a crop minus a soil P test value a recommended P application rate for the particular crop in the specific soil is obtained (Johnston *et al.*, 1991).

94

The fraction of applied P that is released in extractable forms and hence the PRF of soils is determined by the P retention capacities of soils. The P retention capacity of a soil is governed by, *inter alia*, proportions of silicate clay minerals, Fe and Al compounds and colloidal organic matter which participate in soil P reactions that lead to a reduction in P availability (Juo & Fox, 1977; Norrish & Rosser, 1983; Hughes & Hornung, 1987, Loganathan *et al.*, 1987; Nakos, 1987; Johnston *et al.*, 1991; Soon, 1991; Arduino *et al.*, 1993; Ritchie & Weaver, 1993; Agbenin & Tiessen, 1994; Brennan *et al.*, 1994; Bainbridge *et al.*, 1995). Soils rich in these constituents exhibit strong P retention properties such that they exhibit lower plant available P than the soils poor in these constituents after P application. Thus, soils with high P retention capacity have larger PRF's. Evidence in support of this was observed by Johnston *et al.* (1991) from their study where the 13 soils that exhibited the highest PRF had more than 39% clay and there was a strong correlation between PRF and clay content. The study on P retention by the benchmark soils of Lesotho reported in Chapter 4 indicated that the soils of the Fusi, Thabana, Machache, Sefikeng and Tumo series have higher P retention than the soils of the Khabos, Leribe, Rama, Sephula, Matela and Berea series. Interestingly, those benchmark soil series with high P retention had higher clay and organic matter contents. In addition, their clay fractions were more dominated by Fe and Al oxides (Chapter 2).

The aim of this study was to investigate the PRF of the benchmark soils of Lesotho and identify the soil properties that can be used to predict it. In addition, the relationships between PRF and the P retention properties established in the previous chapter, viz. PRI, PRC at P400 and PBI were also investigated.

5.2. Materials and methods

The results on extracted P from the experiment reported in Chapter 4 for the 56 soils described in Chapter 2 were used in this study. In order to investigate the PRF's of the soils applied P was plotted against P extracted by the Bray and the Olsen procedures for each soil. The actual amounts of applied P (mg P kg^{-1}) considering a fertilizer incorporation depth of 300mm, rather than application levels (kg P ha^{-1}) were used in constructing the plots. Straight line graphs that were fitted by a linear regression model ($y = bx + a$) were

95

obtained for all the soils. The slopes of those graphs were used to express PRF of the soils.

Variations in PRF between soil series were tested with ANOVA, viz. general linear models and Tukey–Kramer multiple comparison test, using the NCSS 2000. Correlations between PRF and the P retention properties, viz. PRI, PRC at P400 and PBI were investigated using the correlation/regression analysis in Microsoft Excel. Further, correlations and regressions were conducted between PRF and some selected soil properties reported in Chapter 2, with the simple linear, simple non-linear and multiple linear regression analyses using Microsoft Excel and NCSS 2000.

5.3. Results and discussions

As already mentioned plots of applied P against P extracted with both the Bray and Olsen extractants gave straight line relationships for all the soils and their slopes were used to express the PRF's of the soils. Linear regression models with very large r^2 of 0.93 to 1.00 for the Bray method and 0.94 to 1.00 for the Olsen method, with only two exceptions of lower r^2 values, viz. 0.67 for Bray and 0.69 for Olsen, described these relationships. Some selected plots of these relationships are shown in Figures 5.1 and 5.2 while the PRF's for all the soils are given in Appendix 5.1.

Since the PRF is estimated from plots of applied P (mg P kg^{-1}) against extracted P (mg P kg^{-1}) this factor is basically dimensionless. Again, theoretical PRF's of the study soils, as estimated from the mass of soil per 300mm hectare–furrow–slice, calculated from the sample densities of the soils, should vary from 3.08 to 4.60, assuming 0% sorption and 100% recovery of applied P. However, due to the high activity of P in soils and differences in P retention capacities between the soils, PRF's different from the theoretical ones were obtained. The PRF's determined by the Bray procedure ranged from 0.85 to 11.39 while the PRF's determined by the Olsen procedure ranged from 1.45 to 9.07. The distribution of the soils according to PRF's is shown in Table 5.1. For both extraction procedures more than 80% of the soils had PRF's of 5 and below. Further, the 13 soils that were not compatible for investigating PRI and PBI using the Bray method as reported in Chapter 4 had PRF's (Bray) of 1.00 or less. Those PRF's were, however, statistically significant at
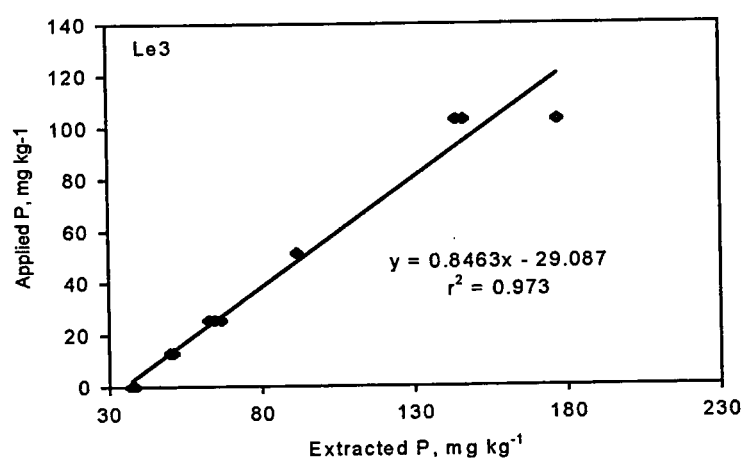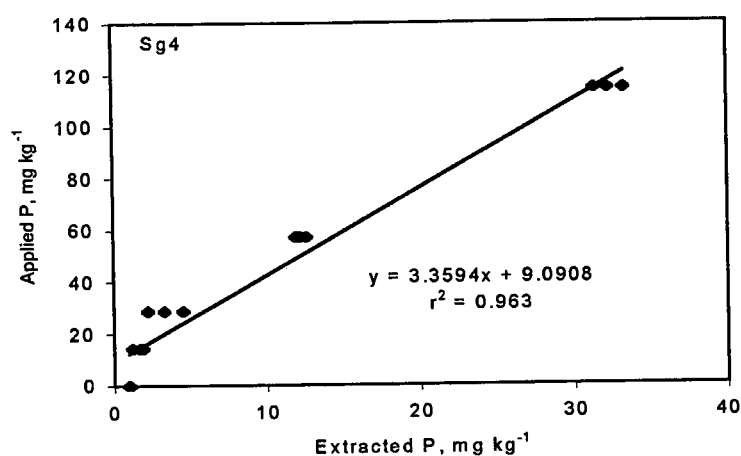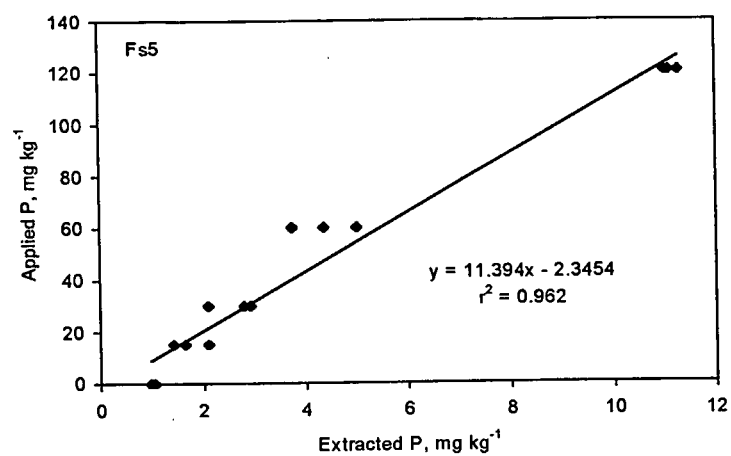
Figure 5.1. Selected plots of applied P against extractable P, each representing soils with large (Fs5), intermediate (Sg4) and small (Le3) slopes (Bray method).
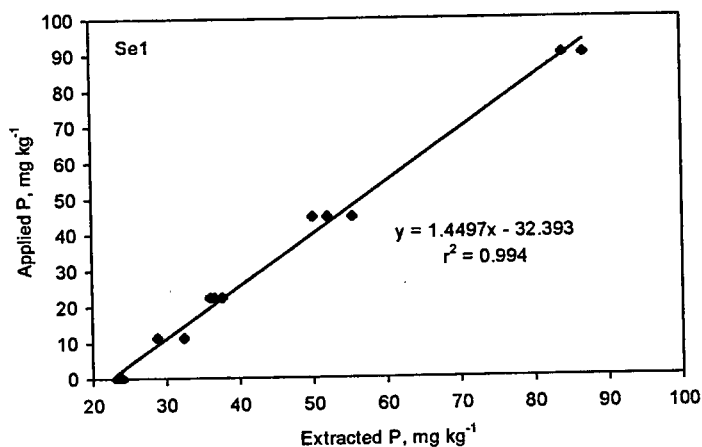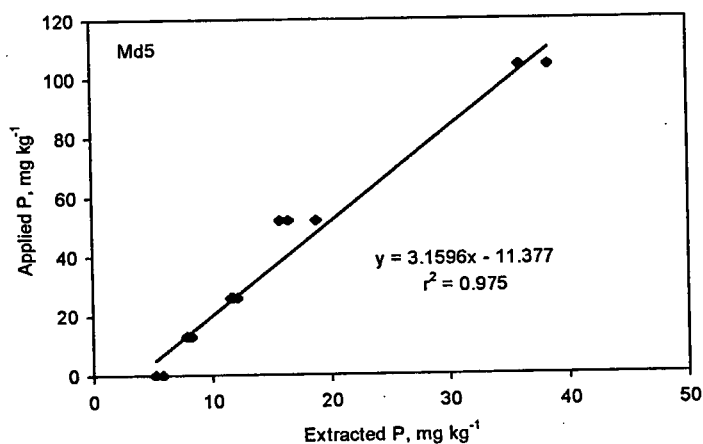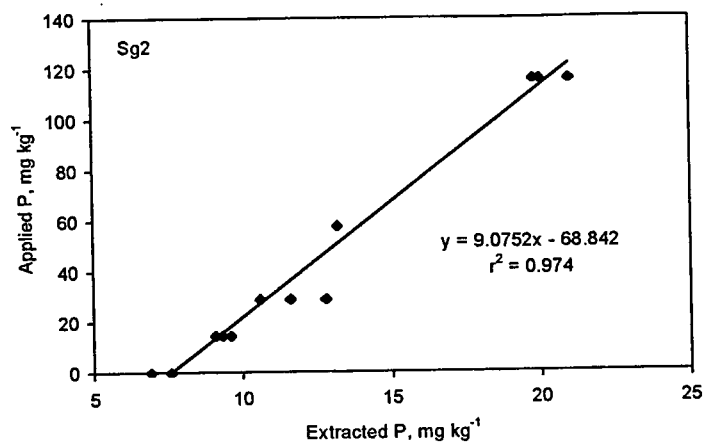
Figure 5.2. Selected plots of applied P against extractable P, each representing soils with large (Sg2), intermediate (Md5) and small (Se1) slopes (Olsen method).

0.050 probability level or less.

Table 5.1. Distribution of the soils according to phosphorus requirement factors (PRF's).

PRF	Occurrence of soils	
	Bray method	Olsen method
>10	3	0
7.5 – 10	3	1
5.0 – 7.5	4	6
2.5 – 5.0	7	20
0 – 2.5	39	29
n	56	56

The arrangement of the soil series in decreasing order of their PRF's based on both extraction procedures and the mean comparisons between the series is shown in Table 5.2. In the case of the Bray method the series Fusi, Thabana and Machache had the highest mean PRF's ranging from 5.67 to 7.13 while the series Khabos, Leribe, Rama, Sephula, Tumo, Matela and Berea had the lowest mean PRF's ranging from 0.96 and 1.66 with the series Sefikeng intermediate with a mean PRF of 3.36. In the case of the Olsen method, however, the series Fusi, Thabana, Machache and Sefikeng had the highest mean PRF's of 3.85 to 5.47 and the series Sephula and Rama had the lowest mean PRF's of 1.86 and less. The other five series, viz. Leribe, Matela, Berea, Khabos and Tumo had intermediate mean PRF's ranging from 1.89 to 2.92. Though there were some variations between the Bray and Olsen methods with respect to Tukey–Kramer multiple comparison between the series the two methods were very strongly correlated ($r = 0.85$; $n = 56$). As seen from Table 5.2 there was considerable consistence between the two methods, particularly in the order of the soil series according to their PRF's.

There was a direct relationship between PRF and the three P retention properties established in Chapter 4, viz. PRI, PRC at P400 and PBI as shown in Figures 5.3, 5.4 and 5.5, respectively. The higher and faster P retaining soil series Fusi, Thabana, Machache and Sefikeng had higher PRF's while the low and moderate to slow P retaining Khabos, Leribe, Rama, Sephula, Tumo, Matela and Berea series had lower PRF's. All the relationships were best described by a logarithmic regression model, $y = b \ln x + a$, regardless of the extraction method. Relationships between PRF and either PRI or PRC at P400 were

stronger ($r^2 > 0.9$) than relationships between PRF and PBI ($r^2 = 0.7$ to 0.8) for both the Bray and the Olsen methods. This probably suggests that PRF can be used interchangeably with either PRI or PRC at P400 to indicate P retention of soils as used by Johnston *et al.* (1991). Further, PRF's of the benchmark soils of Lesotho established in this study were within the ranges of PRF's of the soils from Kwazulu–Natal in South Africa, studied by the previous authors.

Table 5.2. The ranges and means of phosphorus requirement factors of the benchmark soil series and the mean comparisons between the series according to Tukey–Kramer.

Extraction method	Soil series	Range	Mean
Bray	Thabana	2.59 – 10.03	7.13 c
	Fusi	2.30 – 11.40	6.91bc
	Machache	2.42 – 10.36	5.67bc
	Sefikeng	2.25 – 5.29	3.36ab
	Khabos	1.28 – 2.25	1.66 a
	Tumo	1.09 – 2.22	1.37 a
	Sephula	0.95 – 1.90	1.33 a
	Matela	0.95 – 1.32	1.12 a
	Rama	0.86 – 1.16	1.01 a
	Berea	0.91 – 1.09	0.99 a
	Leribe	0.85 – 1.08	0.96 a
Olsen	Sefikeng	2.73 – 9.07	5.47 c
	Machache	4.35 – 5.96	5.18 c
	Thabana	3.36 – 6.81	5.05 c
	Fusi	3.01 – 4.78	3.85bc
	Tumo	2.42 – 3.34	2.92ab
	Khabos	2.22 – 2.77	2.41ab
	Matela	2.10 – 3.16	2.39ab
	Berea	1.71 – 2.50	1.99ab
	Leribe	1.71 – 1.99	1.89ab
	Sephula	1.45 – 2.20	1.86 a
	Rama	1.58 – 2.34	1.85 a

Figures carrying the same letter in a column for each extraction method are not significantly different at 0.050 probability level or less.

BRAY

$$y = 0.1143 \ln x + 0.0325$$
$$r^2 = 0.928$$

OLSEN

$$y = 0.1125 \ln x + 0.0479$$
$$r^2 = 0.918$$
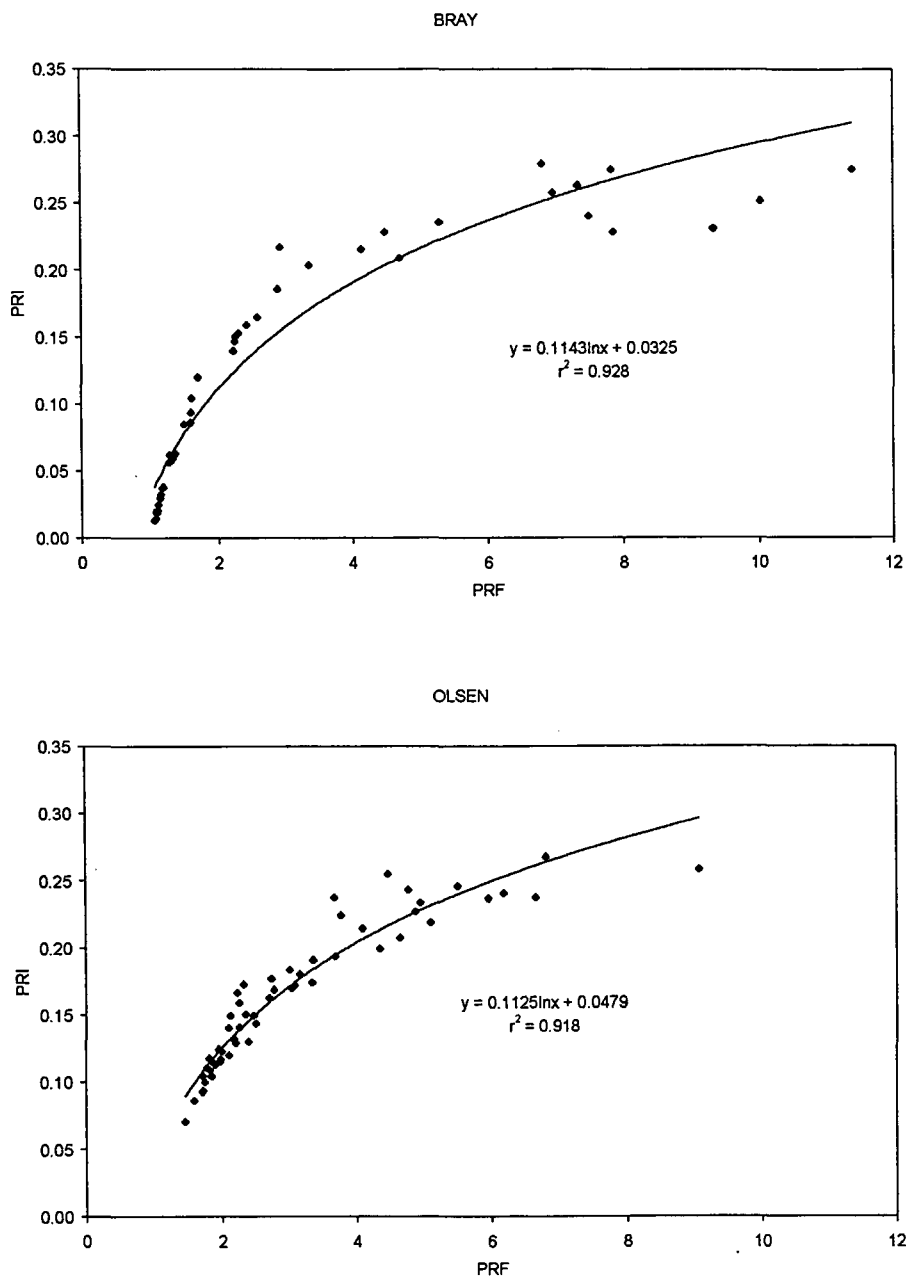
Figure 5.3. Relationship between PRF's and PRI's of the benchmark soils.

101

BRAY

$y = 46.704 \ln x + 11.604$
$r^2 = 0.912$

OLSEN

$y = 43.911 \ln x + 20.815$
$r^2 = 0.903$
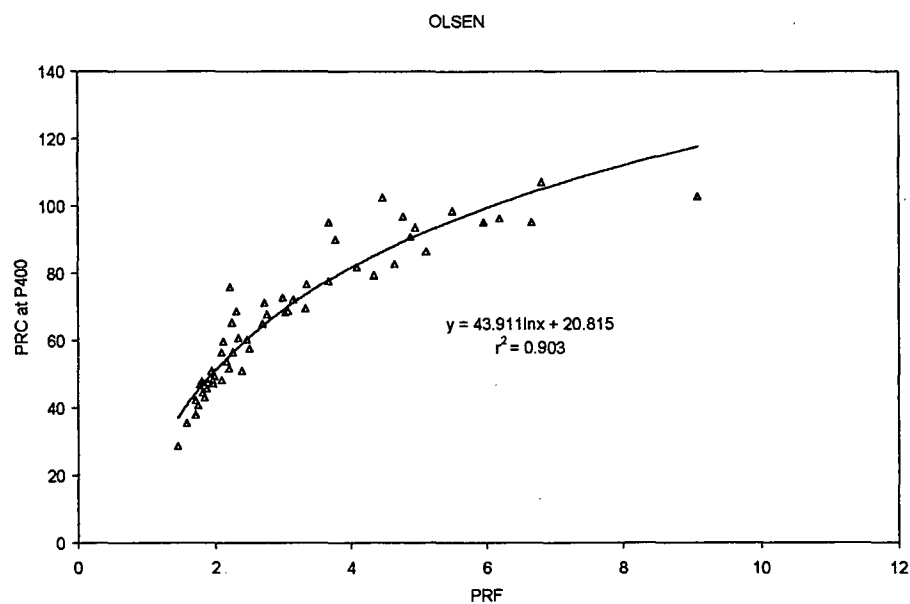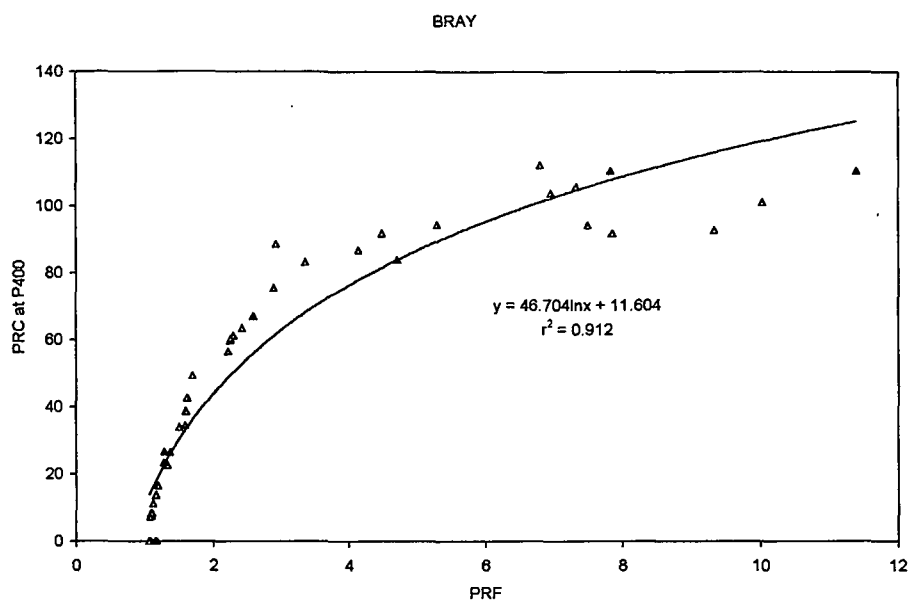
Figure 5.4. Relationship between PRF's and PRC at P400's of the benchmark soils.

BRAY

$y = 18.395\ln x + 8.2026$
$r^2 = 0.796$

OLSEN

$y = 31.524\ln x + 6.0795$
$r^2 = 0.694$
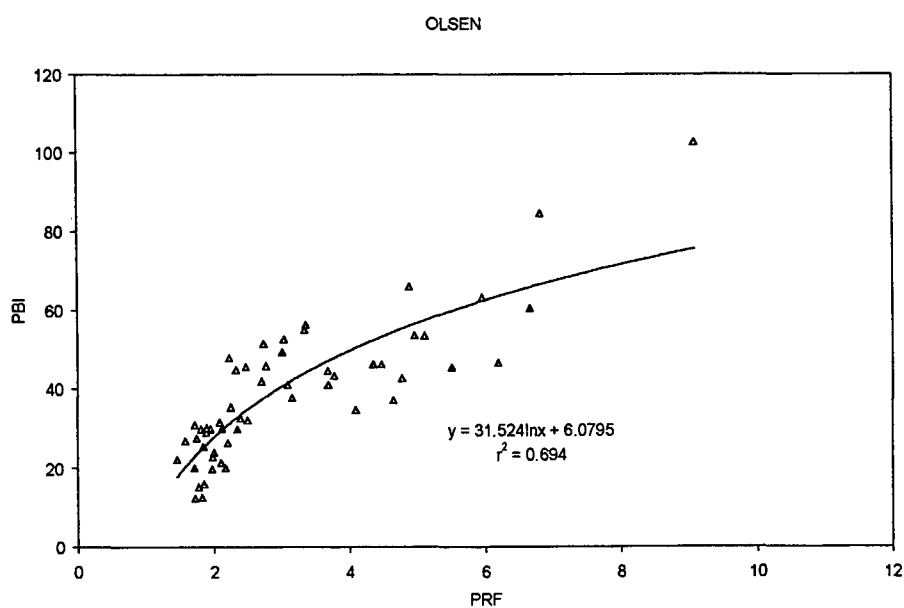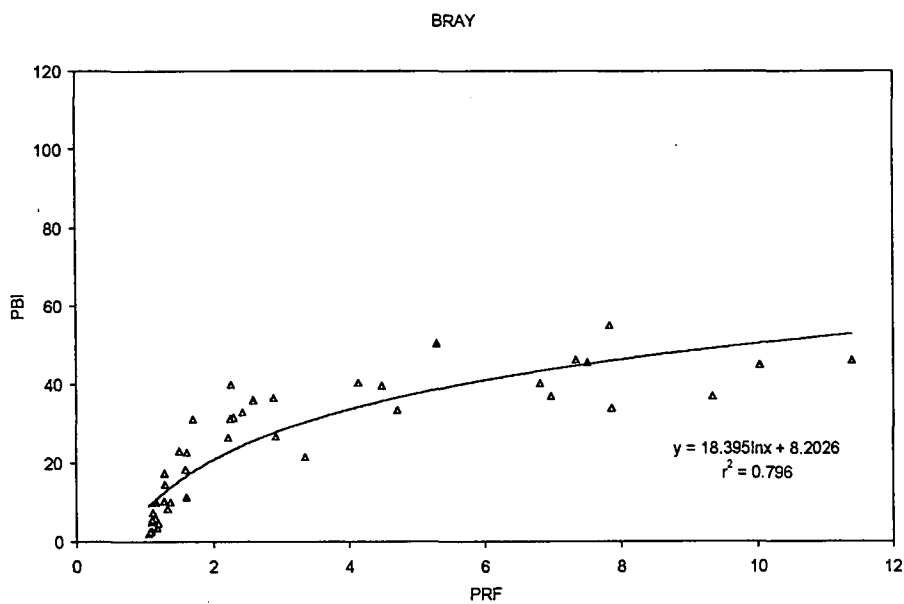
Figure 5.5. Relationship between PRF's and PBI's of the benchmark soils.

The relationships between PRF and the soil properties reported in Chapter 2 were also investigated. Most of those soil properties were significantly correlated with PRF as indicated by the coefficient of determination (r^2 values) obtained with different regression models (Table 5.3). Except for sample density (ρ_s) and sand, all other listed soil properties were positively correlated with PRF. Sand, clay, Fe_o, Al_o, OC, CEC and Bray extractable P, singly, explained more than 60% of the variation in PRF determined by the Bray method. However, in the case of the Olsen method only sand, clay, Al_o and OC as well as Fe_d explained more than 60% of the variation in PRF. The lack of contribution from Al_d and pH to the variation in PRF was consistent with the lack of contribution from these two soil properties to the variation in neither of the PRI, PRC at P400 or PBI as reported in Chapter 4.

Table 5.3. The order of contribution from selected soil properties to the variation in PRF as indicated by r^2 values, which were all significant at $P \leq 0.001$.

| Rank | Bray method | | | Olsen method | | |
	Soil property	r^2	Model	Soil property	r^2	Model
1	Sand	0.74	Power	Clay	0.74	Exp
2	Fe_o	0.73	Exp	Al_o	0.72	Exp
3	OC	0.72	Exp	Fe_d	0.69	Exp
4	Clay	0.71	Exp	Sand	0.64	Power
5	Al_o	0.68	Exp	OC	0.63	Power
6	CEC	0.67	Power	ρ_s	0.53	Exp
7	P	0.65	Power	Fe_o	0.53	Power
8	ρ_s	0.50	Power	CEC	0.50	Power
9	Mg	0.47	Power	Silt	0.26	Power
10	TEB	0.47	Power	P	0.22	Exp
11	Ca	0.46	Power	TEB	0.21	Power
12	Silt	0.38	Exp	Mg	0.21	Power
13	Fe_d	0.38	Power	Ca	0.21	Power
14	CEC–clay	0.34	Power	K	0.16	Power
15	AS	0.30	Quadratic			
16	BS	0.17	Linear			
17	Na	0.16	Exp			
18	$pH(H_2O)$	0.10	Linear			

Linear: $y = bx + a$; Power: $y = ax^b$; Exp: $y = ae^{bx}$; Quadratic: $y = cx^2 + bx + a$; n = 56 for both extraction methods

These results concurred with other studies that reported the positive correlation between P retention and contents of clay, OM and Fe and/or Al oxides (Ahenkorah, 1968; Juo & Fox, 1977; Burnham & Lopez–Hernandez, 1982; Loganathan *et al.*, 1987; Nakos, 1987; Torrent, 1987; Johnston *et al.*, 1991; Soon, 1991; Arduino *et al.*, 1993; Osodeke *et al.*, 1993; Ritchie & Weaver, 1993; Agbenin & Tiessen, 1994; Brennan *et al.*, 1994; Bainbridge *et al.*, 1995). The importance of exchangeable cations in P retention by weak acid soils is also well reported (Ryden & Syers, 1975; Curtin *et al.*, 1987; Smillie *et al.*, 1987; Agbenin, 1996). The negative correlation between PRF and sand arises from the fact that sandy soils as opposed to clayey soils have low P retention capacities and of course low P buffering capacities (see Chapter 4). The P fertility management of these soils should require small and frequent P fertilizer applications to maintain the soil solution P at sufficiency level. Large P fertilization of sandy soils with low P retention will result in accumulation of P, which might leach out into the ground water or be lost through run–off as noted by Ritchie & Weaver (1993) for the Peel–Harvey catchment in Western Australia. This is of course a disadvantage from the viewpoint of P fertility status of these soils and has also an environmental impact as it may result in pollution of surrounding water bodies.

Table 5.4. Multiple linear regression models for estimating the phosphorus requirement factors of the benchmark soils.

Model	Regression models and their r^2 values		Order of soil properties included in the models
	Bray method		
Full	PRF = 3.264 + 14.65 Fe_o – 0.02243 BS – 0.03098 P – 0.07927 silt;	$r^2 = 0.74$	Fe_o>BS>P>Silt
Partial	PRF = 0.2223 + 0.01885 BS – 0.07783 P + 0.1033 silt;	$r^2 = 0.46$	BS>P>Silt
	Olsen method		
Full	PRF = 1.734 + 0.7996 Fe_d + 3.687 Fe_o – 2.768 K – 0.03537 P;	$r^2 = 0.84$	Fe_d>Fe_o>K>P
Partial	PRF = 3.304 + 4.099 K – 0.1331 P;	$r^2 = 0.27$	K>P

All models significant at P < 0.001 and variables in the models are entered at P = 0.1500, n = 56 for both extraction methods.

Stepwise multiple regression analysis involving all those soil properties which correlated with PRF selected only the silt, Fe_o, base saturation and extractable P in the case of the Bray method and the Fe_o, Fe_d, exchangeable K and extractable P in the case of the Olsen method as soil properties which had a collective influence on PRF (Table 5.4). The r^2 values for

105

multiple linear regression models were 0.74 and 0.84 for the Bray and the Olsen methods, respectively. Excluding the Fe_o and Fe_d from the multiple linear regression models resulted in a great reduction in r^2 values, viz. 0.74 to 0.46 and 0.84 to 0.27, indicating high significance of the Fe compounds in determining the PRF's of the soils. On the contrary, the reduction in r^2 values when compounds of Fe and Al were removed from multiple linear regression models describing the P retention properties in Chapter 4 (except PBI in the case of the Olsen method) was very small. This implies that the soil properties that can be used to described or predict P retention depend on the index of P retention used.

5.4. Conclusions

A wide variation in PRF's was observed for the benchmark soils of Lesotho. The high P retaining soil series, viz. Fusi, Thabana, Machache and Sefikeng have large PRF's that ranged from 3.36 to 7.13 for the Bray method and from 3.85 to 5.47 for the Olsen method, on average. Likewise, the low P retaining soil series, viz. Khabos, Leribe, Sephula, Tumo, Matela and Berea as well as the non P retaining series, viz. Rama have low PRF's of about 0.96 to 1.66 and 1.85 to 2.92, on average, for the Bray and Olsen methods, respectively.

It was evident from this study that PRF can also be used as an index of P retention properties of soils. Like the P retention properties, viz. PRI, PRC at P400 and PBI (Chapter 4), PRF is ascribed to other soil properties such as texture, compounds of Fe and Al, exchangeable cations and the level of extractable P. As judged from the differences between the r^2 values for the full and partial multiple linear regression models, the amorphous and free Fe oxides were more important in determining PRF than PRI, PRC at P400 and PBI. It is, therefore, strongly suggested that where PRF is predicted from other soil properties, such properties must include amorphous and free Fe oxides.

CHAPTER 6

SUMMARY AND RECOMMENDATIONS

Phosphorus is an essential nutrient for good crop growth and development to ensure high yields. The content of P in soils and its availability for plant uptake is, however, usually low. This is mainly due to the low content of P in most parent materials as well as the high activity of P in soils (Norrish and Rosser, 1983). The total P content of most agricultural soils is in the order of 100 mg P kg^{-1} soil (Nye and Bertheux, 1957; Cooke, 1958) while soil solution P concentrations are in the order of $10^{-8} - 10^{-5}$M (Wild, 1988). The low availability of P in soils limits replenishment of the soil solution P during plant uptake, resulting in poor crop growth and development with low yields. The use of P fertilizers to correct P deficiencies and hence improve crop production is, therefore, a vital soil P fertility management practice worldwide. Nevertheless, because of the complicated behaviour of P in soils, it is not always easy to predict the response of plants to P fertilizer applications. Thus, to date a lot of research has been done to elucidate the biological, chemical and physical reactions of P in soils (Saunders, 1965; Ahenkorah, 1968; Hall & Baker, 1971; Rajan et al., 1974; Rajan, 1975; Wada & Gunjigake, 1979; Haynes, 1982; Ritchie & Weaver, 1983; Smillie et al., 1987; Parfitt, 1989; Parfitt et al., 1989; Guertal et al., 1991; Soon, 1991; Arduino et al., 1993; Bainbridge et al., 1995).

Studies on P retention broadly suggest that P reaction in soils is a two–phase process. The first phase, which is commonly known as an initial rapid phase, involves low energy surface adsorption and precipitation reactions of applied P by soil constituents (Taylor & Gurney, 1965; Russell et al., 1974; Parfitt et al., 1975; Goldberg & Sposito, 1985; Tisdale et al., 1985; Nanzyo, 1986; Wild, 1988; Parfitt, 1989). This phase lasts for less than an hour to a maximum of six days after P fertilizer application (Fox & Kamprath, 1970; Reeve & Sumner, 1970; Chen et al., 1973; Goncalves et al., 1985; 1989). With increasing time of contact between applied P and soil and as the low energy adsorptive sites become saturated with P, surface adsorbed P migrates into the high energy adsorptive sites and becomes chemisorbed (Kuo & Lotse, 1974; Munns & Fox, 1976; McLaughlin et al., 1977; Ryden et al., 1977b; Cabrera et al., 1981; Parfitt, 1989). Similarly, chemisorption of precipitated P is

also possible through the conversion of the sparingly soluble phosphate precipitates into less soluble phosphate minerals such as octacalcium phosphate and hydroxyapatite minerals (Eanes et al., 1965; Barrow, 1980; Tisdale et al., 1985; Wild, 1988). The chemisorption reactions of P adsorbed or precipitated during the initial rapid reaction phase comprise a second phase of reactions of applied P in soils, commonly known as a slow phase of P reaction. This is a continuous process, which does not appear to stop although its reaction rate decreases with increasing time of contact.

There is extensive literature explaining the mechanisms of both P reaction phases (Manning, 1968; Kuo & Lotse, 1974; Ryden et al., 1977a; b; Goldberg & Sposito, 1985; Parfitt, 1989; Agbenin & Tiessen, 1995). The initial rapid P reactions are responsible for reserving applied P as labile pool that replenishes soil solution P during plant uptake whereas the slow P reactions are responsible for retention of P in non–labile forms, hence determine the effectiveness of P fertilizers and their residual effects (Munns & Fox, 1976; Mattingly, 1975; Williams et al., 1980; Parfitt, 1989; Dalal, 1997). In the present study the retention and release of applied P by the benchmark soil series of Lesotho were investigated and the major soil properties implicated therein were identified. Thus, the focus of this study was mainly on the slow phase reaction of applied P.

In order to achieve the above mentioned objectives, soils were incubated with varying amounts of P, applied as KH_2PO_4, for 42 days after proving that this was a practical optimum incubation period for the soils studied. The retention of P was determined by extracting incubated soils with the Bray (0.03N NH_4F and 0.025N HCl) and Olsen (0.5N $NaHCO_3$) extractants according to Bray & Kurtz (1945) and Olsen et al. (1954), respectively and determining P with a modified method of Murphy & Riley (1962). The slope of retained P against applied P was used as a P retention index (PRI) and the slope of retained P against extracted P was used as a P buffering index (PBI) while the percentage of P retained at the highest P application level (400 kg P ha^{-1}) was used as P retention capacity (PRC at P400). The three parameters were used to express P retention properties of the benchmark soils. In addition, the slope of applied P against extracted P was used to obtain the P requirement factor (PRF) of a soil.

Across all P application levels, the Fusi, Thabana, Machache and Sefikeng were high P retaining series according to the Bray method whereas according to the Olsen method those four series plus the Tumo were high P retaining series. All these series retained, on average, 70% or more of applied P against the respective extraction methods. Nevertheless, when using PRC at P400 only Fusi, Thabana, Machache and Sefikeng were high P retaining series with mean PRC at P400 of about 70% or more, regardless of the extraction method. The series Khabos, Leribe, Sephula, Tumo, Matela and Berea were low sorbing (8 – 39%) and Rama series was non-sorbing according to the Bray method while the series Rama and Sephula were low sorbing (47%) and Leribe, Khabos, Tumo, Matela and Berea series were intermediate (48 – 66%) according to the Olsen method. The high P retaining series have higher PRI's than the rest of the series indicating high rate of retention. There was a close, positive correlation for either PRI or PRC at P400 with PBI such that the high and fast P retaining series Fusi, Thabana, Machache and Sefikeng exhibited higher mean PBI's than the rest of the series.

Consistent with their high rate of P retention (PRI) in particular, the Fusi, Thabana and Machache series had the highest mean PRF's according to the Bray method. The series Khabos, Leribe, Rama, Sephula, Tumo, Matela and Berea retained the applied P at slower rates and consequently had low mean PRF's according to the Bray method. While the mean PRI for the Sefikeng was comparable to those of the Fusi, Thabana and Machache series regardless of which extraction method was used, its mean PRF was only intermediate according to the Bray method. In the case of the Olsen method, however, the PRF and PRI for the Sefikeng were comparable to those of the Fusi, Thabana and Machache series. The series Rama and Sephula had the lowest PRI's and PRF's, the series Leribe, Matela and Berea had intermediate PRI's and PRF's while the series Khabos and Tumo had moderate PRI's but intermediate PRF's just like the latter three series according to the Olsen method. The two extraction methods were consistent in indicating which soils have high and which have low PRI, PRC at P400, PBI and PRF's. The respective correlation coefficients were 0.89 (n = 43), 0.81 (n = 39), 0.72 (n = 43) and 0.85 (n = 56) at $P < 0.001$. This study indicated that not only Machahce and Sefikeng series have high P retention as was previously established (Cauley, 1986; Schmitz & Rooyani, 1978; Arduino *et al.*, 1993) but the series Fusi and Thabana also have high capacities to retain P.

Characterization of the soils indicated that the high P sorbing soil series in particular, have high clay content and larger amounts of OM (Fusi and Thabana) or larger proportions of amorphous and crystalline Fe and Al oxides in their clay fractions (Machache and Sefikeng). The other soil series, viz. Khabos, Leribe, Rama, Sephula, Tumo, Matela and Berea had lower contents of clay, OM and Fe and Al oxides, hence their lower P retention and requirements. Significant correlations were obtained for PRI, PRC at P400, PBI and PRF with many soil properties but sample density, sand, clay, OC, CEC, Al_o, Fe_o, Fe_d and extractable P prior to treatment, consistently had higher correlations ($r^2 > 0.60$). The relationships between the retention and release of applied P by soils and soil properties is one of the topics which has received wide attention in soil science as well as in other related sciences.

Retention of P is more enhanced in clayey and loamy soils than in sandy soils (Ritchie & Weaver, 1993) or in red and/or yellow soils with large proportions of crystalline and poorly crystalline Fe and Al oxides (Gunjigake & Wada, 1981; Hue, 1991). Soils susceptible to alternating waterlogging and drying are also prone to high P retention (Khalid et al., 1977; Holford & Patrick, 1979; 1981; Phillips, 1998; Phillips & Greenway, 1998). Similarly, soils rich in OM, particularly if they also have high contents of Fe and Al in their clay fractions, have higher P retention than otherwise (Saunders, 1965; Lopez–Hernandez & Burnham, 1974a; Holford & Mattingly, 1975c; Wada & Gunjigake, 1979; Le Mare, 1982; Agbenin & Tiessen, 1994; Samadi & Gilkes, 1999). Further, at high levels of extractable P (which includes soil solution P, adsorbed P and P in sparingly soluble phosphate minerals) chemisorption of adsorbed and precipitated P proceeds until the sorption matrix of the soil is saturated. Thus, extractable P and hence the saturation of the sorption matrix also determine the retention of applied P (Munns & Fox, 1976; Ryden et al., 1977b; Gunjigake & Wada, 1981; Le Mare, 1982; Tisdale et al., 1985; Torrent, 1987; Parfitt, 1989; Agbenin & Tiessen, 1994).

As is often the case, significant correlation between P retention and soil pH was not observed in this study (Lopez–Hernandez & Burnham, 1974b). The high retention of P in strong acid soils with high contents of Fe and Al (Machache and Sefikeng) as well as in

weak acid soils with high contents of Ca and Mg (Fusi and Thabana) suggested that soil pH possibly affected P retention through its effects on the solubility and activity of phosphate ions (Mengel & Kirkby, 1987) and of Fe, Al, Ca and Mg cations that react with P (Brady & Weil, 1996).

The low and non P sorbing soil series (Khabos, Leribe, Rama, Sephula, Tumo, Matela and Berea) require lower management input than the high P sorbing soil series (Fusi, Thabana, Machache and Sefikeng) to optimize their productivity as indicated by their PRF's, viz. 0.85 to 2.25 compared to 2.42 to 10.03 (Bray). Low and non P sorbing soils require small P fertilizer applications to raise plant available P to an optimum level and to maintain it at that level while high P sorbing soils require large P fertilizer applications that should satisfy their P sorption capacities and then increase plant available P to the optimum level. The former soils have negligible residual P and as a result, they require repeated P fertilizer applications every growing season to increase and maintain plant available P at optimum. This was consistent with the low PBI's of the Khabos, Leribe, Rama, Sephula, Tumo, Matela and Berea series. In contrast, high P sorbing soils tend to have high residual P after large P fertilizer applications. Therefore, once their P sorption capacities are saturated, it may not be necessary to apply P every growing season as the residual P, through desorption and dissolution reactions, can effectively replenish the plant available P during the seasons of no P application. This conceded with the high PBI's of the Fusi, Thabana, Machache and Sefikeng series. The effectiveness of the residual P in the Fusi, Thabana, Machache and Sefikeng series, however, still needs to be investigated with crop trials. Also, further research is needed to elucidate the correlation between the PBI's and the effectiveness of the residual P for the benchmark soil series.

Whether it is possible or not to saturate the P sorption capacities of high P sorbing soils is a problem which has to be addressed not only by researchers or farmers but by different government sectors. The economic status of a country for instance, determines whether it is possible to buy and transport the fertilizers. It also decides on whether to improve crop production within the country or to import the grain or grain products.

The normal practice is that the amount of P fertilizer required to saturate the P sorption

capacity of a soil is split over some years. The actual number of years that it will take for the P sorption capacities to become saturated depends on annual application rates of P. Thus, it will take a shorter duration when large annual application rates are used than when small rates are used. This is, of course, an important issue to take into consideration with the potential use of the soils. Once saturation of the P sorption capacity is achieved relatively smaller application levels are required to increase and maintain plant available P at optimum. In the process caution should be taken not to over saturate the soils as some P may leach out to the ground water and contaminate the rivers.

An alternative to saturating P sorption capacities of the high P sorbing soils and increasing plant available P to optimum level in the entire soil is to band the fertilizer and increase P availability in the rhizosphere only. This might be less expensive and would probably not take years before the soils could be used to their optimum productivity. Besides, it is possible to increase P availability in the rhizosphere without losing much of applied P into the bulk soil because of the low mobility for P in soils. Further, the ability of plant roots to absorb P against a very steep concentration gradient between the roots and the surrounding soil solution (Higinbothan, 1973; Mengel & Kirkby, 1987) is a distinct advantage as plant roots will have access to applied P that is adsorbed in the band.

However, under very high economic constraints, where it is not possible to even increase the availability of P in the rhizosphere without first saturating the sorption capacity of a soil, then the low and non P sorbing soils, which have cheaper P fertility management are better off for intensive cropping than the high P sorbing soils. This may not be a problem in the lowlands but in the foothills where the Fusi, Thabana, Machache and Sefikeng series are the main cropping soils. Perhaps it is important that landholders in the foothills where the cropping soils are mainly of the Fusi, Thabana, Machache and Sefikeng series get subsidies from the government so that they are able to apply enough fertilizer, or else only small—scale farming can be practiced in those areas.

Finally, the possibility of employing other soil management strategies rather than application of chemical P fertilizers, which could reduce the retention and increase availability of P for plant uptake should also not be overlooked. These include increasing

112

organic matter content of the soil so as to increase organically adsorbed P relative to chemisorbed P. The assumption here is that organically adsorbed P is more readily available than chemisorbed P (Weir & Soper, 1962; 1963; Holford & Mattingly, 1975c; Le Mare, 1982; Agbenin & Tiessen, 1994). Strategies such as stubble return or application of farmyard manure can be used to increase soil organic matter content (Weir & Soper, 1962; Anderson, 1980). There is also an advantage of returning some organic P in the stubble or manure to the soil, hence increasing P content of the soils. Minimum tillage techniques as opposed to conventional tillage improve and maintain organic residues and consequently increase the proportion of applied P that is adsorbed in exchangeable forms relative to the proportion that is adsorbed in non–exchangeable forms (Lal, 1976; Guertal et al., 1991).

The present study highlighted the P retention properties and requirements of the benchmark soil series and their relationships with other soil properties. Thus, it is in a way, a foundation for future studies that should be conducted both under greenhouse and field conditions to establish properly justified P application levels for different crops on specific soils. This study can also be used as a basis for comparing other soils besides the benchmark soils, which are used for crop production and hence to broaden the knowledge of the P behaviour in and its requirement by the soils of Lesotho, at large. However, since this study was conducted in a laboratory it is important to verify the present results under field conditions. In the meanwhile, the results obtained herein can be used with caution to advise farmers on P fertility management of their soils. Recommendations were made for the management of P fertility of different categories of the benchmark soils, under the circumstances that might prevail and thus affect crop production in a country. Suggestions were also put forward for selective use of the benchmark soils under different conditions.

At this point I wish to challenge all the parties involved in improving agricultural production, self–reliance of the Basotho nation or the economy of the countr,y to take action.

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APPENDICES

Appendix 2.1. The physical properties of the 56 study soils.

Soil ID	Sample density (kg m^{-3})	Particle size distribution (%)		
		Sand	Silt	clay
Fs1	1262	25.66	28.77	45.33
Fs2	1292	17.80	35.98	46.00
Fs3	1240	22.93	32.40	44.50
Fs4	1023	29.73	26.27	43.67
Fs5	1107	28.95	28.27	42.67
Khs1	1340	40.35	25.82	33.67
Khs2	1188	47.59	23.49	28.00
Khs3	1147	34.65	28.46	36.67
Khs4	1263	37.02	24.05	38.67
Khs5	1210	41.91	30.41	27.50
Ta1	1277	23.82	30.04	46.00
Ta2	1193	22.72	31.80	45.33
Ta3	1243	21.55	31.32	47.00
Ta4	1100	15.93	29.16	55.67
Ta5	1070	21.82	29.21	48.67
Le1	1360	51.66	24.08	24.00
Le2	1407	60.96	20.81	18.00
Le3	1297	55.90	23.62	20.33
Le4	1350	65.44	20.76	17.67
Le5	1330	54.85	20.24	24.67
Ma1	1113	31.27	28.23	40.33
Ma2	1177	31.11	30.34	38.33
Ma3	1237	33.42	26.40	39.33
Ma4	1307	36.34	25.91	37.50
Ma5	1140	32.49	28.29	39.33
Rm1	1440	78.39	12.24	9.33
Rm2	1270	50.68	28.86	20.33
Rm3	1533	63.42	21.81	14.67
Rm4	1387	57.32	26.20	16.33
Rm5	1347	74.89	12.99	12.00
Rm6	1500	37.82	17.93	8.67
Sg1	1027	28.49	28.34	43.00
Sg2	1153	19.79	31.16	48.67
Sg3	1180	24.68	32.42	42.67
Sg4	1167	34.47	21.06	44.33
Sg5	1237	31.61	27.22	40.33
Se1	1483	62.61	25.14	12.00
Se2	1433	52.86	31.14	15.67
Se3	1397	66.15	25.49	12.00
Se4	1357	45.40	37.99	16.33
Se5	1443	52.83	26.36	20.67
Tm1	1307	51.74	21.40	26.67
Tm2	1343	47.03	22.08	30.67

Appendix 2.1. (continues)

Soil ID	Sample density	Particle size distribution (%)		
	$(kg\ m^{-3})$	Sand	Silt	clay
Tm3	1320	48.98	23.81	27.00
Tm4	1403	55.85	21.90	22.00
Tm5	1327	34.27	33.57	32.00
Md1	1470	66.02	18.09	15.67
Md2	1207	64.08	15.37	20.33
Md3	1523	59.64	21.18	19.00
Md4	1390	68.18	15.67	16.00
Md5	1280	57.34	19.56	22.67
Ba1	1433	66.17	17.67	16.00
Ba2	1397	65.40	18.42	16.00
Ba3	1533e	68.32	20.77	10.67
Ba4	1253	65.78	16.42	17.67
Ba5	1460	56.69	24.85	18.33

Appendix 2.2. The mineralogical properties of the 56 study soils.

Soil ID	Amorphous oxides (%)		Free oxides (%)		Aluminosilicate clays (cmol$_c$ kg^{-1})
	Al	Fe	Al	Fe	
Fs1	0.36	0.62	0.00	1.32	65.14
Fs2	0.18	0.71	0.09	1.70	59.55
Fs3	0.27	0.49	0.00	1.15	83.03
Fs4	0.31	0.57	0.00	1.94	80.94
Fs5	0.30	0.57	0.11	2.73	68.66
Khs1	0.17	0.46	0.05	1.48	46.58
Khs2	0.14	0.36	0.05	1.16	77.64
Khs3	0.16	0.35	0.07	1.85	67.37
Khs4	0.19	0.38	0.09	0.86	74.99
Khs5	0.13	0.35	0.12	1.45	71.32
Ta1	0.32	0.62	0.00	2.29	64.24
Ta2	0.24	0.64	0.10	2.53	59.15
Ta3	0.17	0.45	0.04	1.30	78.94
Ta4	0.21	0.43	0.07	1.37	77.01
Ta5	0.29	0.67	0.18	2.95	59.84
Le1	0.12	0.08	0.05	1.13	19.69
Le2	0.07	0.10	0.07	0.77	24.48
Le3	0.09	0.14	0.08	1.01	28.66
Le4	0.06	0.10	0.11	0.75	30.32
Le5	0.07	0.11	0.16	1.20	25.19
Ma1	0.22	0.40	0.29	4.34	44.85
Ma2	0.36	0.24	0.24	5.19	38.23
Ma3	0.22	0.23	0.27	3.28	37.20
Ma4	0.20	0.20	0.30	3.48	36.52
Ma5	0.29	0.37	0.12	4.40	44.93
Rm1	0.09	0.06	0.07	0.79	31.76
Rm2	0.06	0.06	0.10	0.88	27.83
Rm3	0.05	0.05	0.11	0.74	31.03
Rm4	0.05	0.07	0.12	0.78	30.77
Rm5	0.05	0.03	0.13	0.86	40.82
Rm6	0.06	0.04	0.10	0.63	39.85
Sg1	0.22	0.22	0.31	4.81	37.28
Sg2	0.30	0.49	0.27	5.28	33.74
Sg3	0.22	0.25	0.22	4.60	34.75
Sg4	0.23	0.21	0.25	3.89	39.28
Sg5	0.20	0.20	0.18	4.04	45.93
Se1	0.04	0.06	0.17	0.31	27.78
Se2	0.04	0.16	0.10	0.24	51.47
Se3	0.02	0.10	0.07	0.29	58.46
Se4	0.04	0.17	0.07	0.30	55.71
Se5	0.06	0.13	0.10	0.58	50.88
Tm1	0.19	0.11	0.13	2.76	26.40
Tm2	0.16	0.15	0.14	3.23	29.54

Appendix 2.2. (continues)

Soil ID	Amorphous oxides (%)		Free oxides (%)		Aluminosilicate clays (cmol$_c$ kg^{-1})
	Al	Fe	Al	Fe	
Tm3	0.13	0.11	0.16	2.48	28.56
Tm4	0.12	0.09	0.17	1.72	27.82
Tm5	0.16	0.24	0.14	3.12	36.14
Md1	0.10	0.08	0.11	0.93	20.92
Md2	0.05	0.06	0.17	0.93	31.67
Md3	0.05	0.07	0.21	0.88	25.48
Md4	0.04	0.06	0.23	0.95	35.15
Md5	0.12	0.08	0.35	1.31	36.91
Ba1	0.09	0.06	0.19	0.72	23.91
Ba2	0.05	0.07	0.24	0.80	33.88
Ba3	0.04	0.04	0.25	0.47	42.40
Ba4	0.07	0.07	0.25	1.13	33.86
Ba5	0.06b	0.10	0.25	0.75	34.89

Appendix 2.3. The chemical properties of the 56 study soils.

Soil ID	PH		CEC	Ca	Mg	K	Na	TEB	BS	AS	OC	P (mg kg^{-1})	
	(H$_2$O)	(1N KCl)	(cmol$_c$ kg^{-1})						(%)			Bray	Olsen
Fs1	6.47	4.70	29.57	25.13	11.44	0.25	0.19	37.01	126.43	0.00	2.58	2.48	6.07
Fs2	6.33	4.76	33.92	18.13	8.78	0.28	0.22	27.41	85.89	0.00	2.23	1.87	4.53
Fs3	6.82	5.02	36.52	35.30	17.63	0.21	0.21	53.35	146.32	0.00	2.79	9.45	11.40
Fs4	6.48	4.46	34.49	30.50	10.61	0.26	0.19	41.56	121.03	0.00	2.96	1.80	3.73
Fs5	6.54	4.51	29.27	21.27	10.39	0.19	0.19	32.03	110.80	0.00	2.05	0.75	2.13
Khs1	6.60	5.20	15.65	12.47	6.67	0.26	0.17	19.56	126.84	0.00	1.40	20.91	15.81
Khs2	6.72	5.38	21.74	17.55	8.11	0.33	0.17	26.16	122.04	0.00	1.46	37.98	18.80
Khs3	6.43	5.01	24.64	20.73	9.11	0.41	0.21	30.46	127.47	0.00	1.58	20.09	18.13
Khs4	6.43a	4.70	28.99	26.23	8.83	0.23	0.19	35.48	122.75	0.00	2.12	11.24	10.53
Khs5	6.78	5.46	21.45	21.07	7.66	0.60	0.17	29.51	140.12	0.00	1.67	12.79	10.44
Ta1	5.82	4.40	29.57	19.20	11.94	0.36	0.19	31.70	107.50	0.00	2.39	0.67	2.76
Ta2	6.12	4.45	26.96	23.67	9.44	0.15	0.18	33.45	129.51	0.00	2.61	1.92	3.87
Ta3	6.36	4.74	37.10	31.10	12.83	0.31	0.24	44.48	121.41	0.00	2.54	21.19	18.33
Ta4	6.68	5.33	41.74	44.17	16.22	0.43	0.24	61.06	146.50	0.00	3.47	2.25	5.20
Ta5	5.79	4.15	28.99	27.83	9.06	0.19	0.14	37.22	129.51	0.00	2.91	3.60	4.47
Le1	5.57	4.10	4.73	1.91	0.67	0.20	0.13	2.91	61.88	38.12	0.46	15.11	7.28
Le2	5.04	3.90	4.41	1.78	0.40	0.23	0.14	2.55	58.33	41.67	0.43	16.79	6.32
Le3	4.96	3.86	5.83	2.39	0.52	0.26	0.13	3.28	56.40	43.60	0.54	36.48	12.67
Le4	5.67	4.15	5.36	2.66	0.59	0.36	0.11	3.73	69.83	30.17	0.56	48.72	17.07
Le5	5.34	4.02	6.20	4.16	1.28	0.31	0.12	5.87	97.58	15.05	0.64	21.29	7.93
Ma1	5.17	3.87	18.09	7.64	2.17	0.49	0.12	10.43	57.74	42.26	1.94	1.32	2.27
Ma2	4.70	3.72	14.67	1.48	0.49	0.21	0.15	2.33	16.05	83.95	1.84	6.40	4.60
Ma3	4.91	3.75	14.64	4.93	1.00	0.26	0.12	6.30	43.13	56.87	1.77	8.60	5.27
Ma4	4.66	3.66	13.68	1.44	0.49	0.15	0.11	2.20	16.17	83.83	1.31	4.32	3.87
Ma5	5.60	4.15	17.68	9.01	4.52	0.28	0.14	13.95	78.92	20.81	1.72	2.51	4.93
Rm1	5.20	3.90	2.96	1.06	0.31	0.13	0.13	1.63	55.18	44.82	0.38	61.52	20.13

Appendix 2.3. (continues)

Soil ID	PH		CEC	Ca	Mg	K	Na	TEB	BS	AS	OC	P (mg kg^{-1})	
	(H$_2$O)	(1N KCl)				(cmol$_c$ kg^{-1})				(%)		Bray	Olsen
Rm2	5.28	3.97	5.65	2.01	0.68	0.10	0.18	2.98	52.88	47.12	0.50	16.29	6.80
Rm3	5.09	3.83	4.55	1.05	0.35	0.10	0.18	1.68	37.08	62.92	0.35	34.48	12.47
Rm4	5.07	3.86	5.01	1.25	0.39	0.26	0.18	2.08	41.52	58.48	0.54	26.99	11.20
Rm5	5.66	4.08	4.90	1.57	0.60	0.10	0.14	2.42	49.63	50.37	0.36	4.37	1.80
Rm6	5.93	4.30	3.45	1.20	0.55	0.15	0.11	1.91	55.81	44.19	0.42	5.62	1.67
Sg1	4.87	3.66	16.03	3.00	1.18	0.26	0.16	4.60	28.66	71.34	1.94	4.07	3.17
Sg2	5.07	3.74	16.44	6.06	1.82	0.29	0.13	8.30	51.29	48.71	1.92	4.30	5.93
Sg3	4.74	3.68	14.84	2.04	0.61	0.31	0.13	3.10	21.22	78.78	1.56	9.42	6.73
Sg4	5.04	3.81	17.39	3.11	2.49	0.41	0.14	6.15	36.43	63.57	1.69	2.70	2.91
Sg5	5.53	4.08	18.52	6.08	2.27	0.48	0.13	8.95	48.33	51.67	1.67	15.59	9.51
Se1	6.03	4.95	3.33	1.92	0.72	0.12	0.13	2.89	86.79	13.21	0.19	55.32	23.33
Se2	4.91	3.86	8.07	1.13	0.45	0.10	0.18	1.87	23.28	76.72	0.56	11.99	8.93
Se3	5.75	4.29	7.01	2.25	0.77	0.10	0.19	3.31	47.27	52.73	0.54	2.02	1.87
Se4	5.56	4.07	9.10	2.34	0.70	0.13	0.18	3.36	36.95	63.05	0.75	1.52	2.87
Se5	5.61	4.08	10.52	2.71	0.90	0.15	0.17	3.93	37.46	62.54	0.53	4.80	3.61
Tm1	4.80	3.80	7.04	1.26	0.45	0.18	0.12	2.01	28.66	71.34	0.98	19.87	9.27
Tm2	4.61	3.66	9.07	1.11	0.29	0.21	0.14	1.74	19.50	80.50	0.99	31.43	11.17
Tm3	4.69	3.71	7.71	0.96	0.28	0.15	0.14	1.54	20.12	79.88	0.90	36.98	12.53
Tm4	4.52	3.70	6.09	0.92	0.22	0.15	0.14	1.43	23.79	76.21	0.83	25.39	9.73
Tm5	5.05	3.79	11.56	3.28	0.93	0.36	0.15	4.72	41.17	58.83	0.95	6.15	5.47
Md1	5.83	4.25	3.27	1.40	0.53	0.15	0.12	2.20	67.02	32.98	0.37	10.71	7.04
Md2	5.22	3.87	6.43	1.98	0.69	0.15	0.13	2.96	46.05	53.95	0.52	35.23	9.27
Md3	4.92	3.81	4.84	0.96	0.32	0.15	0.13	1.57	32.52	67.48	0.41	28.74	9.40
Md4	5.65	4.20	5.62	1.86	0.54	0.21	0.12	2.74	48.70	51.30	0.41	5.87	2.44
Md5	4.60	3.82	8.38	0.64	0.22	0.15	0.13	1.14	13.72	86.28	1.00	12.19	4.20
Ba1	5.33	4.08	3.83	1.55	0.56	0.13	0.12	2.37	61.87	38.13	0.34	34.12	18.47
Ba2	5.18	3.91	5.42	1.28	0.44	0.10	0.13	1.95	37.23	62.77	0.34	20.69	7.67

Appendix 2.3. (continues)

Soil ID	PH		CEC	Ca	Mg	K	Na	TEB	BS	AS	OC	P (mg kg^{-1})	
	(H$_2$O)	(1N KCl)	(cmol$_c$ kg^{-1})						(%)			Bray	Olsen
Ba3	5.29	3.95	4.49	1.19	0.35	0.08	0.13	1.75	40.17	59.83	0.33	28.29	11.60
Ba4	4.90	3.86	5.97	1.06	0.32	0.21	0.14	1.72	29.09	70.91	0.52	24.29	8.20
Ba5	5.28	3.95	6.38	2.04	0.54	0.21	0.13	2.93	46.82	53.18	0.51	22.89	10.47

Appendix 3.1. Phosphorus retention (mg P kg^{-1}) by the eleven benchmark soils from four phosphorus application levels and mean comparisons between the sampling times (days) according to Tukey–Kramer.

Soil	Sampling time	P50	P100	P200	P400
Fusi	7d	12.64a	24.53b	48.10a	91.90b
	14d	12.66a	25.23b	49.63ab	95.02b
	21d	13.07a	25.33b	49.06a	98.03b
	28d	13.59a	26.40b	53.74bc	101.91b
	42d	13.70a	26.90b	50.93abc	102.81b
	63d	12.23a	12.72a	54.12c	42.95a
	Prob level	0.884289	0.000000	0.002903	0.000002
	[1]q$_{(0.05)}$	4.91	5.02	4.91	5.02
Khabos	7d	3.37ab	6.74a	14.87a	38.74a
	14d	11.30c	16.20ab	30.07a	47.81a
	21d	5.63ab	12.20ab	23.27a	46.54a
	28d	8.40bc	17.70b	23.40a	47.38a
	42d	9.33bc	19.66b	30.01a	54.87a
	63d	0.00a	40.43c	73.23b	122.31b
	Prob level	0.001281	0.000004	0.000049	0.000001
	q$_{(0.05)}$	5.17	4.82	4.82	4.82
Thabana	7d	10.44ab	20.22a	38.60a	76.66a
	14d	11.50bc	21.59ab	43.56bc	82.51bc
	21d	12.96c	23.92b	44.99c	83.91cd
	28d	11.61bc	22.55ab	44.32bc	86.35d
	42d	11.76bc	22.75ab	40.15ab	80.06b
	63d	8.98a	20.66ab	42.77abc	86.76d
	Prob level	0.003677	0.029524	0.003988	0.000001
	q$_{(0.05)}$	5.02	5.02	4.82	4.75
Leribe	7d	5.63a	7.78a	16.33a	36.13a
	14d	5.17a	11.39a	23.49a	46.93a
	21d	4.79a	12.65a	24.75a	34.52a
	28d	6.83a	8.96a	26.28a	49.80a
	42d	5.68a	15.50a	28.95a	48.85a
	63d	6.85a	11.85a	16.94a	44.66a
	Prob level	0.848219	0.157262	0.095746	0.290588
	q$_{(0.05)}$	4.91	5.36	5.17	5.02
Machache	7d	17.42c	27.44c	59.46b	103.05b
	14d	13.12b	24.74bc	48.64a	94.37ab

Soil	Sampling time	P50	P100	P200	P400
	21d	13.11b	25.16bc	49.27a	77.27a
	28d	12.82b	24.92bc	47.87a	89.85ab
	42d	10.82a	19.76a	44.80a	94.05ab
	63d	13.45b	21.90ab	48.11a	75.93a
	Prob level	0.000002	0.005610	0.000015	0.006764
	$q_{(0.05)}$	4.91	5.17	4.91	5.02
Rama	7d	2.64a	8.34ab	38.48b	51.93a
	14d	3.22a	18.08b	19.09a	23.24a
	21d	14.51b	14.14ab	41.11b	51.80a
	28d	0.00a	0.00a	25.75ab	37.04a
	42d	12.53b	20.48b	19.06a	42.34a
	63d	10.94b	10.70ab	29.54ab	15.76a
	Prob level	0.000031	0.017916	0.004666	0.027362
	$q_{(0.05)}$	5.02	4.91	4.91	4.91
Sefikeng	7d	14.40a	28.17a	58.89b	109.58a
	14d	13.31a	27.18a	50.86a	102.38a
	21d	13.99a	27.00a	51.34a	103.23a
	28d	13.76a	27.40a	59.03b	100.93a
	42d	12.03a	27.69a	54.67ab	100.15a
	63d	14.36a	26.04a	55.37ab	101.96a
	Prob level	0.763676	0.454764	0.003050	0.313108
	$q_{(0.05)}$	4.91	5.02	5.02	5.02
Sephula	7d	4.78abc	6.02ab	9.09a	9.33a
	14d	3.07ab	3.31ab	5.55a	15.95ab
	21d	5.21bc	3.78ab	6.65a	22.06ab
	28d	7.34c	9.31b	16.52a	29.32ab
	42d	0.00a	4.54ab	12.07a	18.09ab
	63d	18.97d	0.00a	11.38a	36.62b
	Prob level	0.000278	0.056146	0.291632	0.018575
	$q_{(0.05)}$	6.03	5.02	4.82	4.82
Tumo	7d	13.15bc	23.32c	36.80a	67.04b
	14d	9.70ab	17.89bc	31.81a	25.45a
	21d	19.14d	8.72a	34.33a	66.50b
	28d	9.80ab	9.96ab	14.98a	49.74ab
	42d	13.66c	21.47c	22.91a	26.85a
	63d	6.60a	18.10abc	17.90a	36.47ab
	Prob level	0.000003	0.002483	0.037910	0.001130
	$q_{(0.05)}$	4.75	5.17	5.17	4.91

Appendix 3.1. (continues)

Soil	Sampling time	P50	P100	P200	P400
Matela	7d	6.47a	12.62bc	22.98ab	41.35b
	14d	7.71ab	13.12bc	22.55ab	39.43b
	21d	4.60a	10.74ab	20.49ab	34.23ab
	28d	12.10c	8.10a	15.42a	10.10ab
	42d	10.53bc	15.80c	22.60ab	3.80a
	63d	13.40c	19.48d	23.73b	41.40b
	Prob level	0.000435	0.000008	0.047191	0.019030
	$q_{(0.05)}$	5.17	4.91	4.82	5.63
Berea	7d	6.60a	12.62b	21.94a	40.03b
	14d	5.32a	10.65b	21.55a	40.01b
	21d	4.81a	0.00a	17.80a	32.36b
	28d	1.72a	18.25b	25.60a	7.99a
	42d	2.88a	11.21b	20.96a	36.86b
	63d	5.60a	10.64b	7.70a	36.29b
	Prob level	0.313903	0.000891	0.531480	0.004154
	$q_{(0.05)}$	4.91	4.82	5.17	5.36

Figures carrying the same letter in a column, for each soil, are not significantly different at 0.050 probability level or less; [1]Studentized range for k treatment means with v error degrees of freedom at alpha = 0.050

Appendix 4.1. Mean percentage of phosphorus retained at four phosphorus application levels and across all application levels for 43 of the 56 study soils, with mean comparisons between application levels according to Tukey–Kramer (Bray method).

SoilID	P50	P100	P200	P400	P level	[1]$q_{(0.05)}$	Mean
Fs1	87.02a	86.74b	84.41ab	79.49a	0.004543	4.53	84.41
Fs2	93.22a	92.62a	91.58a	89.83a	0.093061	4.53	91.81
Fs3	58.93a	63.39a	60.88a	56.98a	0.424111	4.53	60.05
Fs4	92.96b	92.53b	90.68b	86.23a	0.000616	4.53	90.60
Fs5	95.36a	94.74a	94.44a	91.61a	0.055122	4.53	94.04
Khs1	50.78a	45.15a	48.56a	34.15a	0.166798	4.53	44.66
Khs2	45.83b	33.36ab	24.72a	23.69a	0.008633	4.53	31.90
Khs3	66.21c	57.85bc	50.57ab	42.53a	0.000128	4.53	54.29
Khs4	71.27b	64.45ab	58.35a	56.67a	0.001473	4.53	62.69
Khs5	51.73c	45.92bc	41.57ab	38.66a	0.000908	4.53	44.47
Ta1	91.96b	92.00b	89.54ab	87.86a	0.002939	4.53	90.34
Ta2	93.49b	94.04b	93.26b	90.36a	0.008499	4.53	92.79
Ta3	72.55b	71.08ab	63.30a	62.44a	0.014188	4.53	67.34
Ta4	94.55b	93.89b	92.75b	87.23a	0.000070	4.53	92.11
Ta5	96.64c	94.71bc	93.25b	88.34a	0.000152	4.53	93.24
Le1	9.54a	13.42a	7.60a	*	0.118429	4.34	[2]10.19
Le5	30.83b	15.39a	17.73a	8.18a	0.000867	4.53	18.03
Ma1	91.46b	90.06ab	88.14ab	86.48a	0.025210	4.53	89.04
Ma2	85.46b	84.20b	80.60ab	76.62a	0.001918	4.53	81.72
Ma3	64.83ab	64.11ab	67.42b	59.03a	0.033027	4.53	63.85
Ma4	79.11a	77.24a	98.58c	92.31b	0.000001	4.53	86.81
Ma5	87.80c	86.74c	84.32b	78.52a	0.000003	4.53	84.34
Rm2	19.86b	8.60ab	6.12a	*	0.025157	4.34	[2]11.52
Rm4	6.37a	15.94a	11.78a	*	0.225287	4.34	[2]11.36
Rm5	43.98c	29.19b	16.72a	*	0.000013	4.34	[2]29.96
Sg1	84.63bc	90.02c	74.42ab	68.33a	0.001612	4.53	79.35
Sg2	85.39a	85.13a	86.67a	81.57a	0.233120	4.53	84.69
Sg3	83.97c	78.59bc	73.29b	66.74a	0.001355	4.53	75.65
Sg4	95.91c	91.85c	80.47b	72.68a	0.000008	4.53	85.23
Sg5	58.89a	64.81b	61.13ab	56.01a	0.005967	4.53	60.21
Se2	38.64a	37.60a	38.70a	37.04a	0.935518	4.53	38.00
Se3	43.32d	34.81c	26.13b	17.28a	0.000037	4.53	30.39
Se4	63.42c	56.55bc	47.96ab	39.33a	0.000296	4.53	51.82
Se5	52.49c	54.83c	40.80b	28.57a	0.000001	4.53	44.18
Tm1	27.39ab	31.41b	29.11b	22.28a	0.007239	4.53	27.55
Tm2	22.82a	23.92a	16.52a	13.93a	0.218077	4.53	19.30
Tm3	14.15a	26.15b	9.21a	11.09a	0.001237	4.53	15.22
Tm4	26.22b	13.61a	12.66a	7.93a	0.005930	5.22	16.87
Tm5	76.15c	69.41b	66.74b	56.33a	0.000001	4.53	67.16

Appendix 4.1. (continues)

SoilID	P50	P100	P200	P400	P level	[1]$q_{(0.05)}$	Mean
Md1	18.73b	21.46b	6.08a	7.98a	0.001352	4.68	14.07
Md4	21.75b	8.66a	25.83b	23.62b	0.001719	4.53	19.97
Md5	23.83ab	30.00b	18.90a	22.46ab	0.036808	4.53	23.80
Ba5	22.66ab	27.79b	18.56ab	9.14a	0.016840	4.90	20.68

Figures carrying the same letter in a row are not significantly different at 0.050 probability level or less, [1]Studentized range for k treatment means with v error degrees of freedom at alpha = 0.050, [2]Based on P50, P100 and P200 only.

Appendix 4.2. Mean percentage of phosphorus retained at four phosphorus application levels and across all application levels for the 56 study soils, with mean comparisons between application levels according to Tukey–Kramer (Olsen method).

Soil ID	P50	P100	P200	P400	P level	$^1q_{(0.05)}$	Mean
Fs1	79.90a	76.72a	76.42a	73.49a	0.055727	4.53	76.64
Fs2	21.34a	61.29b	78.96b	79.34b	0.001528	4.53	60.23
Fs3	63.61a	68.61a	72.78a	67.61a	0.364045	4.53	68.15
Fs4	78.02b	75.76ab	75.76ab	73.18a	0.045077	4.53	75.68
Fs5	80.71a	85.26a	84.89a	80.44a	0.285145	4.53	82.82
Khs1	69.77a	70.41a	64.03a	60.71a	0.524851	4.68	66.43
Khs2	37.96a	41.41a	34.22a	57.54a	0.148602	5.22	44.81
Khs3	64.86a	49.55a	59.71a	59.27a	0.734428	4.53	58.35
Khs4	69.26a	67.44a	65.57a	64.28a	0.379936	4.53	66.64
Khs5	52.26a	62.48a	48.56a	59.42a	0.676877	4.68	55.34
Ta1	88.56b	87.79b	84.81ab	79.28a	0.011979	4.68	85.64
Ta2	87.21a	87.40a	85.97a	85.17a	0.231766	4.53	86.44
Ta3	66.17a	83.58a	72.51a	71.52a	0.150384	4.53	73.45
Ta4	80.19a	80.80a	76.99a	74.32a	0.138581	4.53	78.08
Ta5	88.31a	90.83a	88.08a	85.71a	0.090456	4.53	88.23
Le1	58.92ab	62.85b	56.09ab	50.67a	0.047978	4.53	57.13
Le2	56.92b	57.09b	53.01ab	49.87a	0.005767	4.53	54.22
Le3	54.30a	60.31a	49.72a	49.49a	0.338551	4.53	52.71
Le4	59.90a	56.50a	48.58a	45.33a	0.297802	4.68	52.79
Le5	72.67c	64.47bc	58.95ab	51.02a	0.001445	4.53	61.71
Ma1	90.92b	85.23a	85.38a	82.29a	0.000587	4.53	85.96
Ma2	91.53b	88.70ab	85.82ab	84.05a	0.022172	4.68	87.68
Ma3	82.24b	72.63a	84.77b	80.42b	0.000126	4.68	79.98
Ma4	82.01a	78.46a	82.12a	77.93a	0.534271	4.53	80.13
Ma5	80.84a	84.22b	80.36a	80.10a	0.000004	4.53	81.38
Rm1	59.43a	49.86a	41.04a	38.61a	0.060882	4.53	47.23
Rm2	68.34b	66.50b	61.59a	58.07a	0.000150	4.53	63.62
Rm3	60.25a	48.78a	48.32a	47.17a	0.375590	4.53	51.13
Rm4	50.70a	53.48a	48.99a	47.64a	0.724292	4.53	50.20
Rm5	69.31c	64.74bc	56.80ab	46.43a	0.001176	4.53	59.32
Rm6	61.38c	56.09b	52.33b	42.86a	0.000019	4.53	53.16
Sg1	88.56b	86.99b	83.48ab	79.12a	0.002499	4.53	84.54
Sg2	86.45a	85.16a	89.93a	88.86a	0.085412	4.53	87.60
Sg3	88.39a	80.98a	84.12a	80.38a	0.303077	4.53	83.46
Sg4	90.41b	86.96ab	86.47ab	84.24a	0.010181	4.53	87.02
Sg5	78.15a	77.00a	75.75a	65.94a	0.048563	4.53	74.21
Se1	37.80a	41.71a	35.87a	31.87a	0.655280	4.68	36.72
Se2	53.88a	49.81a	52.10a	55.69a	0.894786	4.68	52.61
Se3	61.49b	58.03ab	49.18ab	46.75a	0.023454	4.68	53.48

Appendix 4.2. (continues)

SoilID	P50	P100	P200	P400	P level	$^1q_{(0.05)}$	Mean
Se4	61.51a	60.26a	53.62a	47.41a	0.075228	4.53	55.70
Se5	65.72b	66.70b	59.72ab	51.13a	0.006276	4.53	60.82
Tm1	75.67b	66.17ab	71.65ab	63.69a	0.015017	4.53	69.29
Tm2	71.18a	73.76a	72.50a	70.19a	0.279785	4.53	71.91
Tm3	75.09c	74.77bc	69.58ab	67.77a	0.005680	4.53	71.80
Tm4	73.87a	55.92a	62.15a	59.62a	0.179951	4.90	63.29
Tm5	85.66b	76.74ab	75.86a	68.44a	0.005664	4.90	77.49
Md1	65.55a	63.55a	59.61a	53.33a	0.100509	4.53	60.51
Md2	54.08a	57.26a	55.47a	54.10a	0.862449	4.53	55.23
Md3	43.20a	60.61a	61.22a	58.55a	0.338313	4.53	55.89
Md4	77.43b	69.03ab	63.60ab	56.18a	0.032042	4.53	66.56
Md5	80.16b	75.25b	77.76b	69.14a	0.000647	4.53	75.58
Ba1	63.04a	50.08a	47.66a	43.98a	0.138292	4.53	51.19
Ba2	61.48a	69.91a	63.85a	60.50a	0.078829	4.53	63.93
Ba3	65.87a	48.92a	48.99a	43.49a	0.088385	4.53	51.82
Ba4	64.26a	64.31a	59.48a	53.15a	0.133252	4.53	60.30
Ba5	62.05a	57.01a	63.23a	49.78a	0.229927	4.68	57.54

Figures carrying the same letter in a row are not significantly different at 0.050 probability level or less,

[1]Studentized range for k treatment means with v error degrees of freedom at alpha = 0.050.

Appendix 4.3. The phosphorus retention and buffering indices and retention capacity at P400 for some of the study soils (Bray method).

Soil ID	[1]PRI Bray	[2]PRC at P400	[1]PBI Bray
Fs1	0.209 ± 0.005	79.49 ± 1.43	33.495 ± 4.107
Fs2	0.231 ± 0.003	89.83 ± 1.68	37.084 ± 6.208
Fs3	0.153 ± 0.007	56.98 ± 3.17	31.634 ± 4.678
Fs4	0.280 ± 0.006	86.23 ± 1.83	40.366 ± 4.930
Fs5	0.276 ± 0.003	91.61 ± 0.11	46.226 ± 5.733
Khs1	0.085 ± 0.012	34.15 ± 1.04	23.133 ± 3.366
Khs2	0.062 ± 0.010	23.69 ± 4.32	17.517 ± 3.445
Khs3	0.120 ± 0.010	42.53 ± 1.79	31.171 ± 2.003
Khs4	0.147 ± 0.005	56.67 ± 1.81	31.254 ± 4.012
Khs5	0.105 ± 0.004	38.66 ± 0.89	22.702 ± 2.508
Ta1	0.229 ± 0.003	87.86 ± 1.62	33.980 ± 5.678
Ta2	0.252 ± 0.003	90.36 ± 0.27	45.040 ± 5.133
Ta3	0.165 ± 0.005	62.44 ± 1.50	36.024 ± 4.644
Ta4	0.264 ± 0.006	87.23 ± 0.44	46.387 ± 2.612
Ta5	0.275 ± 0.006	88.34 ± 1.69	55.177 ± 3.778
Le1	0.019 ± 0.007	*	2.645 ± 0.822
Le5	0.019 ± 0.009	8.18 ± 1.21	4.989 ± 1.800
Ma1	0.258 ± 0.005	86.48 ± 2.35	37.128 ± 6.881
Ma2	0.216 ± 0.005	76.62 ± 0.98	40.519 ± 4.292
Ma3	0.160 ± 0.008	59.03 ± 0.98	32.963 ± 4.025
Ma4	0.241 ± 0.010	92.31 ± 2.33	45.671 ± 42.056
Ma5	0.229 ± 0.006	78.52 ± 0.52	39.772 ± 3.415
Rm2	0.013 ± 0.011	*	2.071 ± 1.719
Rm4	0.030 ± 0.009	*	6.082 ± 2.074
Rm5	0.037 ± 0.016	*	3.543 ± 0.863
Sg1	0.217 ± 0.012	68.33 ± 1.95	26.814 ± 5.725
Sg2	0.236 ± 0.006	81.57 ± 0.22	50.540 ± 7.109
Sg3	0.186 ± 0.008	66.74 ± 1.81	36.648 ± 3.119
Sg4	0.204 ± 0.010	72.68 ± 0.85	21.654 ± 3.007
Sg5	0.151 ± 0.06	56.01 ± 1.77	40.026 ± 3.446
Se2	0.086 ± 0.005	37.04 ± 1.48	18.357 ± 3.167
Se3	0.038 ± 0.010	17.28 ± 3.91	4.747 ± 0.919
Se4	0.094 ± 0.009	39.33 ± 1.32	11.392 ± 1.659
Se5	0.063 ± 0.012	28.57 ± 2.27	10.093 ± 0.847
Tm1	0.057 ± 0.007	22.28 ± 1.36	14.629 ± 1.630
Tm2	0.033 ± 0.008	13.93 ± 3.10	9.971 ± 2.341
Tm3	0.025 ± 0.08	11.09 ± 2.57	7.446 ± 2.778
Tm4	0.020 ± 0.006	7.93 ± 0.00	5.139 ± 1.119
Tm5	0.140 ± 0.009	56.33 ± 0.69	26.478 ± 1.543
Md1	0.015 ± 0.007	7.98 ± 1.87	2.495 ± 1.180

Appendix 4.3. (continues)

Soil ID	[1]PRI Bray	[2]PRC at P400	[1]PBI Bray
Md4	0.059 ± 0.008	23.62 ± 2.19	8.415 ± 3.026
Md5	0.057 ± 0.010	22.46 ± 5.06	10.329 ± 2.933
Ba5	0.021 ± 0.010	9.14 ± 0.00	5.653 ± 1.961

[1]PRI and PBI with 95% confidence limits for the 43 of the study soils. [2]Mean PRC at P400 with standard deviations for 39 of the study soils. *Soils not responsive to application of phosphorus at P400 while other soils not included in the list were Soils not responsive to application of phosphorus at all P levels.

Appendix 4.4. The phosphorus retention and buffering indices and retention capacity at P400 for the 56 study soils (Olsen method).

Soil ID	[1]PRI Olsen	[2]PRC at P400	[1]PBI Olsen
Fs1	0.194 ± 0.005	73.49 ± 2.51	40.990 ± 5.698
Fs2	0.214 ± 0.017	79.34 ± 0.90	34.736 ± 23.989
Fs3	0.184 ± 0.011	67.61 ± 4.85	49.357 ± 9.505
Fs4	0.238 ± 0.005	73.18 ± 1.67	44.585 ± 7.014
Fs5	0.243 ± 0.010	80.44 ± 4.60	42.666 ± 8.730
Khs1	0.149 ± 0.008	60.71 ± 2.66	45.565 ± 6.019
Khs2	0.166 ± 0.026	57.54 ± 4.79	47.891 ± 24.457
Khs3	0.173 ± 0.018	59.27 ± 6.53	44.831 ± 13.897
Khs4	0.169 ± 0.004	64.28 ± 0.95	45.833 ± 5.501
Khs5	0.159 ± 0.017	59.42 ± 2.95	35.077 ± 12.127
Ta1	0.207 ± 0.007	79.28 ± 2.11	37.164 ± 7.840
Ta2	0.238 ± 0.001	85.17 ± 0.00	60.469 ± 7.196
Ta3	0.191 ± 0.009	71.52 ± 2.87	56.429 ± 10.016
Ta4	0.224 ± 0.006	74.32 ± 1.32	43.329 ± 6.975
Ta5	0.267 ± 0.004	85.71 ± 0.67	84.611 ± 6.527
Le1	0.123 ± 0.006	50.67 ± 0.35	23.862 ± 2.704
Le2	0.117 ± 0.003	49.87 ± 0.85	22.782 ± 2.995
Le3	0.118 ± 0.012	49.49 ± 5.38	29.886 ± 5.543
Le4	0.105 ± 0.011	45.33 ± 1.72	30.939 ± 5.791
Le5	0.125 ± 0.011	51.02 ± 4.21	29.904 ± 4.184
Ma1	0.246 ± 0.003	82.29 ± 0.51	45.458 ± 6.017
Ma2	0.237 ± 0.004	84.05 ± 1.90	63.160 ± 6.734
Ma3	0.219 ± 0.007	80.42 ± 1.05	53.535 ± 12.957
Ma4	0.199 ± 0.008	77.93 ± 3.31	46.237 ± 8.081
Ma5	0.234 ± 0.002	80.10 ± 0.20	53.582 ± 7.021
Rm1	0.086 ± 0.009	38.61 ± 1.85	26.893 ± 4.489
Rm2	0.151 ± 0.004	58.07 ± 1.10	29.820 ± 3.471
Rm3	0.101 ± 0.008	47.17 ± 0.66	25.362 ± 5.277
Rm4	0.114 ± 0.007	47.64 ± 3.02	28.975 ± 4.595
Rm5	0.111 ± 0.012	46.43 ± 4.66	15.188 ± 2.291
Rm6	0.094 ± 0.008	42.86 ± 3.16	12.345 ± 1.893
Sg1	0.255 ± 0.009	79.12 ± 3.76	46.291 ± 5.538
Sg2	0.258 ± 0.003	88.86 ± 0.56	102.720 ± 16.472
Sg3	0.227 ± 0.007	80.38 ± 2.75	65.954 ± 9.966
Sg4	0.241 ± 0.003	84.24 ± 0.61	46.598 ± 6.327
Sg5	0.177 ± 0.015	65.94 ± 6.96	51.524 ± 7.654
Se1	0.071 ± 0.007	31.87 ± 1.80	22.096 ± 3.090
Se2	0.129 ± 0.009	55.69 ± 3.04	26.386 ± 7.279
Se3	0.109 ± 0.010	46.75 ± 4.85	12.549 ± 3.183
Se4	0.115 ± 0.009	47.41 ± 3.67	16.013 ± 3.001

Appendix 4.4. (continues)

Soil ID	[1]PRI Olsen	[2]PRC at P400	[1]PBI Olsen
Se5	0.115 ± 0.009	51.13 ± 1.63	19.658 ± 2.436
Tm1	0.163 ± 0.008	63.69 ± 1.81	41.979 ± 5.238
Tm2	0.174 ± 0.003	70.19 ± 0.47	54.972 ± 4.749
Tm3	0.170 ± 0.003	67.77 ± 0.23	52.568 ± 4.350
Tm4	0.141 ± 0.008	59.62 ± 0.00	35.507 ± 11.016
Tm5	0.172 ± 0.009	68.44 ± 3.52	41.024 ± 4.155
Md1	0.120 ± 0.007	53.33 ± 0.89	21.320 ± 3.276
Md2	0.150 ± 0.013	54.10 ± 6.90	30.043 ± 6.477
Md3	0.130 ± 0.009	58.55 ± 1.98	32.552 ± 7.763
Md4	0.132 ± 0.012	56.18 ± 5.57	20.021 ± 3.518
Md5	0.180 ± 0.008	69.14 ± 1.33	37.818 ± 3.860
Ba1	0.100 ± 0.007	43.98 ± 1.76	27.424 ± 3.773
Ba2	0.144 ± 0.005	60.50 ± 0.24	32.040 ± 4.078
Ba3	0.093 ± 0.011	43.49 ± 5.79	20.083 ± 4.309
Ba4	0.140 ± 0.009	53.15 ± 3.25	31.539 ± 3.544
Ba5	0.113 ± 0.016	49.78 ± 7.67	30.216 ± 6.462

[1]PRI and PBI with 95% confidence limits. [2]Mean PRC at P400 with standard deviations.

Appendix 5.1. The phosphorus requirement factors and their 95% confidence limits of the 56 study soils based on the Bray and Olsen extraction methods.

Soil ID	PRF Bray	PRF Olsen
Fs1	4.71 ± 0.43	3.69 ± 0.28
Fs2	9.33 ± 1.12	4.10 ± 1.64
Fs3	2.30 ± 0.15	3.01 ± 0.40
Fs4	6.81 ± 0.93	3.68 ± 0.20
Fs5	11.40 ± 1.35	4.78 ± 0.81
Khs1	1.50 ± 0.11	2.47 ± 0.19
Khs2	1.28 ± 0.06	2.22 ± 0.51
Khs3	1.69 ± 0.10	2.32 ± 0.35
Khs4	2.25 ± 0.10	2.77 ± 0.11
Khs5	1.61 ± 0.04	2.25 ± 0.32
Ta1	7.85 ± 0.79	4.65 ± 0.61
Ta2	10.03 ± 1.03	6.66 ± 0.22
Ta3	2.59 ± 0.12	3.36 ± 0.38
Ta4	7.33 ± 1.03	3.78 ± 0.29
Ta5	7.83 ± 1.27	6.81 ± 0.53
Le1	1.08 ± 0.03	1.99 ± 0.10
Le2	0.89 ± 0.02	1.97 ± 0.06
Le3	0.85 ± 0.09	1.81 ± 0.15
Le4	0.93 ± 0.03	1.71 ± 0.13
Le5	1.08 ± 0.04	1.95 ± 0.17
Ma1	6.97 ± 0.85	5.50 ± 0.34
Ma2	4.14 ± 0.30	5.96 ± 0.57
Ma3	2.42 ± 0.17	5.11 ± 0.73
Ma4	10.36 ± 5.07	4.35 ± 0.59
Ma5	4.49 ± 0.41	4.96 ± 0.17
Rm1	0.86 ± 0.05	1.58 ± 0.09
Rm2	1.05 ± 0.05	2.34 ± 0.09
Rm3	0.87 ± 0.03	1.84 ± 0.13
Rm4	1.14 ± 0.05	1.88 ± 0.11
Rm5	1.16 ± 0.09	1.77 ± 0.16
Rm6	1.00 ± 0.02	1.71 ± 0.11
Sg1	3.01 ± 0.28	4.47 ± 0.60
Sg2	5.29 ± 0.57	9.07 ± 0.90
Sg3	2.89 ± 0.23	4.88 ± 0.59
Sg4	3.36 ± 0.40	6.19 ± 0.39
Sg5	2.25 ± 0.12	2.73 ± 0.43
Se1	0.95 ± 0.03	1.45 ± 0.07
Se2	1.59 ± 0.05	2.20 ± 0.19
Se3	1.18 ± 0.06	1.82 ± 0.14
Se4	1.60 ± 0.09	1.85 ± 0.13

Appendix 5.1. (continues)

Soil ID	PRF Bray	PRF Olsen
Se5	1.36 ± 0.09	1.97 ± 0.15
Tm1	1.28 ± 0.05	2.70 ± 0.24
Tm2	1.15 ± 0.04	3.34 ± 0.13
Tm3	1.11 ± 0.04	3.04 ± 0.12
Tm4	1.09 ± 0.03	2.42 ± 0.21
Tm5	2.22 ± 0.17	3.09 ± 0.35
Md1	1.07 ± 0.04	2.10 ± 0.13
Md2	0.95 ± 0.05	2.12 ± 0.21
Md3	0.99 ± 0.03	2.39 ± 0.25
Md4	1.32 ± 0.06	2.16 ± 0.23
Md5	1.27 ± 0.06	3.16 ± 0.30
Ba1	0.97 ± 0.05	1.74 ± 0.09
Ba2	0.97 ± 0.03	2.50 ± 0.14
Ba3	0.91 ± 0.03	1.71 ± 0.15
Ba4	1.00 ± 0.04	2.09 ± 0.14
Ba5	1.09 ± 0.05	1.90 ± 0.26