CORRELATION BETWEEN AGRONOMIC AND ENVIRONMENTAL PHOSPHORUS ANALYSES OF SELECTED SOILS

by

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DECLARATION

I declare that the dissertation hereby handed in for the qualification at the University of the Free State, is my own independent work and that I have not previously submitted the same work for a qualification at/in another University/faculty. I furthermore cede copyright of the dissertation in favour of the University of the Free State.

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ABSTRACT

Correlation between agronomic and environmental phosphorus analyses of selected soils

In crop production phosphorus (P) is an essential nutrient for crop growth, and hence P fertilization is necessary to achieve optimum yields. However, this can induces in soil a P concentration which may contributes to eutrophication of fresh water bodies. Soil P tests are therefore considered very useful in setting threshold values important for both agronomic and environmental management purposes. Soil P tests developed from a water pollution protection point unlike agronomic P tests are not easily adapted for use on a routine basis because they are not considered, for this purpose, and this could make agronomic P tests more practical for routine environmental P assessment also. Determination of appropriate agronomic P tests for this purpose however, involves evaluating the potential use of the tests for environmental purposes. Hence, the objective of this study was to review the current methods used to determine the agronomic and environmental P status of soils, and to establish whether P extracted from a range of soils by various agronomic and/or environmental P determination methods are related or not.

Soil samples from the orthic A horison were collected in three cropping areas in the Free State province, namely Jacobsdal, Bloemfontein, and Ficksburg. These samples were treated with K_2HPO_4 to induce different phosphorus concentration levels and then incubated at room temperature for three months. During incubation the samples were subjected to several wetting and drying cycles to ensure that the applied phosphorus equilibrated. The samples were then analysed for P using the extractants of Olsen, Bray 1, Truog, ISFEI and citric acid commonly employed for routine analysis to establish the agronomic P status of soils. In order to establish the environmental P status of the soils, the samples were analysed for using the extractants calcium chloride ($CaCl_2$) and ammonium oxalate [$(NH_4)_2C_2O_4.H_2O$]. The latter was used to calculate the degree of phosphorus saturation (DPS_{ox}).

The results showed significant relationships among agronomic P tests when data of individual soils were analysed separately (r^2=0.65-0.99) and, when data of all soils from a sampling area were pooled (r^2=0.52-0.87). All the relationships were significant for the Ficksburg soils (r^2≥0.55) and for the Bloemfontein soils (r^2≥0.82) but not for the Jacobsdal soils. For the latter soils the Truog-P correlations with Olsen-P (r^2=0.44), Bray 1-P (r^2=0.42) and ISFEI-P (r^2=0.35) were not significant, probably due to that they are calcareous.

Significant relationships were also obtained for P extracted by the environmental P tests when regression analysis was done for each individual soil ($r^2 \geq 0.80$). However, when data of soils from a sampling area were pooled significant relationships were obtained for Bloemfontein soils ($r^2=0.92$) and Ficksburg soils ($r^2=0.56$) while Jacbosdal soils ($r^2=0.33$) showed an insignificant relationship. Pooling data of all soils from the three sampling areas also resulted with a lower correlation coefficient ($r^2=0.40$) implying a poor relationship between the environmental P tests.

The correlation between P extracted by the agronomic tests and $CaCl_2$-P showed positive relationships ($r^2 \geq 0.57$) except in a few instances. Truog-P and citric acid-P showed a poor correlation with $CaCl_2$-P when the Jacobsdal soils' data were pooled ($r^2=0.22$ and 0.35 respectively). Pooling of all soils' data resulted also in a poor correlation between $CaCl_2$-P and Truog –P ($r^2= 0.28$). The DPS_{ox} correlated significantly with the extractable P of all agronomic tests when the individual soil's data were analysed separately ($r^2 \geq 0.73$). However, when data of all soils from a sampling areas were pooled for regression analysis, all relationships were significant for the Bloemfontein soils ($r^2 \geq 0.70$), but not for the Jacobsdal soils, and Ficksburg soils. Pooling data of all soils from the three sites resulted with a positive relationship between DPS_{ox} and the extractable P of all agronomic tests ($r^2 \geq 0.50$), except ISFEI ($r^2 \geq 0.45$).

The threshold values estimated for agronomic tests with regression equations from $CaCl_2$-P DPS_{ox} threshold values varied greatly between individual soils and even the soils groups of a sampling area. The threshold values for all soils when based on $CaCl_2$ implied that if the extractable P status of cropped soils are maintained at optimum levels for Bray 1, Truog, ISFEI and citric acid the soils may be a threat to water pollution. The opposite is true with the estimated threshold values when based on DPS_{ox}. The results therefore showed that agronomic tests can be used also for environmental management of P although only the Olsen test showed the potential for developing a single threshold value for all soils.

Keywords: soil phosphorus test, crop production, water pollution, threshold value

UITTREKSEL

Korrelasie tussen agronomiese en omgewingsfosforontledings van geselekteerde gronde

In gewasproduksie is fosfor (P) ‘n essensiële voedingstof vir gewasgroei en daarom is P bemesting nodig om optimum opbrengste te kry. Nietemin, dit kan in grond ‘n P konsentrasie induseer wat mag bydrae tot die eutrofikasie van varswaterliggame. Grond P toetse word daarom as nuttig beskou om drumpelwaardes vir agronomiese en omgewingsbestuur daar te stel. Grond P toetse wat ontwikkel is met die oog daarop om waterbesoedeling te verhoed word nie oorwag om soos agronomiese P toetse op ‘n roetine basis gebruik te word nie, en dit maak agronomiese P toetse moontlik geskik vir roetine omgewing P assessering ook. Dus was die doel met die studie om ‘n oorsig te kry van die huidige metodes wat gebruik word om die agronomiese en omgewing P status van gronde te bepaal, en vas te stel of die geëkstraheerde P deur die verskillende agronomiese en omgewing P bepalingsmetodes verwant is of nie.

Grondmonsters van die ortiese A horison is in drie gewasverbouiingsgebiede in die Vrystaat provinsie ingesamel, naamlik Jacobsdal, Bloemfontein en Ficksburg. Hierdie monsters is met K_2HPO_4 behandel om fosforkonsentrasievlakke te induseer en daarna by kamertemperatuur vir drie maande geïnkubeer. Gedurende inkubasie is die monsters aan verskeie benatting- en uitdrogingsiklusse onderwerp om te verseker dat die toegediende fosfor ewewig bereik. Die monsters is daarna vir P ontleed deur die ekstraheermiddels van Olsen, Bray 1, Truog, ISFEI en sitroensuur te gebruik omdat hulle algemeen vir roetine ontledings aangewend word om die agronomiese P status van gronde vas te stel. Om die omgewing P status van die gronde vas te stel, is die ekstraheermiddels kalsiumchloried ($CaCl_2$) en ammoniumoksalaat [$(NH_4)_2C_2O_4.H_2O$] gebruik. Laasgenoemde is gebruik om die graad van fosforversading (DPS_{ox}) te berken.

Die resultate het getoon dat daar tussen die agronomiese P toetse betekenisvolle verwantskappe is wanneer die data van die indiwiduele gronde ontleed is (r^2 = 0.65-0.99), en wanneer die data van al die gronde van ‘n monsteringsgebied gepoel is (r^2 = 0.52-0.87). Al die verwantskappe vir die Ficksburggronde ($r^2 \geq 0.55$) en vir die Bloemfonteingronde ($r^2 \geq 0.82$) was betekenisvol, maar nie vir die Jacobsdalgronde nie. Vir laasgenoemde gronde was die Truog-P korrelasies met Olsen-P (r^2 = 0.44), Bray 1-P (r^2 = 0.42) en ISFEI-P (r^2 = 0.35) nie betekenisvol nie, moontlik omdat hulle kalkhoudend is.

Betekenisvolle interaksies is ook gekry vir geëkstraheerde P met omgewing P toetse wanneer regressie-ontledings vir elke indiwiduele grond gedoen is ($r^2 \geq 0.80$). Nietemin, wanneer data van gronde vanaf ‘n monteringsgebied gepoel is, is betekenisvolle verwantskappe vir Bloemfonteingronde ($r^2 = 0.92$) en Ficksburggronde ($r^2 = 0.56$) gekry terwyl Jacobsdalgronde ($r^2 = 0.33$) nie ‘n betekenisvolle verwantskap getoon het. Poel van data van al die gronde van die drie monsteringsgebiede het ‘n laer korrelasiekoeffisiënt gegee ($r^2 = 0.40$) wat ‘n swak verwantskap tussen die omgewing P toetse impliseer.

Die korrelasie van geëkstraheerde P met die agronomiese toetse en $CaCl_2$-P het behalwe vir enkele gevalle ‘n positiewe verwantskap ($r^2 \geq 0.57$) gegee. Truog-P en sitroensuur-P het ‘n swak korrelasie met $CaCl_2$-P gegee wanneer die Jacobsdalgronde se data gepoel is ($r^2 = 0.22$ en 0.35 onderskeidelik). Poel van al die gronde se data het tot ‘n swak korrelasie tussen $CaCl_2$-P en Truog-P ($r^2 = 0.28$) gelei. Die DPS_{ox} het betekenisvol met die ekstraheerbare P van al die agronomiese toetse gekorreleer wanneer die indiwiduele gronde se data afsonderlik ontleed is ($r^2 \geq 0.73$). Nietemin, wanneer die data van al die gronde van ‘n monsteringsgebied gepoel is vir regressie-ontleding, was al die verwantskappe vir die Bloemfonteingronde ($r^2 \geq 0.70$) betekenisvol, maar nie vir die Jacobsdalgronde en Ficksburggronde nie. Poel van die data van al die gronde vanaf die drie monsteringsgebiede het ‘n positiewe verwantskap tussen DPS_{ox} en die ekstrheerbare P van al die agronomiese toetse ($r^2 \geq 0.50$) gegee, behalwe ISFEI ($r^2 \geq 0.45$).

Die drumpelwaardes wat vir agronomiese toetse met regressievergelykings beraam is vanaf $CaCl_2$-P en DPS_{ox} drumpelwaardes het baie tussen indiwiduele gronde en selfs grondgroepe van monsteringsgebiede gevarieer. Die drumpelwaardes vir al die gronde wanneer gebaseer op $CaCl_2$ impliseer dat as die ekstraheerbare P status van verboude gronde by optimum vlakke vir Bray 1, Truog, ISFEI en sitroensuur gehou word die gronde ‘n bedreiging vir waterbesoedeling is. Die teenoorgestelde het gemanifesteer met die beraamde drumpelwaardes wanneer op DPS_{ox} gebaseer. Die resultate toon derhalwe dat agronomiese toetse ook gebruik kan word vir die omgewingsbestuur van P alhoewel slegs die Olsen toets die potensiaal getoon het vir die ontwikkeling van ‘n enkele drumpelwaarde vir al die gronde.

Sleutelwoorde: grondfosfortoets, gewasproduksie, waterbesoedeling, drumpelwaarde.

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DEDICATION

This thesis is dedicated to my mother Mrs Anna Nthejane and my father the late Ntate Mareka Gerard Nthejane whose love and guidance made me who I am today.

CHAPTER ONE

INTRODUCTION

1.1 Motivation

Phosphorus (P) is a key element in both crop production and environmental sustainability. It has been recognised as one of the important elements required to maintain profitable crop production (Sharpley & Tunney, 2000). Phosphorus is classified as a macronutrient in agronomy because of the relatively large amounts in which it is needed by plants. It is therefore an integral part of many soil fertility programmes and hence is applied to agricultural land as either manure or inorganic fertilizer to improve P status of the soil required to meet crop production goals (Schindler *et al.,* 2009). However, the long term and excessive use of fertilizers and manure may result in an increase in the soil P concentration (Shigaki *et al.,* 2006; Toor *et al*., 2006). High soil P concentrations, to levels beyond the crop needs, increase the risk of agriculture nonpoint source pollution (Lzu *et al.,* 2007). Phosphorus is also a principal nutrient associated with eutrophication of recipient water bodies (Rossouw *et al.,* 2008).

Loss of phosphorus from agricultural land to surface water bodies has been a concern in South Africa (Harding *et al.,* 2009). Freshwater pollution is estimated to be 4.74 t P km^{-3} and the average P concentration in the natural water resources of South Africa (as orthophosphate) has been estimated at 0.73 mg $liter^{-1}$ (Nationmaster.com, 2003). The report of De Villiers and Thiart (2007) on the nutrient status of the twenty largest river catchments in South Africa indicates that 60% of the rivers showed statistically significant ($P < 0.05$) upward trends in dissolved orthophosphate (PO_4^{3-}) content. Harding *et al.*(2009) also stated that 35% of total water resources are eutrophic, further indicating that South Africa's freshwater resources are being enriched with P. Phosphorus is considered a undesirable nutrient in water bodies as it results in ecological, economical and social problems. It accelerates cyanobacteria (blue-green algae) and various aquatic vegetative growths (Rossouw *et al.,* 2008). The dissolved oxygen levels of water bodies under these eutrophic conditions diminish quickly as micro-organisms decompose the vegetative matter. Oxygen depletion impairs the water body and restricts its use for drinking, fishery, industry, and recreation (Rossouw *et al.,* 2008).

The environmental problems associated with P losses from agricultural soils have a significant negative economic impact on water quality (Walmsley, 2000). Cyanobacteria release substances into the water that are harmful or toxic to aquatic biota, livestock, and human

beings. This increases the costs of water treatment and maintenance of water supplies, causing problems in meeting the ever-increasing demand for water (Oberholster *et al.,* 2004). Loss of P due to agricultural runoff is also of economic importance to the farmers (Rossouw *et al.,* 2008). The costs associated with soil nutrient loss by runoff equates to a significant loss in terms of fertilizer costs and therefore the financial contribution of agriculture to the national economy (De Villiers & Thiart, 2007).

Increased concern on the environmental impact of agricultural soil P has intensified the need for determining appropriate management strategies for P, which includes the methods that can accurately measure soil P susceptible to runoff (Horta & Torrent, 2006). The challenge is amplified by the fact that the existing environmental soil P testing methods are tedious and time consuming, which therefore contribute to their unlikely use in routine soil P testing (McDowell & Sharpley, 2001). Unlike the environmental soil P tests, various routine agronomic methods have been recommended and used, which effectively assess the P status of soils and are calibrated for making fertilization recommendations (Sharpley & Tunney, 2000). These methods can be used in the management of soil P sources to address water quality issues and also to maintain the productive agronomic potential of soils which are similarly important. They can also be implemented where limited resources are available, making them appropriate for agro-environmental soil P tests. However, agronomic soil P tests require more evaluation in terms of accuracy in measuring P susceptible to runoff (Magyar *et al*., 2006).

The purpose of this study is therefore to provide information that authenticates the importance of agronomic and environmental soil tests in measuring the concentration of available P in the surface layer of soils for determining threshold values critical for proper regulatory and management of P sources for both agronomic and environmental purposes.

1.2 Hypothesis

The phosphorus fraction which is agronomically significant in soil is the same which contributes to environmental pollution. Therefore, it may be possible to use only one chemical test to establish both the agronomic as well as the environmental threshold values.

1.3 Objectives

- To review the current methods used to determine the agronomic and environmental phosphorus status of soils.
- To establish whether phosphorus extracted from a range of soils by various agronomic and/or environmental phosphorus determination methods is related or not.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Phosphorus is a very reactive, naturally occurring element in soil. It originates from the weathering of igneous, sedimentary, and metamorphic rocks, which release the main phosphorus containing mineral, apatite and other phosphate minerals into the environment (Troeh & Thompson, 2005). These primary minerals weather over time and release P into the soil. Phosphorus in the environment also exists as a result of anthropogenic processes because it is added to the soil as fertilizers and manure to improve the fertility of soils (Troeh & Thompson, 2005).

Phosphorus is considered as one of the most limiting nutrients in agricultural soils because most P compounds are insoluble or strongly bound onto soil particle surfaces (Ratchaneeporn, 2009). The formation of these insoluble phosphates depend on the complex dynamics of P in soil, which involve several physico-chemical (sorption-desorption) and biological (immobilization-mineralisation) reactions (Sims, 1998). The rate and direction of these reactions are influenced by the properties of soil and microbiological components (Campbell & Edwards, 2001).

Low P concentration in soil may resulted in an over application of fertilizers and manure in crop production areas (Shigaki *et al.*, 2006; Toor *et al.*, 2006). Over application of P also occurs when manure is applied based on crop nitrogen requirement. The low N/P ratio of manure (2:1 to 6:1) as compared to crop uptake ratio (7:1 to 11:1) contributes to the N-based manure management which results in more P being added to the soil than the crop requires (Sharpley *et al*., 1996; Gburek *et al*., 2000). In addition, increased animal production results in excessive manure production, which is then habitually applied at frequencies exceeding P requirement of the crops (Mallarino *et al*., 2001).

The application of fertilizers and manure P is required to maintain adequate amounts of P in soil for sustainable crop production. However, their contribution to the environmental risk of excessive soil P loading is also crucial and hence must be considered (Ratchaneeporn, 2009). Several research studies have been done locally and internationally on nonpoint P pollution of water and therefore a lot of literature on various aspects of this topic exists.

In this review the focus will be on the cycle of phosphorus in soil-plant systems, especially the essentiality of phosphorus in plants and the dynamics of phosphorus in soil. The management of phosphorus in soil with regard to crop production and environmental protection will be dealt with next, including the use of soil phosphorus tests.

2.2 Phosphorus cycle in soil-plant systems

Phosphorus is usually a scarce resource and is fairly efficiently recycled in natural ecosystems (Haygarth & Jarvis, 1999). This cycling includes interactions and transformations occurring through physical, chemical, and microbiological processes that determine the forms of P, its availability to plants and its transport in runoff or leaching (Campbell & Edwards, 2001). The processes and different P pools that make up the P cycle are illustrated in Figure 2.1.

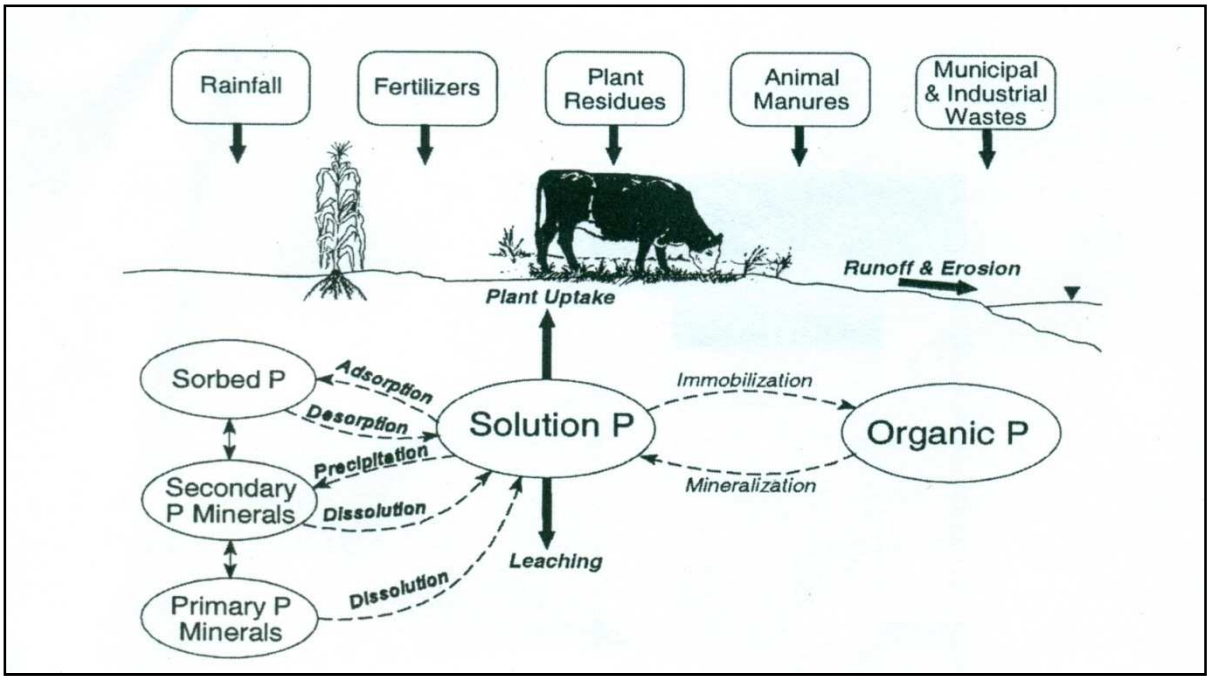

Figure 2.1 Phosphorus cycle in soil-plant systems (Campbell & Edwards, 2001).

Phosphorus in soil originates from the weathering of residual minerals and from other sources like fertilizers, animal manure, plant residues, and industrial wastes (Campbell & Edwards, 2001). Phosphorus is released into the soil solution in forms available for plant up-take through the following processes that are reversible: (1) dissolution of primary and secondary minerals; (2) desorption of P from clays, oxides, and minerals; and (3) mineralisation of P in organic materials to inorganic forms (Sims, 1998). Precipitation and sorption of dissolved P are the

reversible chemical processes that regulate soil solution P concentrations (Campbell & Edwards, 2001).

Phosphorus in soil solution is either found as a monovalent ($H_2PO_4^-$; in acid soils) or a divalent (HPO_4^{2-}; in alkaline soils) anion (Hiradate *et al.*, 2007). These phosphate ions in the soil solution are readily absorbed by plants, and animals can utilise the P in plants. The P is ultimately returned back to the soils as organic phosphates in either plant or animal residues. These are slowly released as inorganic phosphate during mineralisation by microbial biomass or may be incorporated into more stable organic materials and become part of the soil organic matter (Whitelaw, 2000). Inorganic P also may be converted to organic P through immobilisation by soil microbes. Mineralisation and immobilisation rates depend on the C:P ratio of residues in the soil. Immobilisation occurs when the C:P ratio exceeds 300:1 while mineralisation is rapid when the C:P ratio is less than 200:1. These processes are in approximate balance when the C:P ratio ranges between 200:1 and 300:1. Mineralisation and immobilisation are also affected by factors such as temperature, moisture, aeration, pH, cultivation intensity, and P fertilisation (Campbell & Edwards, 2001).

Phosphates in the soil can potentially be lost to fresh water sources through several transport processes in the form of either particulate P or dissolved P. This results in higher levels of P available to organisms like algae in streams, lakes or rivers. The ultimate effect is the eutrophication of these water sources (Sims, 1998).

2.2.1 Essentiality of phosphorus for plants

Phosphorus is a plant nutrient that affects biological processes and hence is essential for plant growth. It is required for the biosynthesis of nucleotides, nucleic acids, coenzymes, phosphoproteins, phospholipids, and sugar phosphates. Energy produced during photosynthesis and metabolism of carbohydrates is stored in phosphate compounds. The nucleotides, adenosine di- and tri-phosphates (ADP and ATP) are important for energy storage and transfer in plant biochemical processes. Phosphorus is also required for phosphorylation, the reaction in which ATP is converted back to ADP (Havlin *et al.,* 1999). Adequate P availability for plants is important for root growth and development of plant reproductive parts (seeds and fruits). It therefore improves the quality of fruit, forage, vegetables, and grain crops (Sanchez, 2006). Phosphorus increases the tolerance of grain crops to fungal disease (root-rot) and also reduces the risk of cold damage to small grain crops (Havlin *et al.,* 1999).

Phosphorus deficiency in plants results in low yields and poor quality as the vegetative and reproductive growth is depressed, because of impaired protein synthesis. Plants are stunted with limited root systems, thin stems and smaller leaves. In many plants seedlings also look stunted and older leaves turn purple or sometimes bluish-green because of anthocyanin accumulation (Sharma, 2002). Since P is mobile in plants, it is translocated from older to younger leaves resulting in deficiency symptoms, such as chlorosis and necrosis occurring on older leaves. Sustained P deficiency in fruit bearing plants result in few and short new shoots and malformed fruits and seeds (Sanchez, 2006).

2.2.2 Dynamics of phosphorus in soils

2.2.2.1 Phosphorus forms

Soil P exists in organic and inorganic forms (Troeh & Thompson, 2005). The total P concentration of soil ranges from 50 to 3000 mg kg^{-1}, of which 15-80% occurs in the organic form composed of the complex compounds inositol phosphates, phospholipids and nucleic acids (Sims, 2000; Pierzynski *et al.,* 2005). These forms of organic P compounds differ in their concentration in soil. The inositol phosphates are mainly sugar molecules with one or more phosphate groups replacing hydrogen and are the most dominant form of organic phosphorus in soil. Phospholipids which are formed from phosphorus and fatty compounds account for about 1-10% of the organic phosphorus. Nucleic acids from plant, animal, and microbial biomass including their decomposition products contain up to 10% of soil's organic phosphorus (Troeh & Thompson, 2005). Microbial activity is responsible for organic P turnover in the soil through decomposition, immobilisation, and mineralisation (Sims, 2000; Hiradate *et al*., 2007; Hariprasad & Niranjana, 2008). The extent and rate of conversion of organic P into soluble or stable inorganic P forms depend on environmental factors such as temperature and soil water and also on the amount and nature of organic material in the soil (Sharma, 2002).

Inorganic P forms in the soil solution exist as monovalent ($H_2PO_4^-$) ions in acid soils or divalent (HPO_4^{2-}) ions in alkaline soils. As discussed earlier, these ions can be adsorbed on clay minerals or precipitate forming complex minerals with a wide variety of elements depending on the soil pH. The most common phosphate minerals are the variscite (Al-PO_4) and strengite (Fe-PO_4) minerals formed in acid soils and the different forms of apatite (Ca-PO_4) found in neutral and calcareous soils (Table 2.1). The solubility of these minerals in the soil depends on the concentration of the solution P ion supported by the mineral form in the soil which is in turn

dependent on pH (Havlin *et al.,* 1999). The minerals are listed in Table 2.1 in the order of their decreasing solubility. Solubility of the minerals also differs as a function of time and development stage of the soil. The dominant minerals in less weathered or moderately weathered soils are the apatites comprising of Ca-PO_4 (Hariprasad & Niranjana, 2008). In highly weathered acidic soils variscite and strengite exist, because the Ca and other basic minerals were leached, resulting in Fe and Al dissolving as the pH decreases (Pierzynski *et al.,* 2005). Phosphorus exists in non-labile, occluded or stable forms in highly weathered soils. Neutral and slightly acidic soils contain all P forms in comparable amounts.

Table 2.1 Common phosphate minerals found in acid and neutral to calcareous soils (Havlin *et al.,* 1999)

Acid soils	
Variscite	$AlPO_4 \cdot 2H_2O$
Strengite	$FePO_4 \cdot 2H_2O$
Neutral and calcareous soils	
Dicalcium phosphate dehydrate (DCPD)	$CaHPO_4 \cdot 2H_2O$
Dicalcium phosphate (DCP)	$CaHPO_4$
Octacalcium phosphate (OCP)	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$
β-tricalcium phosphate (βTCP)	$Ca_3 (PO_4)_2$
Hydroxyapatite (HA)	$Ca_5 (PO_4)_3OH$
Fluorapatite (FA)	$Ca_5 (PO_4)_3F$

2.2.2.2 Phosphorus pools

The P compounds found in soil are often grouped into three pools, namely soil solution P, labile P, and non-labile P where the latter two pools represent both inorganic and organic compounds (Figure 2.2). The P in these three pools is continuously converted from one to another. For example, the soil solution P can be taken up by plants or be transformed into secondary minerals, an unavailable form for plant uptake. The plant available P, viz. orthophosphate HPO_4^{2-} or $H_2PO_4^-$ constitute a small fraction of P dissolved in soil solution. As the plant depletes orthophosphate in the soil solution, the second labile or active P pool replenishes the dissolved P (Hocking, 2001). Labile P consists of adsorbed P on the surfaces of more crystalline compounds like sequioxides or carbonates. This P is held by relatively weak bonds to soil particles and organic matter. The non-labile or stable P in the third soil P pool contains inorganic

phosphate compounds that are very insoluble and organic compounds that are resistant to mineralisation by microorganisms. Phosphorus in this pool is held strongly to soil particles in the form of iron and aluminium phosphates in acid soils, calcium phosphates in calcareous soils, and in highly recalcitrant bonds to organic matter. Stable P is considered unavailable to plants and is released at a very slow rate to the labile and soluble P pools (Sharma, 2002).

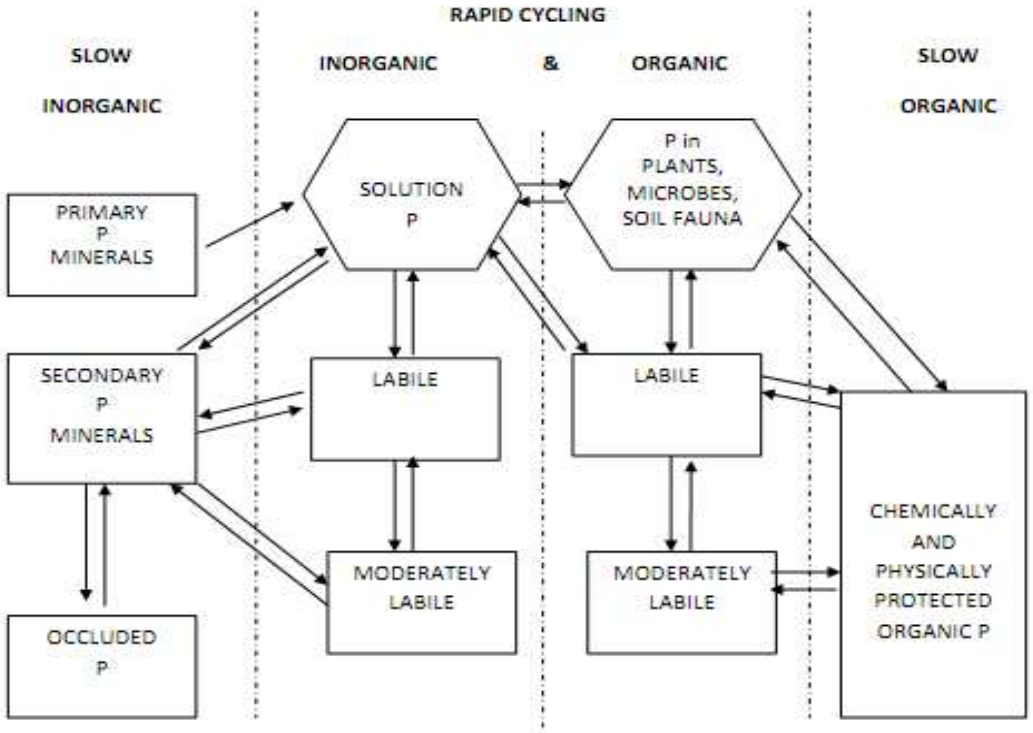

Figure 2.2 Phosphorus pools in soils (Tiessen *et al.,* 1984).

2.2.2.3 Phosphorus availability

The three P pools have different plant availabilities and are in equilibrium with each other. Absorption of P by plants is determined by the concentration of phosphate ions in the soil solution, rate of diffusion of phosphate ions, and capacity of the solid phase to renew the content of phosphate ions in the soil solution. Availability of P to the plants is influenced by properties of soil determining the sorbability or desorbability of P (Griffin *et al*., 2006) which include clay content and mineralogy, organic matter, soil pH, and exchangeable Al, Fe, and Ca concentration in the soil solution (Whitelaw, 2000; Arai & Sparks, 2007). These factors, determining the phosphorus availability in soil, are discussed below:

1. Clay content and mineralogy: Phosphorus solubility is strongly controlled by adsorption and desorption on clay minerals in soil. Clay minerals with high Si:Al ratios (2:1 type) like illite and montmorillonite have low P sorption capacities while those with low Si:Al ratios (1:1 type) like kaolinite and allophane have high P sorption capacities. This is because the latter clay minerals have a large number of exposed hydroxyl groups associated with Al, high content of associated hydrated oxides of Fe and Al, and pH dependent charges on the edges of the mineral lattice (Troeh & Thompson, 2005). Clay content of the soil also affects the degree of P fixation. Soils with high clay content have a larger capacity to hold phosphates by adsorption than soils with low clay content, even when the clay mineralogy is similar (Troeh & Thompson, 2005).

2. Organic matter: This fraction in soil contributes to P fixation by forming complex compounds of organic matter, metal cations, and phosphates. Soil organic matter consists of humic and fulvic acids containing functional groups such as $R\text{-}COO^-$, R-C=O, R-COH, R-SH and others. These functional groups are capable of adsorbing metal cations and thus increasing sorption of P in soil (Bianchi *et al.,* 2008). In addition, the low molecular weight organic acids released during decomposition of organic residues increase the P sorption sites on cations by inhibiting polymerization and crystallisation of metal cations. However, most organic matter interaction with soil components is in a manner that mobilises P in soil and hence it greatly increases P uptake by crops (Wandruszka, 2006). Organic acids reduce the adsorption of added phosphorus on soil colloids by competing for binding sites (Hariprasad & Niranjana, 2008). Organic acid anions are more quickly adsorbed on soil surface than P and this increases the P concentration in the soil solution (Wandruszka, 2006). Solubilisation of P compounds by organic acids also occurs through complex formation between organic acid and metal ions, especially Al, Fe, and Ca. Metal complexation and dissolution reactions reduce the number of sorption sites and more P is released for plant uptake (Bolan *et al.,* 1994; Geelhoed *et al.,* 1999; Wandruszka, 2006). Organic acids are also a readily soluble source of carbon for microorganisms and therefore influence the rhizosphere microbial population and consequently increase plant growth (Bolan *et al.,* 1994; Yang *et al.,* 1994).

3. Soil pH and exchangeable Al, Fe, and Ca concentration: The solubility of the compounds holding P is directly related to soil pH. Phosphorus is most available in the pH range of 6.5 to 7.0 (Troeh & Thompson, 2005). A change in soil pH to outside this range affects the charge of the P species in solution and on the surface of the adsorbing particles. An

increase in pH results in P adsorbing sites increasingly being negatively charged. This makes the reaction with negatively charged phosphate ions more difficult and therefore tends to decrease P adsorption and thus changes the proportion of P species in solution (Whitelaw, 2000).

In acidic soils more P reacts with iron (Fe^{3+}) and aluminum (Al^{3+}) to form insoluble phosphate compounds. The solubility of these phosphates increases with increase in soil pH. In alkaline soils and calcareous soils, P reacts with excess calcium (Ca^{2+}) also forming insoluble compounds. The solubility of these phosphates increases with decreasing soil pH. Fixation of P is usually higher in acidic soils than in neutral or calcareous soils (Whitelaw, 2000).

Calcium carbonate serves as the main adsorption site for P in calcareous soils. Soluble P reacts with $CaCO_3$ to form low solubility calcium phosphates which later may crystallise to precipitated P compounds under alkaline soil conditions. In strongly alkaline soil where large amounts of sodium are present sodium phosphates are formed. Sodium phosphates unlike calcium phosphate are soluble. Phosphorus availability is therefore not a major problem at pH values above 9. Plant growth is then, however, affected by other adverse conditions (Troeh & Thompson, 2005). For example an increase in P availability at high pH lowers the concentration of micronutrients (Cu, Fe, and Zn) in soil (Whitelaw, 2000; Hocking, 2001).

2.2.2.4 Phosphorus additions

Soil solution P content is naturally very low in most soils and P sources are therefore used to improve these low levels to the accepted levels for optimum crop growth and yield (Haygarth & Jarvis, 1999). The most commonly used P sources in crop production are either of inorganic or of organic nature. Inorganic sources are rock phosphate, single superphophate, triple superphosphate, mono-ammonium phosphate, di-ammonium phosphate, potassium phosphate and compound fertilizer NPK (Troeh & Thompson, 2005). Most of these inorganic P fertilisers are water soluble, except for rock phosphate. This means they have a high percentage of P immediately available for plant uptake when applied to soil. However, this water soluble P is converted rapidly over time to less soluble forms in soil (Ratchaneeporn, 2009), depending on soil pH, soil water content, and soil temperature. Haygarth and Jarvis (1999) indicate that the plant absorption of applied P fertiliser is only 5 to 10%, while Hiradate *et al. (*2007) stated that it

is lower than 20% because most is fixed by soils as low-solubility Ca-PO_4 and Mg-PO_4 compounds in alkaline soils and Al-PO_4 and Fe-PO_4 compounds in acid soils. The P content of the soil also varies with parent material, texture, and management factors such as rate and type of P applied and soil cultivation (Sims, 1998).

Organic P sources are animal manure, sewage sludge, and plant residues. The P content and chemical composition of organic P sources varies. In animal manures P composition is influenced by the type and age of the animal, diet, and management factors such as type of bedding material and method of manure storage. Sewage sludge variability is influenced by treatment processes (Atia & Mallariono, 2002; Troeh & Thompson, 2005). Phosphorus in organic manure therefore exists in inorganic and organic forms with different solubilities. Most of organic P sources have less P immediately available for plant uptake and have to be mineralised to release plant available P to the soil solution. The rate at which plant available P is released depends on microbial activity in the soil and the form of organic P source used. Pierzynski *et al*. (2005) indicate that fresh plant residues quickly release P into the soil solution while stable forms of organic matter like manure, biosolids, composts, and humus act as long term sources and slowly release P into the soil solution. Organic P sources stimulate this transformation of non-labile P to soluble P by increasing the number of microorganisms and soil enzymes decomposing organic bound P (Bolan *et al*., 1994; Yang *et al*., 1994). Organic manure amendment also increases P mobilisation in the soil through the blockage of P sorption sites by organic acids such as citrate which form complex compounds with exchangeable Al and Fe in soil (Bolan *et al.,* 1994; Geelhoed *et al.,* 1999; Wandruszka, 2006).

The P nutrition of crops therefore depends on the source of P used and the ability of the labile P in soil to quickly replenish P in the soil solution as the plants remove it (Whitelaw, 2000) and on the ability of the plant to produce a healthy and extensive root system for maximum absorption (Sharma, 2002).

2.2.2.5 Phosphorus losses

The main transport pathways through which P can be lost from agricultural fields to fresh water bodies are surface runoff or erosion and subsurface flow (Sims *et al.,* 1998; Haygarth & Sharpley, 2000). Soil erosion or surface runoff may be generated by two nonexclusive mechanisms, infiltration excess runoff which occurs when rainfall intensity exceeds the infiltration capacity of the soil and saturation excess runoff which is when water tables rises to the soil surface so that the soil's water storage capacity is exceeded (Heathwaite *et al.*, 2005;

Kleinman *et al.*, 2006). Soil erosion or surface runoff is often associated with dissolved P and high rates of particulate P or sediment-bound P (Sims *et al.,* 1998; Borling *et al.*, 2004; Heathwaite *et al.*, 2005). Particulate P transfer occurs with colloidal materials associated with >0.45 µm-sized sediments although the operationally defined threshold size is often taken as >0.4 µm and even as >0.2 µm (Horta & Torret, 2006). These include P adsorbed to fine soil particles, mineral P, and organic material eroded during flow events. These sediments provide a long-term source of P to aquatic biota. Dissolved P or soluble P is mainly orthophosphates released from soil, plant material, and applied fertilizer and manure and is available for uptake by aquatic biota (Sharpley & Withers, 1994; Sharpley *et al*., 1996; Haygarth & Jarvis, 1999).

Translocation of colloids depends on the prevailing conditions for transport, such as colloid stability in the soil solution, soil water content, pore size and geometry of the water-conducting pore system. The magnitude of P transfer by erosion is measured by the amount of sediment moved and the dissolved P concentration in runoff, although it may be different from that of the source due to dissolved P enrichment or reduction during transportation (Sharpley *et al.*, 1996). The total amount of dissolved P transported from agricultural soil to water bodies depends on (1) the total desorbable P content of the soil; (2) the proportion of P in the soil solid phase between adsorbed and precipitated form; (3) the rate of phosphate desorption from various adsorption sites in soil colloids; and (4) the metal phosphates dissolution rate mainly rich in Al, Fe, and Ca (Horta & Torret, 2006).

The rate at which P is transported is influenced by various agronomic practices and transport factors. Agronomic factors include soil P levels, P fertilizer source, application rate, method, and time. Transport factors include soil erosion, surface runoff, subsurface drainage, field slope and proximity of the field to surface waters (Allen *et al.*, 2006).

Long-term P fertiliser and manure addition without soil P testing have the effect of concentrating P in the surface layer of agricultural soils, increasing the potential P loss. Lzu *et al.* (2007) found that soluble P in runoff water increased significantly with the increase of phosphate fertiliser and manure application rates, whereas the maximum phosphorus sorption capacity decreased with phosphate fertiliser and manure application rates. Similar results were obtained by Haygarth and Jarvis (1999), although manure application rate was found to have a greater influence on soil P availability and leaching than the application of fertilisers. Surface application of fertiliser and manure without incorporation into the soil also results in a large reservoir of P available for transfer to waters by surface runoff or leaching. Time of manure or fertiliser application is also

crucial as there are vulnerable times, especially in autumn which is a season in which there is frequent heavy rainfall and also any time before irrigation (Haygarth & Jarvis, 1999).

Soil characteristics is another factor which defines the chemical form of P export and the pathway. Highly fertilised sandy soils that are poor in the main P sorbents Fe and Al oxide also often exceeds critical levels and are therefore vulnerable to P loss through leaching (IIg *et al*., 2005; Zheng & Macleod, 2005).

Tillage practices can have a direct effect on P transfer, mostly because of physical effects on vulnerability to soil erosion (Haygarth & Jarvis, 1999). Different tillage methods have varying effects on vulnerability to erosion and P transfer. The use of mould board ploughing for instance creates the greatest soil disturbance and thus the greatest risk of erosion with a high capacity to pulverise and invert the soil surface. It also increases the risks of P loss by removing the crop cover (Haygarth & Jarvis, 1999).

The type of crop grown and landscape position can influence surface runoff generation processes and excess P saturation in surface water. Growing of cover crops can reduce the amount of particle detachment and erosion especially on sloping lands as they are highly susceptible to soil loss through surface flow.

Leaching is the subsurface transportation of P from the soil surface through the soil profile into the water table. It involves transportation of P through saturated flow, common in saturated sandy soils or preferential macropore flow common in clay soils (Sims *et al.,* 1998; Haygarth & Jarvis, 1999). Leaching occurs mostly in soils which easily reach a high degree of phosphorus sorption saturation, such as highly fertilised acidic sandy soils, organic or peaty soils, and also soils with low water holding capacities. These soils have minimal Fe and Al oxides, clay minerals, and carbonates and therefore have low P adsorption sites (Gburek *et al*., 2005).

The availability of P in water systems has received much attention due to its important biogeochemical role in the environment. Phosphorus is an element with very low solubility and thus a unique water pollutant. An increase in the amount of P in soil results mostly in increased levels of phosphate in the soil solution. This result in potentially important increase of P transported from agricultural land by erosion into surface water (Boesch *et al*., 2001). Phosphorus can have detrimental effects on water quality at concentrations as low as 35 µg P L^{-1} although it is not toxic. The accepted critical concentration limit is 100 µg P L^{-1} (Haygarth *et al.*, 2000; Walmsley, 2000; Toor *et al.,* 2006). Soil P is almost entirely associated with particle

size distribution. The fine particles provide the high surface area or affinity sites for P sorption. When soil erosion occurs, the dissolved P and more of the fine particles are transported than the coarse particles causing sediment leaving the soil through erosion or leaching to be enriched with P (Zheng & Macleod, 2005).

The problems associated with eutrophication include high levels of bioavailable P which causes algal blooms or a high phytoplankton population. It is organic matter that is the actual cause of eutrophication. Decomposition of the increased organic matter in water depletes the oxygen concentration within the system. These primary producers continue to consume dissolved oxygen, reducing it to a level exceeding replenishment, when anoxia (lack of oxygen) and even hypoxia (dissolved oxygen concentration is lower than required by indigenous organisms) develops (Boesch *et al*., 2001). The chemical effects of increased de-oxygeneration are production of hydrogen sulphide and elevated levels of heavy metals. Algal blooms are produced which reduce light from entering the system. Light reduction affects photosynthetic organisms like sea grass and other plants growing in water. The loss of aquatic vegetation loosens sediment at the bottom, adding particulate suspension and turbidity, which further block light penetration for photosynthesis (Walmsley, 2000).

Loss of food and oxygen result in death of species or migration to better waters. The habitat becomes less desirable for smaller species because predators dominate and food sources change. The shifted food webs begin to decrease the biodiversity of the system. Another problem associated with eutrophication is harmful algae blooms (microscopic organisms *Pfiesteria*) which differ from other blooms because of their toxic nature (Walmsley, 2000). The toxins of these blooms can work their way through food chains and food webs, killing (marine organisms) fish species, seabirds, and aquatic mammals. It can cause illness and even death of humans through consumption of affected species (Arai & Sparks, 2007).

The economical impact of eutrophication is through its impact on commercial agricultural production such as irrigation based crop production and the fishing industry. Eutrophication results in killing or driving away the desired fish species and thus decreasing production in the fishing industry. The other economic impact is an increase in water treatment costs through filter clogging in water treatment works and increased bad taste and odour problems in drinking water. Other concerns are loss of recreational fishing and other activities affected by toxic algal blooms. The loss of aesthetic value could also lead to reduced tourism to these areas and recreation activities such as swimming, fishing, and boating (Walmsley, 2000).

The detrimental impact of P on water quality can therefore be accelerated by physical, chemical and biological reactions that control P solubility in soils, the transport processes that move soluble and particulate P to surface waters and the effect of bioavailable P on aquatic biota (Pierzynski *et al*., 2005).

2.3 Management of soil phosphorus

2.3.1 For crop production

Inorganic and organic sources of P are used in agronomy to correct nutrient deficiency and increase crop yield to the optimum level. Soil P testing and other diagnostic techniques such as plant tests and deficiency symptoms identification are useful in determining the P status of soil and quantity of P needed for crop grown (Havlin *et al.,*1999). Added P availability is, however, generally dependent on soil P reactions, influenced by the factors discussed in Section 2.2.2.3. In addition P is also immobile in soil. Unlike other nutrients which move through the soil by means of bulk flow and diffusion, P moves mainly by diffusion which is very slow. Therefore for improved efficiency with which fertiliser P can be used by the plants, there should be sufficient P supply close to the root surface (Havlin *et al.,* 1999). Morphology and physiology of the root system determine the total area of roots in contact with the soil. A root system that is extensively branched, development of root hair, and hyphae all increases uptake because more root surfaces will be in contact with the soil. Management of P therefore varies with the kind of plant grown as crops respond differently to fertiliser P application (Sanchez, 2006).

Phosphorus availability after application of a P source depends on the percentage of water soluble P in the source. High water solubility is important for starter fertiliser application, fast growing crops, short season crops, crops with restricted root systems (Sanchez, 2006), and crops grown in cool wet seasons when biological processes including absorption of P is very low (Troeh & Thompson, 2005).

The method and frequency of fertiliser P application are also important in improving P acquisition efficiency. There is high P fixation when more of the added P is in greater contact with soil absorbing surfaces than the roots (Havlin *et al.,* 1999). Fertiliser that is broadcast and ploughed in is in less contact with plant roots than with band application where there is a greater amount of P closer to the roots for absorption. The frequency of P application also depends on the P fixing capacity of the soil. Fine textured soils with high P fixation capacity require more frequent P application than coarse textured soils with low P fixing capacity (Troeh & Thompson,

2005). Soil water and temperature also affect P availability since they determine the rate of soil reactions governing the dissolution, adsorption and diffusion of P in soil solution. In conclusion P availability and uptake efficiency is in general influenced by the interaction of factors such as crop root morphology, length of the crop growing season, soil chemical and physical characteristics and cultural practices (Sanchez, 2006).

2.3.2 For environmental protection

Phosphorus in runoff from agricultural land is considered as non-point source pollution that can be controlled through the use of a proper nutrient management plan (Giasson *et al*., 2003). The main emphasis is on the rate, method, and time of application which all directly influence the P concentration in soil. Routine soil testing for P to determine the plant available amount of P in soil can reduce the risk of P loss as excess amounts will be avoided (Sims *et al*., 2002). The plan should also include management of hydrological factors and other cropping practices which increase vulnerability of fields to P loss (Giasson *et al*., 2003). Hydrologic factors can be managed by practices such as minimum cultivation, contour ploughing, and other management practices which will slow or reduce surface runoff and/or encourage infiltration or sediment trapping. These include measures such as terracing, contour tillage, cover crops, buffer strips, riparian zones, and impoundments or small reservoirs (Haygarth & Jarvis, 1999).

The phosphorus index is often used to assess the potential risk of P loss from agricultural fields to surface water bodies (Giasson *et al.,* 2003). In this index threshold P levels and sediment production estimates are taken into the account. The latter is obtained with the universal soil loss equation (Mallarino *et al*., 2001). By using the phosphorus index it is possible to rate a field's vulnerability to P loss in either water or sediments as very low, low, medium, high or very high (Lemunyon & Gilbert, 1993).

A GIS-based approach can also be used in determining potential problem areas over larger catchments. This approach is based on the qualitative combination of factors that affect the potential availability of sediment (land cover and soil erodibility) and those that affect the potential of sediment removal (slope steepness, and rainfall erosivity). Qualitative assessment of these factors is combined to identify areas of high, medium or low sediment availability and erosion potential (Moolman *et al.*, 2004).

2.4 Soil phosphorus tests

2.4.1 For crop production

Soil P tests are extraction methods comprising of chemicals used to determine the P status of soils (Haygarth & Jarvis, 1999). They are used to extract soil P from different pools that respond similarly to an extractant-induced change in chemical environment. These methods can be categorised into single extractions used to give an estimate of a certain pool of P and sequential extractions which characterise P in more detail and separate P into different pools depending on chemical properties.

Phosphorus extraction methods commonly used in determining soil P status for agronomic purposes are referred to as agronomic P tests. These methods are based on a strong chemical extraction of P fractions seemingly relevant for plant uptake (Klaat *et al*., 2003). In this regard the easily soluble P fraction is the most important since it is considered to be a reflection of the plant available or labile P. The chemical extractants are therefore based on (1) desorbing soil P from the sorption sites by creating circumstances where desorption is enhanced, (2) replacement of weakly bound soil P with a compound having a stronger sorption affinity or (3) solubilisation of sorption components (Kamprath & Watson, 1980).

There are several agronomic soil P tests in use and they extract varying amounts of P in soils, because their extractants differ (Pote *et al*.,1996; Sims, 2000). The extractants are generally grouped into dilute weak acids (e.g. lactate, acetate) with or without a complexing agent (e.g. F, EDTA), dilute strong acids (e.g. HCl, H_2SO_4) with or without a complexing agent (e.g. F, lactate, EDTA) and buffered alkaline solutions (e.g. $NaHCO_3$, NH_4HCO_3) with or without a complexing agent (DTPA) (Kuo, 1996). More detail on some of the extractants is given in Table 2.2. The selection of an appropriate soil P test for a specific soil or cropping system is usually made after field trials on crop responses to fertiliser application. The correlations obtained and interpretations of calibrations of the soil test values against crop response to added P fertiliser are then used for the determination of soil P status and fertiliser recommendations.

Table 2.2 Extractants commonly used to determine plant available phosphorus in soils (Fixen & Grove, 1990)

Extractant name(s)	Extractant composition
AB-DTPA	1 *M* NH_4HCO_3 + 0.005 *M* DTPA – pH7.5
Bray 1	0.03 *M* NH_4F + 0.025 *M* HCl
Bray 2	0.03 *M* NH_4F + 0.1 *M* HCl
Citric acid	1 % citric acid
Egner	0.01 *M* Ca lactate + 0.02 *M* HCl
ISFEI (Hunter)	0.25 *M* $NaHCO_3$ + 0.01 *M* NH_4F + 0.01*M* EDTA – pH 8.5
Mehlich-1	0.05 *M* HCl + 0.0125 *M* H_2SO_4
Mehlich-2	0.015 *M* NH_4F + 0.2 *M* CH_3COOH + 0.2 *M* NH_4Cl + 0.012 *M* HCl
Mehlich-3	0.015 *M* NH_4F + 0.2 *M* CH_3COOH + 0.25 *M* NH_4NO_3 + 0.013 *M* HNO_3 + 0.001 *M* EDTA
Morgan	0.54 *M* CH_3COOH + 0.7 *M* $NaC_2H_3O_2$ – pH 4.8
Olsen	0.5 *M* $NaHCO_3$ – pH 8.5
Truog	0.001 *M* H_2SO_4 + $(NH_4)_2SO_4$ – pH 3

Some of the extractants listed in Table 2.2, namely Bray, citric acid, ISFEI, Olsen, and Truog are used in South Africa (Schmidt *et al.,* 2004). The Department of Agriculture of the Western Cape Province relies on citric acid, while similar departments of the other eight provinces rely on slight modification of ISFEI, locally known as Ambic. The Bray and Truog extractants are used by the South African fertiliser and sugar industries respectively. The use of the Olsen method is limited to the irrigation areas of the Free State and Northern Cape provinces. These five extractants are discussed concisely as they were used in this study.

1. Bray: In both Bray methods P is extracted by a diluted strong acid (more diluted for Bray 1 than Bray 2) plus a complexing ion (Sims, 1998). This extractant enhance the release of P from aluminium phosphates by decreasing Al activity in the soil solution through the formation of various Al-F complexes. The fluoride is also effective at suppressing re-adsorption of solubilised P by soil colloids. The acidity of the extractant (pH 2.6) further contributes to the dissolution of plant available P from Al, Ca, and Fe-bound forms in most soils (Olsen & Sommer, 1982). Sims (1998) indicated that neither of the two Bray tests can be used in calcareous fine-textured soils, clay soils with a moderate high base saturation, soils with calcium carbonate equivalent >7% of the base saturation or soils

with large amounts of lime (>2% $CaCO_3$). Soils of this nature can neutralise the acidity of the extracting solution and lower the soil P test values, as found in several studies (e.g Fernandes *et al*., 1999; Atia & Mallariono, 2002; Fang *et al*., 2002; Allen *et al*., 2006). For use in alkaline soils a considerable increase in the ratio of extractant to soil is required (Sims, 1998).

2. Truog: The extraction of soil P with the Truog method is through the reaction of the hydrogen ion (H^+), which increases the solubility of the different P forms in soil. Ca-P is the main form extracted while Al-P and Fe-P extraction occurs to lesser extent. The sulphate prevents re-adsorption of dissolved P (Kamprath & Watson, 1980). The Truog soil test reagent is a well buffered acid solution and as a result dissolves more apatite in the soil. The method therefore overestimates P in soils high in Ca-P and also soils containing rock phosphate residues (Kumer *et al*., 1994). The efficiency of the extraction solution is affected by pH, Ca saturation level, and the affinity of sesquioxides for P in the soil (Henry *et al*.,1993).

3. Citric acid: This extraction method solubilises P forms in soil through reaction with a weak acid. The organic citrate anion influences P extraction by forming complexes with metal cations on which P is adsorbed. In addition it competes with P for adsorption sites on the soil surface which also enhances release of P into soil solution by replacing adsorbed P and also reducing its re-adsorption (Kamprath & Watson, 1980).

4. Olsen: The extraction method of Olsen is suitable for use in neutral to alkaline or calcareous soils (Tan, 2005; Horta & Torret, 2006). However, according to Kleinman *et al.* (2001) the method performs well in moderately weathered soils, which are acidic. The method is based on the use of a 0.5M $NaHCO_3$ solution which is buffered at pH 8.5. The OH^- and CO_3^{2-} in the $NaHCO_3$ solution decreases the concentration of Ca^{2+}, Fe^{3+}, and Al^{3+}, resulting in increased P solubility in soils. As mentioned above, the extractant is useful for a wide range of soils. In calcareous soils, increased calcium phosphate solubility results from the decreased Ca concentration by the high concentration of CO_3^{2-} and the precipitation of $CaCO_3$. In acid or neutral soils, the solubility of aluminium and iron phosphates increases because an increased OH^- concentration decreases the concentration of Al^{3+} and Fe^{3+} by the formation of oxy-hydroxides (Olsen & Sommer 1982; Sims, 2000). On account of the extractant's high pH it also dissolves organic P and thus increases the amount of P extracted (Tan, 2005). Fernandes *et al.* (1999)

analysed the variability in the amount of P extracted by different extractants including Olsen as a function of soil properties. They concluded that Olsen was least affected (when compared with other tests) by chemical and physical properties of the soil, in particular soil texture, organic matter content, carbonates, pH, and CEC. Delagado *et al.* (2009) showed that the critical values for Olsen P depend on soil properties affecting the relationship between sorbed P and P in soil solution which are P buffering capacity, Na/Ca ratio in the solution and the affinity of the sorbent surfaces for P.

5. ISFEI: The ISFEI method was developed as a modification of the Olsen method by including a chelating agent EDTA and NH_4F in the reagent, which makes it a multi-extractant. The extraction solution also contains hydroxide ions (OH^-), which extract P from Al-P and Fe-P through hydrolysis of these metals. The carbonate (HCO_3^-) in the extractant is useful in replacing adsorbed P, while Na reduces the activity of Ca in solution (Kamprath & Watson, 1980).

Agronomic soil P tests are used for determining threshold or critical values for cropping. Values are considered to be optimal for plant growth when no plant growth responses to additions of the nutrient are likely to occur. Sims (2000) approximates of these optimal values by the different methods are as follows: Bray 1 ≥ 25-30 mg kg^{-1}, Mehlich-1 ≥ 20-25 mg kg^{-1}, Mehlich-3 ≥ 30-50 mg kg^{-1}, Olsen ≥ 10 mg kg^{-1} and Morgan ≥ 4-6 mg kg^{-1}. However, other researchers (Lemunyon & Gilbert, 1993; Schindler *et al.,* 2009) pointed out that the soil P availability indices that exist have been developed based on the inherent chemical character of soils in particular regions and the test's ability to estimate a yield response of a particular crop. Reported agronomic and environmental threshold values for different regions in the USA are presented in Table 2.3. These values show great variability in the amount of P extracted by different methods, which was due to the following soil properties: silt-plus-clay content, pH, CEC, and organic carbon content. The general conclusion from these studies is therefore to consider soil properties when determining extractable P threshold values for different localities.

Table 2.3 Threshold soil test P values and P management recommendations (adopted from Sharpley *et al*., 1996)

State	Agronomic	Environmental	Method	Management recommendations for water quality protection
Arkansas	50	150	Mehlich 3	At or above 150 mg kg^{-1} soil P: Apply no more P, provide buffers next to streams, over seed pastures with legumes to aid P removal, and provide constant soil cover to minimize erosion.
Delaware	25	50	Mehlich 1	Above 50 mg kg^{-1} soil P: Apply no P
Idaho	12	50 – 100	Olsen	Sandy soils - above 50 mg kg^{-1} Silt loam soils - above 100 mg kg^{-1} Apply no more P until soil P is significantly reduced
Ohio	40	150	Bray 1	Above 150 mg kg^{-1} soil P: Reduce erosion and reduce or eliminate P additions
Michigan	40	75	Bray 1	Below 75 mg kg^{-1} soil P: P application not to exceed crop removal. Above 75 mg kg^{-1} soil P:Apply no P from any source
Wisconsin	20	75	Bray 1	Below 75 mg kg^{-1} soil P: Rotate to P demanding crops and reduce P additions. Above 75 mg kg^{-1} soil P: Discontinue P applications

2.4.2 For environmental protection

Environmental or bio-available soil P tests (water or unbuffered salt solutions like $CaCl_2$) are developed with the objective of measuring soluble and easily desorbable P (Schindler *et al.,* 2009). These tests extract a very small portion of plant available P and are therefore usually not used as an index of agronomic P (Olsen & Sommer, 1982). Bio-available soil P is determined also with Fe-oxide impregnated filter paper, an anion-exchange resin membrane, and isotopic exchange method (Kuo, 1996; Kulhanek *et al*., 2009). These methods are not destructive to soil constituents like the other chemical methods. They function as a sink that simulates the action of plant roots by continuously removing dissolved P from the soil solution (Olsen & Sommer, 1982). The P extracted by all these environmental soil P tests represent soil solution concentrations and have been used as an approximation of dissolved reactive P in runoff water (Wang *et al*., 2008).

Agronomic soil P tests extract biologically available P in quantities that are related to the amount of P available to crops during their growth period. These tests can therefore also be used for the measurement of the amount of soluble P released from soils into runoff and leaching or P biologically available to algae. Sims *et al. (*2002) indicate that for an agronomic soil P test to be used for environmental purposes, it should at least be well correlated with soil P saturation and the forms of soil P most susceptible to losses in runoff and leaching, namely the soluble P and desorbable P.

Atia and Mallarino (2002) indicate that several studies show good relationships between the P fractions extracted by agronomic soil P tests and environmental soil P tests. For example, P values determined with either water or $CaCl_2$ extraction correlates well with P values determined with several agronomic soil P tests (Pote et *al.,* 1996; Nair *et al.,* 2004; Nash *et al.,* 2007; Wang *et al*., 2008). These studies including the one of Sharpley (1991) indicate that agronomic soil P tests also correlate well with tests measuring the P buffering capacity of soils, such as the anion-exchange resin and Fe-oxide impregnated paper method which measures potentially desorbable phosphorus. Soil P extracted by environmentally oriented soil tests produce change points when plotted against agronomic soil P test values. The change points provide threshold soil P concentrations above which potential release of soil P to water increases (Sharpley & Tunney, 2000; Davis *et al.,* 2005).

Soil P tests for estimating degree of phosphorus saturation (DPS) are also applied to accurately predict the amount of soluble P, desorbable P, and P loss in runoff (Nair *et al.,* 2004; Ilg *et al*., 2005). However, agronomic soil P tests are preferred over this less frequently used ammonium oxalate extraction approach where DPS is calculated as DPS_{Ox} = [(Ox-P)/α(Ox-Fe + Ox-Al)]×100 (Sims *et al.,* 2002). This is because of practical difficulties in the measurement of parameters in DPS calculations. Nair *et al.* (2004) also pointed out that agronomic soil P tests are far simpler to perform than the measurement of parameters for DPS estimations. According to Nair *et al.* (2004), DPS is also calculated by dividing the soil test P value either by the P sorption index (a rapid measure of P sorption capacity) or P sorption maxima (calculated from a sorption isotherm). Relationships between calculated DPS values and P values determined with either water or $CaCl_2$ extraction also give change points. These change points as mentioned are the DPS values above which there will be a rapid increase in the concentration of dissolved P in soil and therefore the likelihood of a negative impact on water quality also increases (Maguire & Sims, 2002).

Several researchers (e.g. Sharpley & Tunney, 2000; Davis *et al.,* 2005) have, however, shown that physical and chemical properties of soil profoundly influence the relationships between agronomic and environmental P analyses and thus result in site specific critical values as presented in Table 2.3. After analysing several field studies, Sharpley *et al.* (1996) concluded that above mentioned relationships based on data of the 0-5 cm soil layer can be used to determine the critical levels if their r^2 values range between 0.58 and 0.98. The critical levels also known as environmental threshold values are used in P management strategies to regulate manure or fertilizer P application in the soil (Davis *et al.,* 2005).

2.5 Conclusion

In agricultural systems, P is considered an important nutrient because of its role in crop production. Addition of different P sources to the soil helps to maintain P at required level as it is being used by plants. The P status of the soil and the optimum amount required are determined through soil P testing. Adequate P nutrition enhances many aspects of plant development which improves crop yield. The challenge, however, is that the P concentration in the soil solution is very low due to its high fixation and immobility in soil. Farmers must therefore use management practices to improve P availability and its acquisition by plant roots, which are dependent on cultivation practices, crop factors, and soil properties. In addition, the long-term use of different P sources and cultivation practices to improve the low concentration must be considered, because this increases P loss through soil erosion from agricultural fields to surface waters. The problem with water P pollution is that it causes eutrophication, which results in a serious limitation of water uses. Phosphorus losses are generally affected by soil P concentration, P source, management, soil properties, crop grown, tillage systems, and transport factors. Several management practices including soil P testing can be used to control P pollution. However, the soil P tests to be used for determining the concentration at which P poses a threat to the environment still remains to be established. This study therefore serves to substantiate the potential use of routine agronomic soil P tests for environmental P management purposes.

CHAPTER THREE

STUDY AREA AND METHODOLOGY

3.1 Study area

3.1.1 Location

The soils used in this study were collected from three distinct cropping areas in The Free State Province of South Africa, namely Jacobsdal, Bloemfontein, and Ficksburg (Figure 3.1). All three sampling areas are located around the 29° S latitude. Their approximate elevation above sea level increases from 1150 m at Jacobsdal, to 1400 m at Bloemfontein, and 1850 m at Ficksburg.

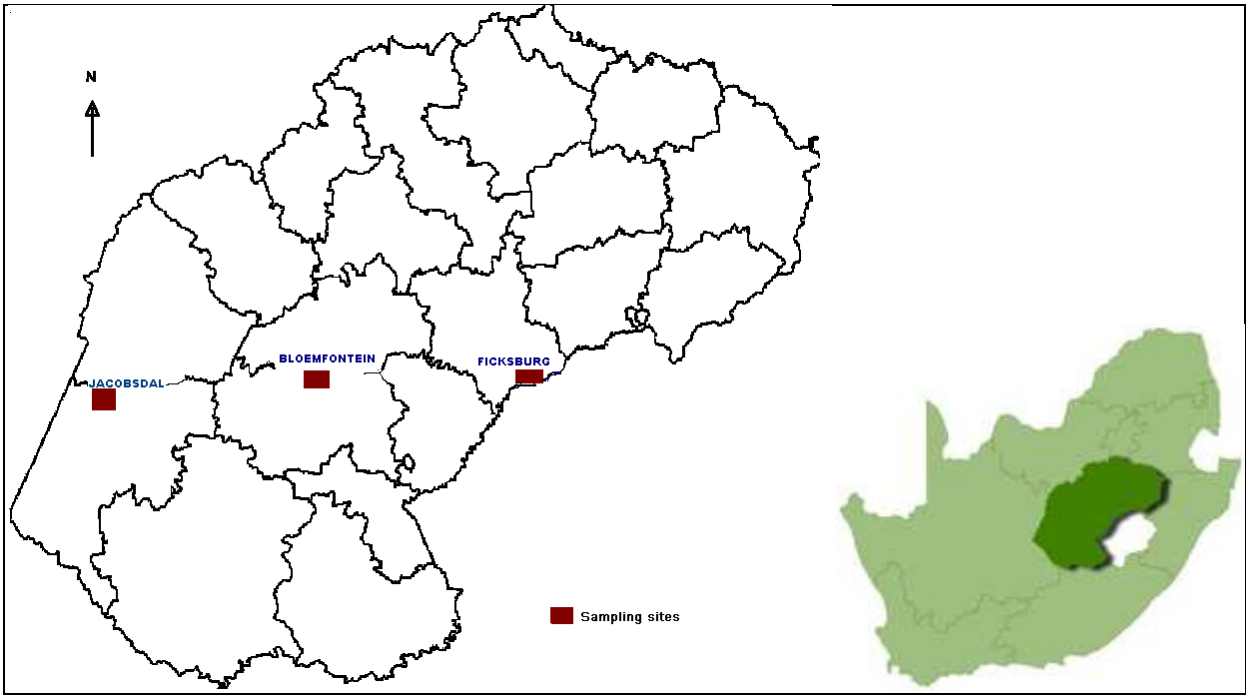

Figure 3.1 Location of the sampling areas in the Free State province

3.1.2 Climate

The mean annual precipitation and evaporation of the three sampling areas are given in Table 3.1. Based on these data the climate of Jacobsdal, Bloemfontein, and Ficksburg are classified as arid, semi-arid, and sub-humid, respectively. Jacobsdal has the least consistent rainfall and most extreme temperatures on a monthly basis (Table 3.2). Ficksburg on the other hand has the most consistent rainfall with the least extreme temperature. However, at all three sampling areas, 94% of the rain fell from September to May with either January or February as the wettest months. July is

the driest month at all the sampling areas. The frequency of frost increases from Jacobsdal in the warmer western part to Ficksburg in the cooler eastern part of the Free State Province (Kruger, 2004).

Table 3.1 Climate of the three sampling areas (Adopted from Midgley *et al.,* 1994)

Sampling area	MAP (mm)	MAE (mm)	Climate
Jacobsdal	200-300	1700-1800	Arid
Bloemfontein	500-600	1600-1700	Semi-arid
Ficksburg	700-800	1300-1400	Sub-humid

MAP = mean annual precipitation; MAE = mean annual evaporation (A-pan)

3.1.3 Geology

The geology at the three sampling areas is typical of the Karoo sequence. In the Jacobsdal sampling area shale of the Ecca Group is dominant. The Bloemfontein sampling area comprises of sandstone, shale, and mudstone of the Beaufort Group. Dolerite intrusions are common in both these sampling areas. In the Ficksburg sampling area Elliot mudstone and sandstone occurs predominantly, with some inliers of Molteno sandstone, mudstone, and grit due to narrow dolerite dykes, as well as small Clarens sandstone outliers (Geological Survey, 1984).

3.1.4 Vegetation

The sampling area at Jacobsdal is on the edge of the Nama Karoo Biome, namely in the Eastern Mixed Nama Karoo vegetation type (Low & Rebelo, 1996). A mixture of grass and shrubs species is therefore common. Shrubs include Kapokbush (*Eriocephalus ericoids*) and Bitterkaroo (*Pentzia incana*). The most dominant grass specie is Redgrass (*Themeda triandra*), while *Acacia* trees are common in the river beds (Kruger, 2004). Both the Bloemfontein (Dry Sandy Highveld vegetation type) and Ficksburg (Moist Cool Highveld vegetation type) sampling areas are in the Grassland Biome (Low & Rebelo, 1996). The vegetation in the Bloemfontein sampling area consists mostly of grass species which include Broadleaf Bluestern (*Diheteropogon amplectens*), Weeping Love Grass (*Eragrostis curvula*), Giant Spear grass (*Trachypogon spicatus*), Caterpillar Grass (*Harpochloa falx*), White Buffalo Grass (*Panicum coloratum*) and Redgrass (*Themeda triandra*). Some woody vegetation such as *Acacia* and Mountain Karee *Rhus leptodictya* also occurs (Kruger, 2004). The Ficksburg sampling area is dominated by grass species including Broom Needlegrass (*Triraphis andropogonoides*), Rolling Grass (*Aristida bipartita*), Redgrass (*Themeda triandra*), Tough Love Grass (*Eragrostis plana*), and Bushveld Turpentinegrass (*Cymbopogon plurinodis*). Forbs including Fishbean (*Tephrosia semiglabra*), Wild Petunia (*Ipomoea obscura*), and Bladderweed (*Hibiscus trionum*) are also widespread (Kruger, 2004).

Table 3.2 Climate data from a representative weather station within each sampling area (ARC-ISCW, 2011)

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
Jacobsdal (weather station 30179: 14 years' data)													
P (mm)	56.37	53.72	43.41	35.17	20.36	11.97	2.99	8.27	16.11	29.93	37.06	48.20	363.56
ETo	5.50	5.19	4.36	3.30	2.51	2.10	2.32	3.11	4.22	5.06	5.77	6.22	49.66
Tx (℃)	32.46	32.28	29.82	26.44	22.39	19.84	19.95	22.28	26.10	29.05	30.89	32.73	27.02
Tn (℃)	16.86	17.28	14.48	9.82	4.81	1.31	1.22	2.58	6.15	11.37	13.19	15.56	9.55
Tm (℃)	24.66	24.78	22.15	18.13	13.60	10.58	10.59	12.43	16.13	20.21	22.04	24.15	18.29
Bloemfontein (weather station 30454: 11 years' data)													
P (mm)	82	111	72	56	17	12	8	15	24	43	58	60	558
ETo	4.11	4.46	3.85	2.72	2.24	2.15	2.39	3.41	5.32	5.21	5.88	5.77	47.51
Tx (℃)	30.17	29.44	27.86	24.30	20.77	17.70	18.32	20.71	25.07	27.54	28.98	30.14	25.08
Tn (℃)	16.19	15.97	13.52	9.68	5.38	2.38	1.50	3.19	6.91	11.51	12.92	15.05	9.52
Tm (℃)	23.18	22.71	20.69	16.99	13.08	10.04	9.91	11.95	15.99	19.53	20.95	22.60	17.30
Ficksburg (weather station 30675: 7 years' data)													
P (mm)	158.58	99.97	67.67	63.51	25.01	21.95	1.87	21.38	23.58	68.38	73.54	105.20	730.64
ETo	4.50	4.25	3.26	2.47	2.36	1.82	2.02	2.69	3.96	4.15	4.65	5.24	41.37
Tx (℃)	27.08	26.85	25.59	21.85	19.42	16.88	17.38	19.82	24.60	24.82	26.07	28.09	23.20
Tn (℃)	14.29	13.90	11.36	7.16	2.77	-0.37	-1.18	1.18	5.21	9.13	10.91	12.97	7.28
Tm (℃)	20.69	20.38	18.48	14.51	11.10	8.26	8.10	10.50	14.91	16.98	18.49	20.53	15.24

P = Mean total precipitation; ETo (mm) = Mean total relative evapotranspiration; Tx = Mean daily maximum temperature; Tn = Mean daily minimum temperature; Tm = (Tx+ Tn)/2

3.1.5 Farming

Mixed farming namely cropping and stocking is practised in all three sampling areas. Stock farming entails grazing of the native vegetation by cattle and/or sheep. Cattle are more dominant in the sub-humid climate of Ficksburg while sheep are more dominant in the arid climate of Jacobsdal. Cropping in the Jacobsdal sampling area is only viable with irrigation. Crops commonly grown are lucern, maize, wheat, potato, peanut, and cotton. In the two other sampling areas cropping is mostly rainfed with maize and wheat as the major crops. However, sunflower and soyabean are planted also often in the sampling areas of Bloemfontein and Ficksburg, respectively.

3.2 Methodology

3.2.1 Site selection

In each of the three sampling areas four sites within a radius of 5 km were selected for the collection of bulk topsoil samples. These sites with native vegetation were selected with the aim to collect bulk soil samples with low extractable P content, while their other properties are similar to that of the cropped soils in the sampling area. Each site's location, land type, and soil form are presented in Table 3.3. The soils at all sites have diagnostic orthic A horizons which was of greater importance in this study than the variation of soil forms and land types within and between the sampling areas. A soil form has a unique vertical sequence of diagnostic horizons and materials (Soil Classification Working Group, 1991) while a land type displays a marked degree of uniformity with respect to terrain form, soil pattern, and climate (Land type Survey Staff, 2002). Cropping is, however, practised on all the listed land types and soil forms, implying fertilizer P application to the orthic A horizon.

Table 3.3 Selected soil sampling sites, locations, land types (Land Type Survey Staff, 2002) and soil forms (Soil Classification Working Group, 1991)

Area	Site	Latitude	Longitude	Land type	Soil form	Diagnostic horizon sequence
Jacobsdal	J1	-29.1751	24.7540	Ae15	Hutton	Orthic A / red apedal B / unspecified material
	J2	-29.1636	24.6999	Ae15	Hutton	Orthic A / red apedal B / unspecified material
	J3	-29.1963	24.6280	Ae279	Hutton	Orthic A / red apedal B / unspecified material
	J4	-29.0527	24.6631	Ag148	Valsrivier	Orthic A / pedocutanic B / unconsolidated material
Bloemfontein	B1	-29.0358	26.1521	Ca8	Bainsvlei	Orthic A / red apedal B / soft plinthic B
	B2	-29.2036	26.1947	Ca22	Hutton	Orthic A / red apedal B / unspecified
	B3	-29.2310	26.2027	Ca22	Valsrivier	Orthic A / pedocutanic B / unconsolidated material
	B4	-29.2757	26.1712	Ca8	Valsrivier	Orthic A / pedocutanic B / unconsolidated material
Ficksburg	F1	-28.7989	27.8591	Bd29	Avalon	Orthic A / yellow-brown apedal B / soft plinthic B
	F2	-28.8038	27.8676	Ad4	Clovelly	Orthic A / yellow-brown apedal B / unspecified material
	F3	-28.8058	27.8727	Ad4	Clovelly	Orthic A / yellow-brown apedal B / unspecified material
	F4	-28.8133	27.8317	Bd29	Avalon	Orthic A / yellow-brown apedal B / soft plinthic B

3.2.2 Soil sampling

At each site a bulk sample of about 150 kg was collected from the orthic A horizon after removal of living plants and plant residues. These bulk samples were transported to a glasshouse at the University of the Free State, where it were spread out in an approximately 100 mm thick layer on plastic sheets and air-dried. Thorough spreading and turning of soil was done on at least five occasions and thereafter the soil from each site was properly mixed. The air-dried soil was crushed, passed through a mechanical 2 mm sieve and again thoroughly mixed before being stored for treatment.

3.2.3 Soil treatment

The aim of soil treatment was to induce seven phosphorus levels to soil from each bulk sample, replicated three times. For this purpose, 21 plastic containers of 500 ml each were filled with 400 g of the relevant soil. The soil in each plastic container was spread evenly in a thin layer on a plastic sheet. Sufficient KH_2PO_4 solution of appropriate concentration was sprayed on the soil to wet it to 70% field capacity. This was done with a sprayer connected to a burette to ensure precision application. After spraying, the soil was mixed thoroughly and then returned to the plastic containers. A lid with holes was put on, which allowed drying during incubation at room temperature. During the three months of incubation the soil was rewetted several times to 70% field capacity with distilled water and mixed as described above. After incubation, the soil were air-dried, sieved, and stored for phosphorus analysis.

3.3.4 Soil analysis

Standard methods (The Non-affiliated Soil Analysis Working Committee, 1990) were used to analyse soil from the bulk samples for particle size distribution (pipette and sieve method), organic carbon (Walkly-Black method), pH (1:2.5 soil to water suspension), exchangeable cations, and cation exchange capacity (1 mol dm^{-3} NH_4OAc at pH 7). Each of these samples were analysed in triplicate.

Soil from the phosphorus treated samples were analysed in triplicate for extractable phosphorus. The extraction methods commonly used in South Africa to determine the agronomic P status of soils were employed namely Bray, Truog, citric acid, Olsen, and ISFEI (Non- affiliated Soil Analysis Working Committee, 1990). In addition to these, two extraction methods for the determination of the

environmental P status, calcium chloride (Kuo, 1996) and ammonium oxalate (Beck *et al.,* 2004), were also employed. The concentration of P in solution was measured irrespective of extraction method with the ammonium molybdate method in which ascorbic acid is the reducing agent (Murphy & Riley, 1962).

3.3.5 Data processing

Linear and non-linear regression models of Microsoft Excel 2007 in Windows XP were used to establish the correlation between P extracted by the soil tests. The most suitable model was selected based on the r^2 value to determine the relationship between and/or among agronomic and environmental P tests for each individual soil's data, when data of all soils from one sampling area are pooled and also when data of all soils from the three sampling areas are combined.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Characteristics of soils under study

The particle size distribution and textural class for each of the 12 soils under study are presented in Table 4.1. Their textures vary from fine sand to fine sandy clay loam. The sand fraction of the soils is therefore dominantly fine, namely in the 0.05 to 0.25 mm range. However, these virgin soils have a wide range of clay content, which is representative of cropped soils at the three localities. For example, the clay content varies between 3.3% (F1 soil) to 27.3% (J3 soil). The texture of a soil has an important impact on several of its properties and hence the processes occurring therein, which may affecting crop production. Sandy soils for instance, have limited plant nutrient availability, a very low water holding capacity, and a high permeability and therefore must receive frequent addition of water and plant nutrients to be highly productive. Phosphorus availability is determined *inter alia* by the clay content of soil. Soils with high clay content have a high capacity for P adsorption and this capacity is enlarged by the presence of Al and Fe oxides. In coarse textured soils P is mainly retained as labile P available for plant uptake (Zheng & Macleod, 2005).

Analyses for the chemical characterization of the bulk soil samples were done in triplicate (Section 3.3.4) and these data are presented in Appendix 1 while the means are given in Table 4.2. The organic matter content of the soils is very low to medium as indicated by the 0.32 to 1.82% organic C. All organic C values were less than 2% which is the threshold value below which the soil's nutrient availability and structural stability is likely to decline and resulting in a loss in the general quality of the soil (Loveland & Webb, 2003). It is therefore important that farming practices such as stubble retention and direct addition of organic material such as compost and manure, which increase the organic matter content are considered in the management of soils across all sites. Soil organic matter is a major source of plant nutrients and improves physical properties of soil such as porosity, structural stability, and water holding capacity (Seremesic *et al.,* 2011). Decomposition of organic matter releases nitrogen, phosphorus, and other nutrients needed for plant growth. In this process, organic acids such as oxalic acid are also released, which have the ability to prevent phosphorus fixation by clay minerals and improve its plant availability. Furthermore it is claimed (Sharma, 2002) that organic carbon compounds, such as polysaccharides bind soil aggregates together and stabilize soil structure, resulting in increased soil permeability and resistance to erosion. Increase in organic

Table 4.1 Particle size distribution and textural class of soils used in study

Soil sample[1]	Particle size distribution (%)							Textural class
	Coarse sand (>0.5mm)	Medium sand (0.25-0.5mm)	Fine sand (0.1-0.25mm)	Very fine sand (0.05-0.1mm)	Coarse silt (0.02-0.05mm)	Fine silt (0.002-0.02mm)	Clay (<0.002mm)	
J1	2.4	16.0	51.5	14.5	2.3	4.5	6.4	Loamy fine sand
J2	15.5	8.0	37.1	18.3	4.6	6.0	8.1	Loamy fine sand
J3	0.9	0.9	18.0	21.2	8.6	19.7	27.3	Fine sandy clay loam
J4	4.7	4.1	38.4	18.7	4.1	10.6	16.4	Fine sandy loam
B1	0.4	3.6	60.4	20.2	1.0	0.0	12.0	Loamy fine sand
B2	1.5	2.1	54.4	24.0	2.1	0.1	13.0	Loamy fine sand
B3	2.0	2.0	52.9	21.7	2.8	2.4	12.2	Loamy fine sand
B4	2.7	3.8	35.5	20.9	3.1	10.5	21.2	Fine sandy clay loam
F1	0.7	14.7	56.8	12.1	5.5	5.1	3.3	Fine sand
F2	1.4	4.8	54.5	16.3	6.4	8.0	4.5	Loamy fine sand
F3	1.1	3.2	47.9	20.7	8.2	9.3	5.8	Loamy fine sand
F4	2.1	3.7	11.6	27.6	21.9	14.7	13.7	Fine sandy loam

[1]J= Jacobsdal, B= Bloemfontein, and F= Ficksburg

matter improves cation exchange capacity and biological diversity of soil. Soil organic matter management is therefore very important for the improvement of soil quality for sustainable crop production in soils very low in organic C (FSSA, 2003).

The results on pH analysis of the soils in Table 4.2 show a range from acidic (F1 soil with pH 5.5) to very alkaline soils (J3 soil with pH 8.6). However, the other soils are within the normal pH range of 6.0 to 7.5 (FSSA, 2003). In this range, nutrient availability is optimal for most crops, implying that there is no threat to plant growth due to nutrient deficiencies. Soil pH mainly influences ions activities and reactions determining P and other nutrients availability and hence is used in soil fertility evaluation (Forth & Ellis, 1996). Low pH increases the aluminium, manganese and iron concentrations to toxic levels and reduces the availability of nutrients such as calcium, magnesium, and potassium. The iron and aluminum in strongly acidic soils react with P to form insoluble phosphates. The availability of these insoluble phosphates improves as pH increases to near neutral. A high concentration of sodium and calcium carbonates results in high pH. In alkaline soils, calcium carbonate reduces P availability by increasing the activity of calcium, which reacts with P to form insoluble calcium phosphates (Troeh & Thompson, 2005; Mahdi *et al.,* 2011).

The exchangeable calcium levels ranged between 352 and 5595 mg kg^{-1} (Table 4.2). An acceptable level for most crops is between 200 and 3000 mg kg^{-1} (FSSA, 2003). This suggests that the soils have enough calcium to support plant growth as it was the dominant cation. However, the high calcium content (5595 mg kg^{-1}) of J3 soil may be inhibiting to other nutrients. Deficiencies of nutrients such as P, K, Mg, and micronutrients are often reported in soils with high calcium content (Troeh & Thompson, 2005). The results also showed high exchangeable magnesium and potassium levels in all soils with values ranging from 80 to 625 and 93 to 519 mg kg^{-1}, respectively (Table 4.2). The recommended level for optimum crop growth is 50 to 300 mg kg^{-1} for magnesium and 40 to 250 mg kg^{-1} for potassium (FSSA, 2003). Thus 25% of the soils may have excessive magnesium (J2, J3, J4, and B4) and potassium (J3, J4, B4, and F2) levels, depending on their cation ratios, which will be dealt with later.

The cation exchange capacity of the soils ranged from 5.5 to 21.1 $cmol_c$ kg^{-1} (Table 4.2). This wide range of negative charges resulted through either isomorphic substitution or deprotonation (Forth & Ellis, 1996). The latter is dependent therefore on the pH, organic matter content, clay

Table 4.2 Some chemical properties of soils used in study

Soil sample[1]	Organic C (%)	pH (H_2O)	Exchangeable cations (mg kg^{-1})				CEC ($cmol_c$ kg^{-1})	
			Ca	Mg	K	Na	Soil	Clay
J1	0.66	6.3	518	159	120	14	6.2	96.9
J2	0.59	7.1	1051	376	257	18	11.5	142.2
J3	0.90	8.6	5592	625	519	71	21.1	77.3
J4	0.78	7.4	2413	517	298	23	16.5	100.7
B1	0.47	6.2	470	153	144	17	6.3	52.5
B2	0.32	6.5	509	170	243	17	6.3	48.5
B3	0.76	6.2	583	178	236	15	7.3	59.7
B4	0.87	6.1	823	375	285	57	12.3	57.9
F1	0.95	5.5	352	80	93	13	5.5	167.9
F2	1.41	6.0	513	128	346	21	7.2	160.0
F3	1.08	6.0	490	96	113	15	6.0	103.1
F4	1.82	6.2	1138	204	208	15	11.5	84.1

content, and mineralogy of each soil. For example, the estimated cation exchange capacity of the clay fraction varied from 48.5 to 167.9 $cmol_c\ kg^{-1}$ (Table 4.2). This is an indication that the clay fraction of the soils is dominated by different types of 2:1 silicate clay minerals. It seems however, that the 2:1 silicate clay minerals make a major contribution to the soils' cation exchange capacity. Soils with high CEC are considered fertile as they can retain more plant nutrients, while soils with a low CEC have little ability to store nutrients and are susceptible to nutrient loss through leaching. Soils with a lower CEC therefore require more frequent fertilizer applications and liming to improve their low yield potential (Forth & Ellis, 1996).

The cation ratios for the soils, as calculated from the average cation concentrations (Table 4.2), are presented in Table 4.3. As shown Ca:Mg ratios ranged between 1.3 and 5.4. All soils were within the recommended range for optimum plant growth (also referred to as normal range) namely, 1.3 to 4.5 (FSSA, 2003), except for the J3 soil (5.4). These ratios indicate that there is sufficient Ca for the plants. However, levels of excess Ca may inhibit the uptake of potassium and magnesium by plants even when their levels are sufficient in soil (Troeh & Thompson, 2005). As mentioned earlier excess Ca could also reduces P availability by increasing the activity of Ca and adsorption of P on $CaCO_3$.

The Mg:K ratios ranged from 1.2 to 5.7 (Table 4.3) while the normal range is 3 to 4 (FSSA, 2003). Compared to the normal range the Mg:K ratios for two Bloemfontein (B2 and B3) and three Ficksburg (F1 to F3) soils were below and that of one Bloemfontein (B4) and four Jacobsdal (J1 to J4) soils above the normal range. The Ca+Mg:K ratios ranged from 4.1 to 24.9 (Table 4.3), while the normal range is 10 to 20 (FSSA, 2003). All four Jacobsdal (J1 to J4) and three Ficksburg (F1, F3, and F4) soil ratios were within this normal range. Below this normal Ca+Mg:K ratio were that of one Ficksburg (F2) and all four Bloemfontein (B1 to B4) soils. The low ratios of Mg:K and Ca+Mg:K implied a shortage of Ca and/or Mg which is often related to a low base saturation percentage and toxic levels of Al and Mn in the soil. Application of agricultural lime is therefore required to improve fertility of these soils. The exchangeable potassium percentage (Table 4.3), however, indicated sufficient K in all soils to support optimal plant growth as the values were within the normal range of 3 to 7 (FSSA, 2003), except for B2, B3 and F2 soils which had slightly excessive amounts.

Besides having sufficient quantities of Ca, Mg, and K in the soil, it is important that they are in balance with each other because, as indicated earlier, excess of one of these can hinder the uptake of another. The Ca:Mg:K:Na ratio of 65:25:8:2 is considered optimal for

Table 4.3 Cation ratios[1] applied in evaluation of soil's fertility

Soil sample[2]	Ca/Mg	Mg/K	(Ca+Mg)/K	100Ca/S:100Mg/S:100K/S:100Na/S	100K/CEC[3]	100S/CEC[4]
J1	2.0	4.3	12.6	61 : 31 : 7 : 1	5.0	68
J2	1.8	4.7	12.7	58 : 34 : 7 : 1	5.7	79
J3	5.4	3.9	24.9	80 : 15 : 4 : 1	6.3	>100
J4	2.8	5.7	21.6	70 : 25 : 4 : 1	4.6	>100
B1	1.9	3.4	9.8	58 : 31 : 9 : 2	5.9	64
B2	1.8	2.3	6.4	55 : 30 : 13 : 2	9.8	74
B3	2.0	2.4	7.2	57 : 29 : 12 : 1	8.4	70
B4	1.3	4.3	9.9	50 : 38 : 9 : 3	5.9	67
F1	2.6	2.8	10.1	65 : 25 : 9 : 2	4.3	49
F2	2.4	1.2	4.1	56 : 23 : 19 : 2	12.4	64
F3	3.1	2.8	10.6	68 : 22 : 8 : 1	4.8	60
F4	3.4	3.2	13.9	71 : 13 : 7 : 1	4.6	69
Norms	1.3 - 4.5	3 - 4	10 - 20	65 : 25 : 8 : 2	3 - 7	70 - 95

[1]For the calculation of these ratios the values in Table 4.2 were converted from mg kg^{-1} to $cmol_c$ kg^{-1} and hence S is the sum of Ca, Mg, K, and Na in the latter unit.

[2]J= Jacobsdal, B= Bloemfontein, and F= Ficksburg

[3]Exchangeable potassium percentage (EPP)

[4] Base saturation (%)

[5]FSSA (2003)

the growth of most crops (FSSA, 2003). In relation to this optimal ratio the general trend for the calculated Ca:Mg:K:Na ratios of the soils (Table 4.3) suggested less favorable conditions for plant growth, as they show the same nutrient imbalances observed with individual nutrient ratios. The base saturation of 3 soils ranged from 70 to 79% (Table 4.3), which is within the recommended range of 70 – 95 (FSSA, 2003). Another 6 soils had a base saturation almost within this range namely, 60 to 69%. The exceptions were the very acidic F1 soil (49%) and the very alkaline J3 and J4 (>100%) soils. High percentage base saturation means there are more basic cations (Ca, Mg, K, and Na) than acid cations (H and Al) adsorbed on the exchange sites of soil colloids. The implication is that displacement of the adsorbed base cations into the soil solution for plant root uptake is more likely. Soils with a high base saturation are considered more fertile than soils with low percent base saturation (Forth & Ellis, 1996).

4.2 Phosphorus contents induced to study soils

Soil from each bulk sample was treated with K_2HPO_4 solution and incubated to induce seven P levels, replicated three times (Section 3.2.3). Extractable P content levels obtained with all P tests following this treatment are displayed in Appendix 2 while the range of extractable P contents are shown in Table 4.4. The induced soil P content levels for all soils varied widely depending on the properties of the soil, which greatly influenced the amount of P the soil test extracted. Considering the amount of P extracted by the soil P tests, the ranges induced with the smallest differences were all in the B4 soil. These differences are in increasing order: 0.5 mg kg^{-1} P for $CaCl_2$, 5.6 mg kg^{-1} P for ammonium oxalate, 9.3 mg kg^{-1} P for ISFEI, 10.6 mg kg^{-1} P for citric acid, 20.2 mg kg^{-1} P for Bray 1, 22.3 mg kg^{-1} P for Olsen, and 31.3 mg kg^{-1} P for Truog. On the other hand ranges induced with the largest differences are in different soils namely J2 ($CaCl_2$), J3 (Olsen, Truog, ISFEI, and ammonium oxalate), B1 (citric acid), and F1 (Bray 1). These differences are in increasing order: 10.2 mg kg^{-1} P for $CaCl_2$, 24.5 mg kg^{-1} P for citric acid, 26.0 mg kg^{-1} P for ammonium oxalate, 55.5 mg kg^{-1} P for ISFEI, 61.2 mg kg^{-1} P for Olsen, 67.7 mg kg^{-1} P for Bray 1, and 85.0 mg kg^{-1} P for Truog.

The degree of P saturation (DPS_{ox}), which is based on measurements of oxalate extractable P, Fe, and Al, was also calculated for all soil samples. Table 4.5 shows the means for oxalate extractable Fe and Al as well as the ranges for oxalate extractable P and DPS_{ox}. The DPS_{ox} range with the smallest difference (1.9%) and the largest difference (18.7%) manifested in soils B4 and F3 respectively.

Table 4.4 Range of extractable phosphorus contents (mg kg^{-1}) induced to soils used in this study

Soil sample[1]	Agronomic tests					Environmental tests	
	Olsen	Bray 1	Truog	ISFEI	Citric acid	Calcium chloride	Ammonium oxalate
J1	2.8 - 57.5	2.2 - 62.0	3.8 - 55.0	0.3 - 36.2	0.5 - 13.5	0.3 - 6.3	1.3 - 12.6
J2	16.3 - 49.2	15.7 - 81.5	47.0 - 121.7	5.8 - 48.5	10.3 - 24.3	0.5 - 10.7	9.9 - 24.3
J3	10.5 - 71.7	8.5 - 61.7	150.0 - 235.0	8.0 - 63.5	17.0 - 30.2	0.3 - 5.1	24.7 - 50.7
J4	12.7 - 61.7	8.6 - 71.5	30.7 - 108.3	7.7 - 50.8	4.2 - 20.0	0.3 - 7.5	6.0 - 19.7
B1	1.7 - 43.8	2.8 - 59.7	1.3 - 60.0	0.0 - 22.8	0.5 - 25.0	0.0 - 4.2	1.1 - 13.8
B2	6.0 - 46.3	6.2 - 58.4	4.2 - 64.0	0.3 - 26.2	1.0 - 15.7	0.3 - 5.6	1.7 - 13.8
B3	2.8 - 32.7	2.3 - 43.5	1.3 - 50.7	0.0 - 17.0	0.5 - 11.6	0.0 - 2.5	1.3 - 7.8
B4	3.9 - 26.2	2.4 - 22.6	5.0 - 36.3	1.5 - 10.8	1.0 - 11.6	0.0 - 0.5	3.3 - 8.9
F1	2.7 - 50.1	1.3 - 69.0	2.0 - 62.0	2.3 - 26.6	1.0 - 17.3	0.0 - 2.1	1.7 - 17.3
F2	5.6 - 61.7	2.7 - 61.0	7.5 - 61.3	2.3 - 49.0	4.2 - 20.0	0.3 - 2.5	3.8 - 20.8
F3	3.6 - 30.4	1.3 - 40.8	3.5 - 47.0	0.0 - 19.3	2.0 -17.1	0.0 - 2.0	4.7 - 27.7
F4	4.8 - 27.5	1.5 - 24.9	25.5 - 70.0	2.3 - 19.5	6.0 - 22.8	0.3 - 4.5	8.4 - 22.1

[1]J= Jacobsdal, B= Bloemfontein, and F= Ficksburg

Table 4.5 Range of degree of phosphorus saturation (DPS_{ox} %) calculated from measured ammonium oxalate extractable phosphorus, iron and aluminium contents (mmol kg^{-1}) of soils used in this study

Soil sample[1]	Phosphorus	Iron	Aluminium	DPS_{ox}
J1	0.04 - 0.41	0.87 ± 0.07	2.00 ± 0.28	1.8 - 11.2
J2	0.32 - 0.78	1.67 ± 0.10	3.06 ± 0.16	6.5 - 16.0
J3	0.80 - 1.64	2.21 ± 0.39	4.08 ± 0.09	12.6 - 21.7
J4	0.19 - 0.64	3.97 ± 0.24	2.14 ± 0.21	3.1 - 10.2
B1	0.04 - 0.45	0.88 ± 0.02	2.24 ± 0.15	1.3 - 13.6
B2	0.05 - 0.45	0.96 ± 0.02	2.73 ± 0.03	1.8 - 14.2
B3	0.04 - 0.25	1.76 ± 0.06	2.35 ± 0.09	1.0 - 5.7
B4	0.11 - 0.29	6.54 ± 0.19	3.61 ± 0.10	1.0 - 2.9
F1	0.05 - 0.56	3.92 ± 0.11	2.52 ± 0.21	0.9 - 8.9
F2	0.12 - 0.67	4.29 ± 0.08	2.69 ± 0.51	1.0 - 8.9
F3	0.09 - 0.90	1.83 ± 0.08	2.94 ± 0.26	1.0 - 19.7
F4	0.27 - 0.71	2.20 ± 0.08	2.42 ± 0.22	5.6 - 16.8

[1]J= Jacobsdal, B= Bloemfontein, and F= Ficksburg

4.3 Correlation between phosphorus tests

Several regression models were used to depict the correlation between P extracted by the different methods applied in this study. These models are *inter alia* linear, exponential, logarithmic, power, and polynomial. The coefficients of determination (r^2) for the relationship between P extractable with the different methods were used for selecting the best fitting model. A second order polynomial model gave the best fit in most instances. Where not applicable, one of the other mentioned models were selected depending on which one is best fitted to the data.

4.3.1 Among agronomic phosphorus tests

All agronomic tests used in this study are significantly and positively correlated with each other (r^2=0.52 - 0.87) when all soils from the three sampling areas were subjected to regression analysis (Table 4.6). Olsen-P values were highly correlated with Bray 1-P values (r^2=0.86). The r^2 value was, however, slightly lower for Jacobsdal (0.80), than for Ficksburg (0.89), and Bloemfontein (0.91), when soils from the three sampling areas were considered separately (Table 4.6). The r^2 values ranged for individual soils in the order from lowest: Jacobsdal (0.73 - 0.97, Table 4.7), Bloemfontein (0.89 - 0.98, Table 4.8), and Ficksburg (0.91 - 0.98, Table 4.9).

The slightly lower r^2 value obtained for the relationship between Olsen-P and Bray-P for the J2 soil from Jacobsdal is probably because of its high pH and $CaCO_3$ content. Other researchers (Mallarino & Atia, 2005; Ebeling *et al.,* 2006) also reported slightly lower r^2 values for the relationship between these methods when the soils have high pH and $CaCO_3$ content. They attributed it to the fact that Bray 1 method extracts a lower amount of P than the Olsen method from calcareous soils which is not the case in other soils. As indicated in section 2.4.1, $CaCO_3$ neutralizes the acidity of the Bray 1 extraction solution and therefore reduces its effectiveness in extracting P in soil. Wang *et al.* (2008) also showed a closely correlated relationship between these extraction methods on acidic to calcareous soils.

The Truog P values of all soils from the three sampling areas correlated well with their citric acid (r^2=0.87), Olsen (r^2=0.70), Bray 1 (r^2=0.58), and ISFEI (r^2=0.52) P values, respectively (Table 4.6). Significant relationships between Truog and the Olsen and Bray extraction methods were also reported by Mamo *et al*. (2002) and Masjkur (2009). The r^2 values that resulted when each sampling area's Truog-P values were regressed with its P values from the other extraction methods, improved substantially for Bloemfontein and to a lesser extent for Ficksburg. For Jacobsdal only the r^2 value of the relationship between the Truog and citric acid P values improved from 0.87 for all soils to 0.92.

The poor correlation between Truog-P values and the P values of Olsen (r^2=0.44), Bray 1 (r^2=0.42) and ISFEI (r^2=0.35) for Jacobsdal may be explained by the fact that on a relative basis a larger amount of Ca-P is dissolved by the acid Truog extractant in soils with high pH and exchangeable Ca (Kumer *et al.,* 1994*;* Gilbert *et al.,* 2009). Analysis for each individual soil, however, resulted in higher significant r^2 values when the Truog-P values were regressed with the other tests P values. The r^2 value ranges obtained were 0.67 to 0.99 for Jacobsdal soils (Table 4.7), 0.91 to 0.99 for Bloemfontein soils (Table 4.8), and 0.71 to 0.99 for Ficksburg soils (Table 4.9).

The ISFEI-P values were well correlated with P values of Olsen (r^2=0.81), Bray 1 (r^2=0.78), and citric acid (r^2=0.71) when all soils from the three sampling areas were subjected to regression analysis (Table 4.6). Islam *et al.* (2001) reported a significant correlation between ISFEI-P values and Olsen-P values in acid to slightly alkaline soils. In support to this, high coefficients of determination for the relationship between ISFEI-P values and Bray 1-P values were found by Schmidt *et al.* (2004) in strongly acidic to highly alkaline soils. Considering Bloemfontein soils only, the three best correlations of ISFEI-P values was obtained with the P values of Olsen (r^2=0.95), Bray 1 (r^2=0.94) and citric acid (r^2=0.82). For the Jacobsdal and Ficksburg soils respectively the P values of ISFEI correlated weaker with Olsen (r^2=0.78 and r^2=0.75), Bray 1 (r^2=0.80 and r^2=0.72) and citric acid (r^2=0.58 and r^2=0.75) P values. This showed that compared to the Olsen, Bray 1, and citric acid methods the amount of P extracted by the ISFEI method decreased as either the acidity or alkalinity of a soil increased. Regression analysis on the individual soils improved the correlation between ISFEI-P values and the P values of the other extraction methods (Table 4.7, 4.8, and 4.9).

Unlike these methods, the correlation of citric acid-P values with ISFEI-P values was highest for the Bloemfontein soils (r^2=0.82), intermediate for the Ficksburg soils (r^2=0.75), and lowest for the Jacobsdal soils (r^2=0.58), implying a decrease in P extraction efficiency by citric acid as the soil's pH increases. Similar observations were made when the P values of the citric acid and Olsen methods were correlated. The resulting r^2 values for Jacobsdal, Ficksburg, and Bloemfontein soils were 0.57, 0.79 and 0.85 respectively. This trend manifested also in the correlation of citric acid and Bray 1-P values with r^2 of 0.84 for Bloemfontein soils, 0.67 for Ficksburg soils, and 0.58 for Jacobsdal soils. However, for all soils from the three sites the P values of citric acid were better correlated with the P values of ISFEI (r^2=0.71) and Olsen (r^2=0.70) than that of Bray 1 (r^2=0.57) (Table 4.6).

Table 4.6 Relationships between amounts of P extracted with agronomic tests from soils of all three sampling areas and each sampling areas separately

Soil P tests	All soils (n=252)	Jacobsdal (n=84)	Bloemfontein (n=84)	Ficksburg (n=84)
Olsen vs. Bray 1	$y = 0.572x^{1.177}$	$y = -0.009x^2 + 1.728x - 7.251$	$y = 0.006x^2 + 1.003x + 0.027$	$y = -0.007x^2 + 1.610x - 6.369$
	$r^2 = 0.862$	$r^2 = 0.797$	$r^2 = 0.914$	$r^2 = 0.892$
Olsen vs. Truog	$y = 0.946x^{1.202}$	$y = 3.078x^{0.940}$	$y = 1.454x - 3.070$	$y = -0.023x^2 + 2.459x - 1.562$
	$r^2 = 0.704$	$r^2 = 0.444$	$r^2 = 0.955$	$r^2 = 0.738$
Olsen vs. ISFEI	$y = 0.004x^2 + 0.423x - 0.427$	$y = 0.004x^2 + 0.432x + 1.211$	$y = 0.005x^2 + 0.287x - 0.631$	$y = 0.002x^2 + 0.505x - 0.704$
	$r^2 = 0.807$	$r^2 = 0.779$	$r^2 = 0.952$	$r^2 = 0.754$
Olsen vs. citric acid	$y = 0.353x^{1.060}$	$y = 0.371x^{1.05}$	$y = 0.163x^{1.230}$	$y = -0.007x^2 + 0.719x + 0.336$
	$r^2 = 0.696$	$r^2 = 0.57$	$r^2 = 0.852$	$r^2 = 0.787$
Bray 1 vs. Truog	$y = 2.531x^{0.859}$	$y = 5.167x^{0.771}$	$y = -0.002x^2 + 1.216x - 0.930$	$y = -0.011x^2 + 1.478x + 9.966$
	$r^2 = 0.578$	$r^2 = 0.421$	$r^2 = 0.930$	$r^2 = 0.588$
Bray 1 vs. ISFEI	$y = 0.003x^2 + 0.313x + 0.962$	$y = 0.003x^2 + 0.397x + 1.767$	$y = 0.002x^2 + 0.275x - 0.243$	$y = 0.000x^2 + 0.444x + 0.834$
	$r^2 = 0.782$	$r^2 = 0.797$	$r^2 = 0.937$	$r^2 = 0.717$
Bray 1 vs. citric acid	$y = -0.002x^2 + 0.437x + 1.942$	$y = 0.597x^{0.896}$	$y = 0.343x - 0.445$	$y = -0.004x^2 + 0.499x + 3.270$
	$r^2 = 0.570$	$r^2 = 0.583$	$r^2 = 0.838$	$r^2 = 0.666$
Truog vs. ISFEI	$y = -0.000x^2 + 0.340x - 0.076$	$y = 8.85\ln(x) - 17.83$	$y = 0.003x^2 + 0.199x + 0.110$	$y = 0.004x^2 + 0.093x + 1.020$
	$r^2 = 0.518$	$r^2 = 0.349$	$r^2 = 0.979$	$r^2 = 0.554$
Truog vs. citric acid	$y = 0.438x^{0.828}$	$y = 0.208x^{0.947}$	$y = 0.300x^{0.964}$	$y = 0.000x^2 + 0.231x + 1.815$
	$r^2 = 0.873$	$r^2 = 0.923$	$r^2 = 0.917$	$r^2 = 0.911$
ISFEI vs. citric acid	$y = -0.009x^2 + 0.899x + 2.005$	$y = -0.006x^2 + 0.756x + 3.377$	$y = -0.015x^2 + 1.144x + 0.057$	$y = -0.013x^2 + 0.980x + 2.869$
	$r^2 = 0.712$	$r^2 = 0.579$	$r^2 = 0.824$	$r^2 = 0.748$

Table 4.7 Relationships between amounts of P extracted with agronomic tests from each of the Jacobsdal soils

Soil P tests	J1(n=21)	J2 (n=21)	J3 (n=21)	J4 (n=21)
Olsen vs. Bray 1	$y = 0.748x^{1.064}$ $r^2 = 0.919$	$y = 0.860x^{1.122}$ $r^2 = 0.734$	$y = -0.003x^2 + 1.078x - 2.349$ $r^2 = 0.938$	$y = -0.011x^2 + 2.154x - 16.57$ $r^2 = 0.966$
Olsen vs. Truog	$y = -0.010x^2 + 1.466x - 0.975$ $r^2 = 0.914$	$y = 9.226x^{0.598}$ $r^2 = 0.669$	$y = -0.009x^2 + 2.064x + 133.7$ $r^2 = 0.957$	$y = 4.371x^{0.773}$ $r^2 = 0.933$
Olsen vs. ISFEI	$y = 0.008x^2 - 0.025x + 2.512$ $r^2 = 0.808$	$y = 0.151x^{1.379}$ $r^2 = 0.710$	$y = 0.785x^{0.989}$ $r^2 = 0.928$	$y = 0.002x^2 + 0.633x - 1.071$ $r^2 = 0.931$
Olsen vs. citric acid	$y = 0.156x^{1.074}$ $r^2 = 0.914$	$y = 2.714x^{0.531}$ $r^2 = 0.647$	$y = -0.001x^2 + 0.337x + 14.43$ $r^2 = 0.925$	$y = 0.295x + 1.070$ $r^2 = 0.948$
Bray 1 vs. Truog	$y = -0.006x^2 + 1.294x + 0.386$ $r^2 = 0.994$	$y = -0.001x^2 + 0.927x - 10.90$ $r^2 = 0.987$	$y = -0.011x^2 + 2.326x + 134.0$ $r^2 = 0.988$	$y = 0.006x^2 + 0.731x + 24.35$ $r^2 = 0.976$
Bray 1 vs. ISFEI	$y = 0.007x^2 + 0.096x + 1.299$ $r^2 = 0.969$	$y = 0.007x^2 - 0.094x + 6.456$ $r^2 = 0.975$	$y = 0.009x^2 + 0.330x + 5.201$ $r^2 = 0.982$	$y = 0.009x^2 - 0.066x + 8.531$ $r^2 = 0.986$
Bray 1 vs. citric acid	$y = 0.217x^{0.992}$ $r^2 = 0.963$	$y = -0.000x^2 + 0.258x + 7.002$ $r^2 = 0.964$	$y = 9.616x^{0.270}$ $r^2 = 0.958$	$y = 0.001x^2 + 0.088x + 4.053$ $r^2 = 0.959$
Truog vs. ISFEI	$y = 0.015x^2 - 0.245x + 2.917$ $r^2 = 0.958$	$y = 0.001x^2 + 0.384x - 14.43$ $r^2 = 0.99$	$y = 8E\text{-}10x^{4.592}$ $r^2 = 0.982$	$y = 0.001x^2 + 0.088x + 4.053$ $r^2 = 0.959$
Truog vs. citric acid	$y = 0.001x^2 + 0.158x - 0.198$ $r^2 = 0.967$	$y = -0.002x^2 + 0.520x - 8.924$ $r^2 = 0.945$	$y = 0.032x^{1.250}$ $r^2 = 0.962$	$y = 0.000x^2 + 0.112x + 1.079$ $r^2 = 0.940$
ISFEI vs. citric acid	$y = -0.012x^2 + 0.840x - 0.597$ $r^2 = 0.948$	$y = -0.007x^2 + 0.730x + 6.992$ $r^2 = 0.953$	$y = 6.271\ln(x) + 4.043$ $r^2 = 0.979$	$y = -0.001x^2 + 0.395x + 2.143$ $r^2 = 0.955$

Table 4.8 Relationships between amounts of P extracted with agronomic tests from each of the Bloemfontein soils

Soil P tests	B1 (n=21)	B2 (n=21)	B3 (n=21)	B4 (n=21)
Olsen vs. Bray 1	$y = -0.007x^2 + 1.672x - 0.498$ $r^2 = 0.980$	$y = 1.270x - 1.166$ $r^2 = 0.959$	$y = 0.026x^2 + 0.443x + 0.755$ $r^2 = 0.982$	$y = 0.633x^{1.098}$ $r^2 = 0.889$
Olsen vs. Truog	$y = 1.428x - 2.738$ $r^2 = 0.987$	$y = -0.009x^2 + 1.979x - 7.988$ $r^2 = 0.937$	$y = 0.027x^2 + 0.639x - 0.532$ $r^2 = 0.982$	$y = 0.017x^2 + 0.784x + 2.247$ $r^2 = 0.947$
Olsen vs. ISFEI	$y = 0.002x^2 + 0.415x - 1.370$ $r^2 = 0.989$	$y = 0.003x^2 + 0.439x - 2.406$ $r^2 = 0.952$	$y = 0.011x^2 + 0.147x - 0.362$ $r^2 = 0.984$	$y = 0.006x^2 + 0.148x + 1.250$ $r^2 = 0.845$
Olsen vs. citric acid	$y = -0.003x^2 + 0.790x - 2.628$ $r^2 = 0.956$	$y = -0.001x^2 + 0.410x - 1.550$ $r^2 = 0.897$	$y = 0.007x^2 + 0.067x + 0.563$ $r^2 = 0.946$	$y = 0.006x^2 + 0.216x + 0.712$ $r^2 = 0.926$
Bray 1 vs. Truog	$y = 0.004x^2 + 0.788x - 1.851$ $r^2 = 0.991$	$y = -0.004x^2 + 1.432x - 4.909$ $r^2 = 0.971$	$y = 1.175x - 0.724$ $r^2 = 0.994$	$y = 4.461e^{0.097x}$ $r^2 = 0.927$
Bray 1 vs. ISFEI	$y = 0.003x^2 + 0.191x - 0.848$ $r^2 = 0.983$	$y = 0.002x^2 + 0.31x - 1.585$ $r^2 = 0.973$	$y = 0.000x^2 + 0.374x - 0.653$ $r^2 = 0.991$	$y = 0.016x^2 - 0.001x + 1.838$ $r^2 = 0.894$
Bray 1 vs. citric acid	$y = 0.468x - 2.308$ $r^2 = 0.959$	$y = 0.283x - 0.809$ $r^2 = 0.948$	$y = 0.001x^2 + 0.163x + 0.557$ $r^2 = 0.978$	$y = 0.013x^2 + 0.141x + 1.149$ $r^2 = 0.906$
Truog vs. ISFEI	$y = 0.001x^2 + 0.280x - 0.441$ $r^2 = 0.993$	$y = 0.003x^2 + 0.188x - 0.239$ $r^2 = 0.991$	$y = 0.345x - 0.539$ $r^2 = 0.983$	$y = 0.003x^2 + 0.110x + 1.349$ $r^2 = 0.916$
Truog vs. citric acid	$y = -0.002x^2 + 0.588x - 1.416$ $r^2 = 0.981$	$y = 0.000x^2 + 0.204x + 0.085$ $r^2 = 0.983$	$y = 0.001x^2 + 0.150x + 0.608$ $r^2 = 0.983$	$y = 0.001x^2 + 0.255x + 0.230$ $r^2 = 0.980$
ISFEI vs. citric acid	$y = -0.030x^2 + 1.826x - 0.345$ $r^2 = 0.981$	$y = 0.056x^2 - 0.504x + 2.066$ $r^2 = 0.954$	$y = 0.007x^2 + 0.470x + 0.861$ $r^2 = 0.959$	$y = -0.041x^2 + 1.636x - 1.312$ $r^2 = 0.952$

Table 4.9 Relationships between amounts of P extracted with agronomic tests from each of the Ficksburg soils

Soil P tests	F1 (n=21)	F2 (n=21)	F3 (n=21)	F4 (n=21)
Olsen vs. Bray 1	$y = 0.518x^{1.265}$ $r^2 = 0.962$	$y = -0.014x^2 + 1.997x - 8.675$ $r^2 = 0.914$	$y = 0.023x^2 + 0.738x - 2.395$ $r^2 = 0.979$	$y = 0.152x^{1.489}$ $r^2 = 0.945$
Olsen vs. Truog	$y = -0.023x^2 + 2.395x - 4.359$ $r^2 = 0.960$	$y = -0.017x^2 + 2.117x - 3.511$ $r^2 = 0.930$	$y = 0.025x^2 + 0.772x + 0.095$ $r^2 = 0.981$	$y = 0.025x^2 + 1.071x + 20.43$ $r^2 = 0.981$
Olsen vs. ISFEI	$y = 1.159x^{0.677}$ $r^2 = 0.668$	$y = -0.001x^2 + 0.875x - 3.519$ $r^2 = 0.914$	$y = 0.023x^2 - 0.120x + 0.634$ $r^2 = 0.973$	$y = 1.383e^{0.091x}$ $r^2 = 0.944$
Olsen vs. citric acid	$y = 0.528x^{0.887}$ $r^2 = 0.937$	$y = -0.004x^2 + 0.548x + 1.659$ $r^2 = 0.929$	$y = 0.003x^2 + 0.409x + 0.805$ $r^2 = 0.972$	$y = 5.205e^{0.050x}$ $r^2 = 0.937$
Bray 1 vs. Truog	$y = -0.007x^2 + 1.354x + 1.069$ $r^2 = 0.992$	$y = 3.754x^{0.671}$ $r^2 = 0.984$	$y = 2.883x^{0.713}$ $r^2 = 0.970$	$y = -0.041x^2 + 3.055x + 20.89$ $r^2 = 0.975$
Bray 1 vs. ISFEI	$y = 1.642x^{0.536}$ $r^2 = 0.697$	$y = 0.013x^2 - 0.115x + 4.002$ $r^2 = 0.972$	$y = 0.007x^2 + 0.136x + 0.469$ $r^2 = 0.986$	$y = 0.014x^2 + 0.349x + 1.638$ $r^2 = 0.978$
Bray 1 vs. citric acid	$y = -0.000x^2 + 0.273x + 1.165$ $r^2 = 0.982$	$y = -0.000x^2 + 0.298x + 3.981$ $r^2 = 0.971$	$y = 0.350x + 2.583$ $r^2 = 0.972$	$y = 0.003x^2 + 0.597x + 5.739$ $r^2 = 0.980$
Truog vs. ISFEI	$y = 2.527e^{0.034x}$ $r^2 = 0.706$	$y = 0.017x^2 - 0.418x + 5.756$ $r^2 = 0.976$	$y = 0.006x^2 + 0.129x - 0.042$ $r^2 = 0.992$	$y = 0.002x^{2.120}$ $r^2 = 0.954$
Truog vs. citric acid	$y = 0.000x^2 + 0.206x + 0.830$ $r^2 = 0.983$	$y = 0.283x + 2.235$ $r^2 = 0.978$	$y = -0.000x^2 + 0.363x + 1.484$ $r^2 = 0.979$	$y = 0.142x^{1.170}$ $r^2 = 0.961$
ISFEI vs. citric acid	$y = 0.861x^{0.919}$ $r^2 = 0.690$	$y = -0.008x^2 + 0.746x + 3.152$ $r^2 = 0.972$	$y = -0.025x^2 + 1.250x + 2.538$ $r^2 = 0.986$	$y = -0.012x^2 + 1.197x + 4.368$ $r^2 = 0.983$

The results indicated that the ability of the employed methods to extract P was different. However, the close correlation between the methods showed that their trends of P displacement into the soil solution were similar (Islam *et al.,* 2001). The strength of the relationships between the methods increased when soils from a site were grouped together (Table 4.6). With individual soils the relationships between methods were even stronger (Table 4.7, 4.8, and 4.9).

The high correlation between the various agronomic phosphorus tests indicate that, even though the extractants have shown to have varying efficiencies in extracting P in different soils, they are capable of estimating plant availability of P and can be used for fertilizer recommendation in the soils under study. In the study area the regression equations for the significant relationships can be used for estimating the amount of plant available P among the agronomic phosphorus tests.

4.3.2 Among environmental phosphorus tests

The regression analysis showed significant relationships between the P values of $CaCl_2$ and DPS_{ox} per individual soil (Table 4.10). Coefficients of determination for these relationships ranged between 0.81 to 0.95, 0.93 to 0.99 and 0.88 to 0.98 for the individual Jacobsdal, Bloemfontein, and Ficksburg soils respectively. However, when data of all soils from one sampling area were regressed, significant relationships (Table 4.11) were obtained for Bloemfontein (r^2=0.92) and Ficksburg (r^2=0.56), but not for Jacobsdal (r^2=0.33). The relationship between the P values of $CaCl_2$ and DPS_{ox} for all soils from the three sampling area was poor (r^2=0.40).

Table 4.10 Relationships between amounts of P extracted with $CaCl_2$ (y) and DPS_{ox} (x) in each soil (n=21) from the three sampling areas

Locality	Soil sample	Equation	r^2
Jacobsdal	J1	$y = 0.111e^{0.361x}$	0.952
	J2	$y = 0.092e^{0.276x}$	0.850
	J3	$y = 0.007e^{0.273x}$	0.813
	J4	$y = 0.095x^2 - 0.287x + 0.027$	0.897
Bloemfontein	B1	$y = 0.021x^2 + 0.009x + 0.036$	0.968
	B2	$y = 0.038x^2 - 0.186x + 0.456$	0.992
	B3	$y = 0.117x^2 - 0.315x + 0.235$	0.934
	B4	$y = 0.175x^2 - 0.444x + 0.272$	0.968
Ficksburg	F1	$y = 0.010x^2 + 0.149x - 0.118$	0.977
	F2	$y = 0.033x^2 - 0.044x + 0.100$	0.881
	F3	$y = 0.003x^2 + 0.026x + 0.006$	0.892
	F4	$y = 0.014x^2 + 0.083x - 0.886$	0.959

Table 4.11 Relationships between amounts of P extracted with $CaCl_2$ (y) and DPS_{ox} (x) from soils of all three sampling areas (n=252) and each sampling area separately (n=84)

Group soils	Equation	r^2
All soils	$y = -0.008x^2 + 0.380x - 0.672$	0.398
Jacobsdal	$y = 0.128x^{1.023}$	0.325
Bloemfontein	$y = 0.019x^2 + 0.088x - 0.095$	0.916
Ficksburg	$y = 0.157x - 0.178$	0.556

4.3.3 Among agronomic and environmental phosphorus tests

In section 2.4.2 it was mentioned that DPS_{ox} and $CaCl_2$ extractable P are used as reliable indicators of a soil's ability to release soluble P in runoff and/or leaching waters (McDowell & Sharpley, 2001; Allen & Mallariono, 2006). However, agronomic tests are considered versatile enough to serve as alternative tools. This is because of the difficulty to perform environmental tests on a routine basis especially the DPS_{ox} method. Thus to evaluate the suitability of agronomic tests as proxy to environmental tests, the P extracted with environmental tests (DPS_{ox} and $CaCl_2$) were regressed to the P extracted with agronomic tests (Olsen, Bray 1, Truog, ISFEI, and citric acid), commonly used in South Africa.

4.3.3.1 Agronomic tests and $CaCl_2$

Figure 4.1 shows the relationships of P extracted with $CaCl_2$ and the different agronomic tests when data of all soils from the three sampling areas were regressed. Significant relationships were obtained with Bray 1 (r^2= 0.80), Olsen (r^2= 0.75), ISFEI (r^2= 0.72), and citric acid (r^2= 0.57). The exception was with Truog which showed a poor correlation (r^2= 0.28).

Regression analysis on extracted P data of all soils from one sampling area resulted in significant relationships between $CaCl_2$ and all agronomic tests for Bloemfontein and Ficksburg soils (Table 4.12). The r^2 values ranges were 0.73 to 0.90 for Bloemfontein soils and 0.59 to 0.93 for Ficksburg soils. Substantially lower r^2 values for the relationship of extracted P with $CaCl_2$ and Truog (r^2= 0.22) or citric acid (r^2= 0.35) were obtained for the Jacobadal soils.

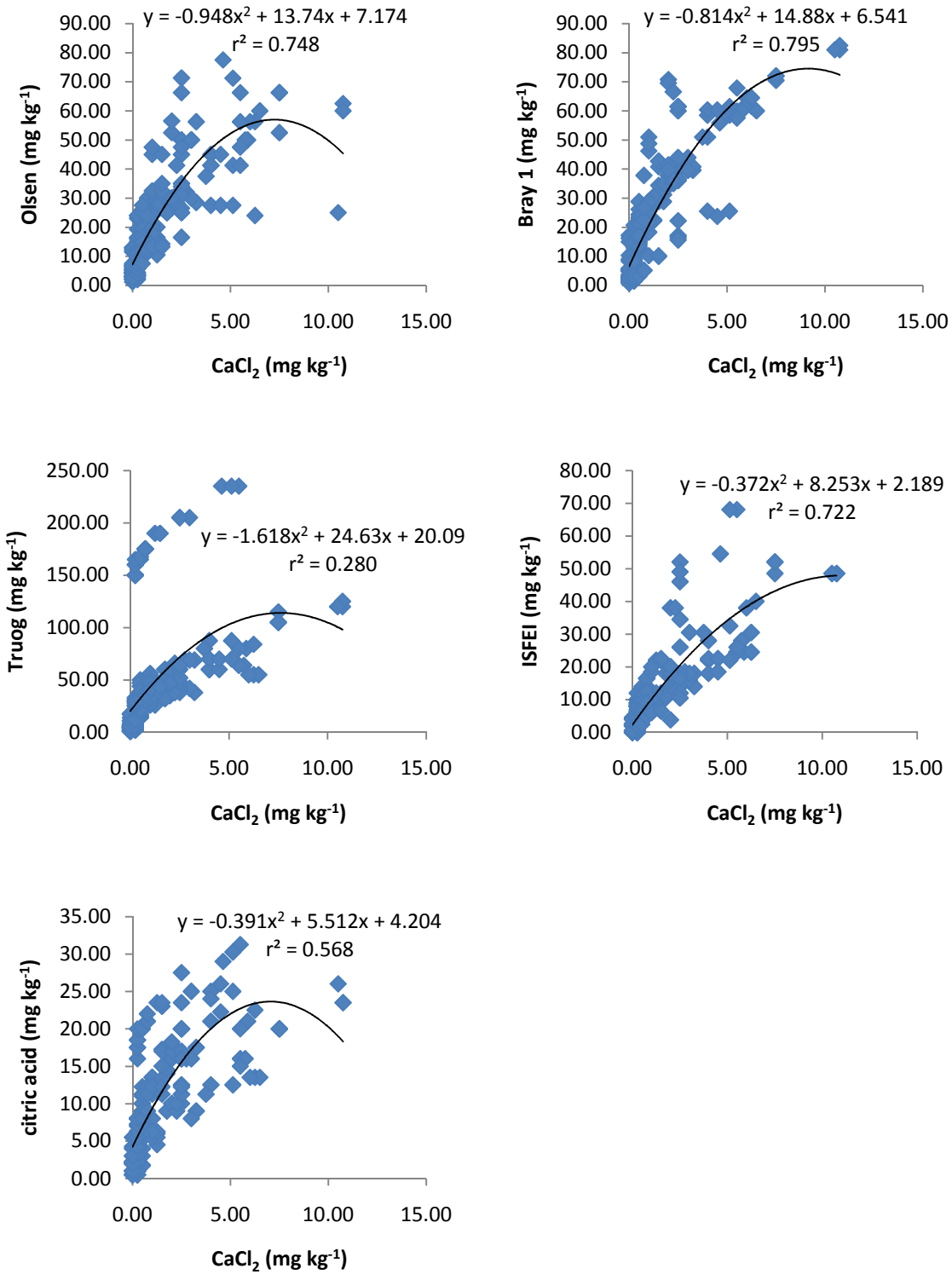

Figure 4.1 Relationships between P extracted with $CaCl_2$ and different agronomic tests for all soils (n=252) from the three sampling areas

Table 4.12 Relationships between P extracted with $CaCl_2$ (y) and the different agronomic tests (x) for Jacobsdal, Bloemfontein and Ficksburg soils (n=84)

Agronomic tests	Jacobsdal	Bloemfontein	Ficksburg
Olsen	$y = -0.929x^2 + 13.79x + 7.660$ $r^2 = 0.802$	$y = -1.140x^2 + 13.22x + 7.324$ $r^2 = 0.810$	$y = -4.492x^2 + 26.79x + 2.343$ $r^2 = 0.698$
Bray 1	$y = -0.633x^2 + 13.53x + 6.908$ $r^2 = 0.977$	$y = -1.825x^2 + 19.58x + 6.289$ $r^2 = 0.900$	$y = -5.963x^2 + 33.41x - 0.519$ $r^2 = 0.633$
Truog	$y = 52.44x^{0.403}$ $r^2 = 0.217$	$y = -2.064x^2 + 21.57x + 6.695$ $r^2 = 0.851$	$y = -4.375x^2 + 33.65x + 7.302$ $r^2 = 0.899$
ISFEI	$y = -0.373x^2 + 8.338x + 3.545$ $r^2 = 0.761$	$y = -0.430x^2 + 6.789x + 1.527$ $r^2 = 0.901$	$y = -2.380x^2 + 16.1x - 0.431$ $r^2 = 0.591$
citric acid	$y = 8.774x^{0.503}$ $r^2 = 0.348$	$y = -0.761x^2 + 7.229x + 1.626$ $r^2 = 0.734$	$y = -1.015x^2 + 8.909x + 3.258$ $r^2 = 0.926$

The regression analysis on each individual soil's extractable P data showed much stronger relationships between $CaCl_2$ and the different agronomic tests (Table 4.13). Coefficients of determination for Jacobsdal soils were above 0.92 except for the Olsen relationship in the J1 (r^2=0.88) and J2 (r^2=0.73) soils. Bloemfontein soils also showed significant relationships between extracted P with $CaCl_2$ and the different agronomic tests with r^2 values in most instances greater than 0.90. Conversely, for the B4 soil the range of r^2 values (0.63 - 0.87) were lower. Slightly lower r^2 values than 0.90 also manifested in a few instances when $CaCl_2$ extractable P values were regressed with that of Olsen (B2 soil: r^2=0.89 and B3 soil: r^2=0.87), Bray 1 (B1 soil: r^2=0.89), and citric acid (B1 soil r^2=0.88).The relationship of $CaCl_2$-P and the different agronomic tests were also high ($r^2 \geq 0.90$) for the Ficksburg soils. However, there were a few exceptions in the case of the F1 soil (Olsen: r^2=0.82 and ISFEI: r^2=0.63).

Table 4.13 Relationships between P extracted with $CaCl_2$ (y) and the different agronomic tests (x) for individual soils (n=21) from Jacobsdal, Bloemfontein and Ficksburg

Agronomic	Jacobsdal			Bloemfontein			Ficksburg		
tests		Equation	r^2		Equation	r^2		Equation	r^2
Olsen	J1	$y = 16.16\ln(x) + 26.46$	0.883	B1	$y = 9.624x + 5.393$	0.936	F1	$y = 24.07x + 4.757$	0.853
Bray 1		$y = 16.41\ln(x) + 25.52$	0.954		$y = 12.82x + 8.842$	0.890		$y = 33.58x + 3.727$	0.938
Truog		$y = 14.75\ln(x) + 25.93$	0.983		$y = 13.78x + 4.929$	0.929		$y = 29.29x + 7.442$	0.903
ISFEI		$y = 5.568x + 0.529$	0.969		$y = 5.366x + 0.696$	0.961		$y = 11.93x + 2.431$	0.633
citric acid		$y = 3.771\ln(x) + 5.707$	0.930		$y = 6.092x + 1.750$	0.878		$y = 7.703x + 2.273$	0.931
Olsen	J2	$y = 2.616x^{0.654}$	0.734	B2	$y = 6.840x + 8.598$	0.888	F2	$y = 23.81x + 1.584$	0.936
Bray 1		$y = 22.61x^{0.550}$	0.982		$y = 9.018x + 9.283$	0.918		$y = 23.41\ln(x) + 35.69$	0.958
Truog		$y = 7.108x + 44.40$	0.980		$y = 16.99\ln(x) + 29.61$	0.961		$y = 21.58\ln(x) + 39.80$	0.973
ISFEI		$y = 3.986x + 4.067$	0.981		$y = 4.618x + 0.894$	0.974		$y = 19.42x - 2.255$	0.970
citric acid		$y = 12.63x^{0.270}$	0.974		$y = 4.208\ln(x) + 7.013$	0.954		$y = 6.108\ln(x) + 13.52$	0.947
Olsen	J3	$y = 11.92x + 11.27$	0.940	B3	$y = 11.52x + 7.120$	0.872	F3	$y = 12.93x + 6.831$	0.897
Bray 1		$y = 10.49x + 9.600$	0.975		$y = 16.57x + 5.019$	0.948		$y = 20.43x + 3.019$	0.939
Truog		$y = 184.5x^{0.128}$	0.958		$y = 19.53x + 5.141$	0.948		$y = 22.04x + 5.736$	0.949
ISFEI		$y = 10.77x + 6.542$	0.969		$y = 6.787x + 1.212$	0.944		$y = 9.674x + 0.158$	0.992
citric acid		$y = 22.38x^{0.160}$	0.922		$y = 4.212x + 1.311$	0.966		$y = 7.262x + 3.591$	0.937
Olsen	J4	$y = 6.436x + 13.42$	0.948	B4	$y = 41.07x + 8.217$	0.800	F4	$y = 7.443\ln(x) + 15.64$	0.915
Bray 1		$y = 22.48x^{0.591}$	0.987		$y = 31.14x + 7.261$	0.634		$y = 5.335x + 1.472$	0.964
Truog		$y = 10.64x + 32.25$	0.967		$y = 56.56x + 9.987$	0.845		$y = 42.46x^{0.329}$	0.951
ISFEI		$y = 5.754x + 6.682$	0.986		$y = 15.43x + 2.846$	0.868		$y = 3.967x + 1.308$	0.990
citric acid		$y = 1.962x + 4.893$	0.959		$y = 17.91x + 2.926$	0.866		$y = 3.699x + 6.379$	0.976

4.3.3.2 Agronomic tests and DPS_{ox}

As displayed in Figure 4.2 the relationship between DPS_{ox} and extractable P with the different agronomic tests on all soils from the three sampling areas were significant for Olsen (r^2=0.60), Bray 1 (r^2=0.51), Truog (r^2=79) and citric acid (r^2=0.82). The exception was with ISFEI which resulted in a poor correlation (r^2=0.45). Regression analysis between DPS_{ox} and the different agronomic tests for all soils of a site resulted in variable significant relationships (Table 4.14). For Jacobsdal Truog and citric acid, for Ficksburg Olsen, Truog and citric acid, and for Bloemfontein Olsen, Bray 1, Truog, ISFEI and citric acid showed strong relationships.

Table 4.14 Relationships between DPS_{ox} (y) and the different agronomic tests (x) for Jacobsdal, Bloemfontein and Ficksburg soils (n=84)

Agronomic tests	Jacobsdal	Bloemfontein	Ficksburg
Olsen	$y = 4.320x^{0.759}$ $r^2 = 0.477$	$y = -0.044x^2 + 3.542x + 2.306$ $r^2 = 0.757$	$y = 3.782x^{0.737}$ $r^2 = 0.530$
Bray 1	$y = 3.186x^{0.902}$ $r^2 = 0.479$	$y = -0.088x^2 + 5.421x - 1.520$ $r^2 = 0.873$	$y = 2.156x^{0.899}$ $r^2 = 0.370$
Truog	$y = 2.770x^{1.42}$ $r^2 = 0.838$	$y = -0.087x^2 + 5.595x - 0.837$ $r^2 = 0.771$	$y = 4.068x^{0.995}$ $r^2 = 0.727$
ISFEI	$y = 0.012x^2 + 1.419x + 1.775$ $r^2 = 0.397$	$y = 0.027x^2 + 1.323x - 0.140$ $r^2 = 0.804$	$y = -0.070x^2 + 2.314x - 1.447$ $r^2 = 0.232$
citric acid	$y = -0.031x^2 + 2.070x - 3.319$ $r^2 = 0.914$	$y = -0.006x^2 + 1.524x - 0.311$ $r^2 = 0.722$	$y = -0.053x^2 + 1.945x - 0.144$ $r^2 = 0.714$

For the individual Jacobsdal soils, the P extracted with DPS_{ox} related well with that of the different agronomic tests with r^2 values ranging from 0.73 to 0.96 (Table 4.15). It was interesting to note that the r^2 values for the slightly acid J1 soil (r^2=0.91-0.96) were higher than for the slightly alkaline J2 (r^2=0.73-0.87), and calcareous J3 (r^2=0.76-0.85) and J4 (r^2=0.82-0.91) soils.

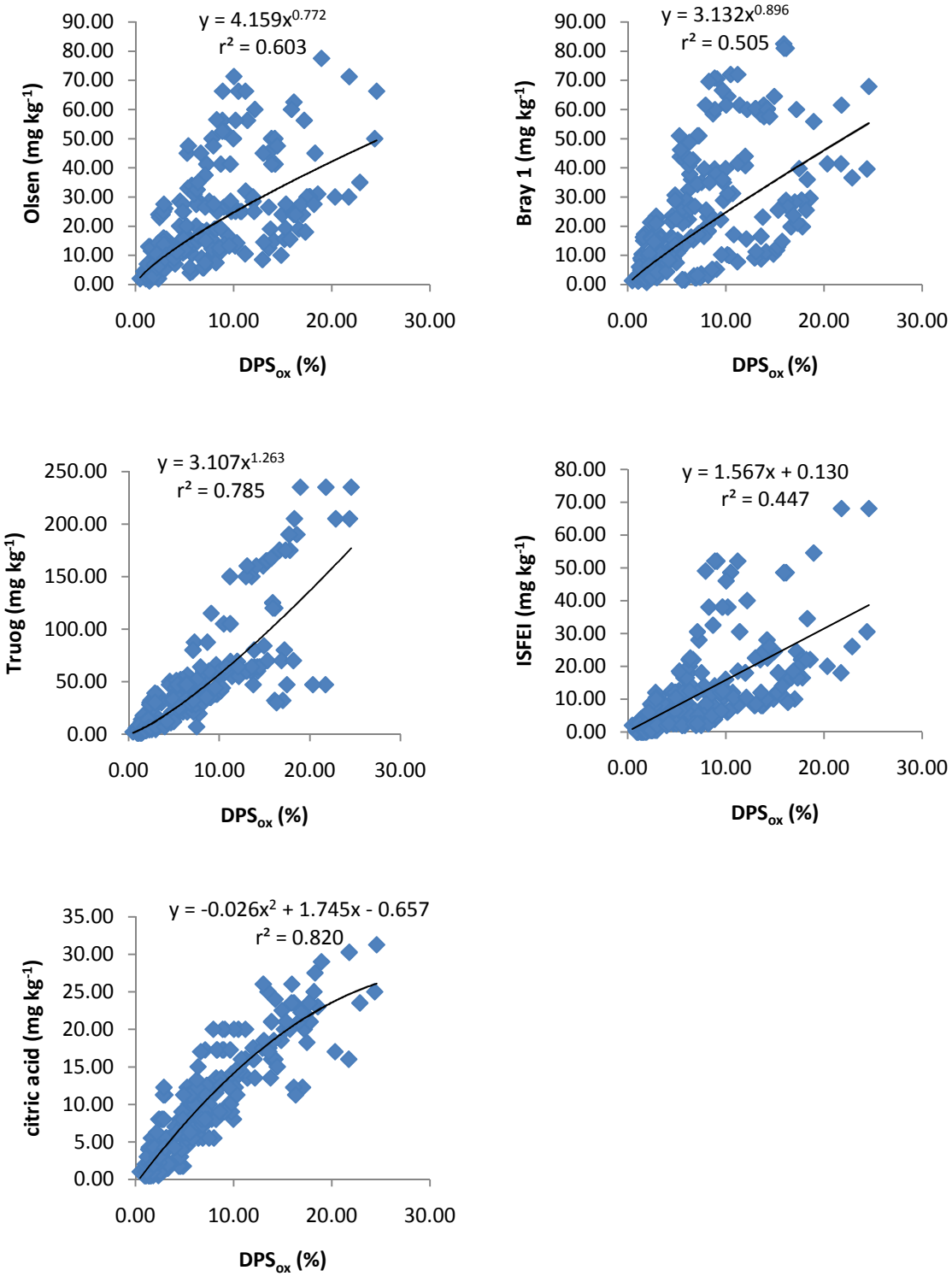

Figure 4.2 Relationships between DPS_{ox} and different agronomic tests for all soils (n=252) from the three sampling sites

Table 4.15 Relationships between DPS_{ox} (y) and the different agronomic tests (x) for individual soils (n=21) from Jacobsdal, Bloemfontein and Ficksburg

Agronomic		Jacobsdal			Bloemfontein			Ficksburg	
tests		Equation	r^2		Equation	r^2		Equation	r^2
Olsen	J1	$y = 6.081x - 10.37$	0.911	B1	$y = 0.007x^2 + 3.193x - 1.497$	0.974	F1	$y = 3.588x^{1.272}$	0.932
Bray 1		$y = 6.060x - 11.25$	0.949		$y = -0.068x^2 + 5.534x - 3.512$	0.992		$y = -0.453x^2 + 13.05x - 11.78$	0.977
Truog		$y = 5.399x - 6.872$	0.96		$y = 4.788x - 5.569$	0.989		$y = 7.571x - 0.875$	0.936
ISFEI		$y = 0.319x^2 - 0.908x + 1.928$	0.907		$y = 0.040x^2 + 1.235x - 1.915$	0.982		$y = 2.648x^{0.908}$	0.691
citric acid		$y = 0.195x^{1.743}$	0.928		$y = -0.048x^2 + 2.852x - 4.549$	0.968		$y = -0.126x^2 + 3.216x - 1.593$	0.976
Olsen	J2	$y = 0.014x^{2.923}$	0.866	B2	$y = 0.129x^2 + 1.065x + 4.746$	0.945	F2	$y = 1.054x^2 - 3.693x + 9.239$	0.916
Bray 1		$y = 5.930e^{0.154x}$	0.861		$y = 0.130x^2 + 2.029x + 2.548$	0.968		$y = 0.617x^{2.085}$	0.904
Truog		$y = 26.64e^{0.079x}$	0.734		$y = 0.068x^2 + 3.788x - 3.656$	0.995		$y = 7.922x - 11.09$	0.891
ISFEI		$y = 1.677e^{0.186x}$	0.806		$y = 0.109x^2 + 0.310x - 0.419$	0.993		$y = 0.956e^{0.438x}$	0.892
citric acid		$y = 6.404e^{0.078x}$	0.868		$y = 0.032x^2 + 0.696x - 0.563$	0.984		$y = 2.298x - 1.159$	0.912
Olsen	J3	$y = 0.010x^{2.747}$	0.762	B3	$y = -0.117x^2 + 7.072x - 4.683$	0.978	F3	$y = -0.023x^2 + 1.823x + 1.751$	0.944
Bray 1		$y = 0.004x^{2.959}$	0.848		$y = 1.999x^{1.736}$	0.984		$y = 2.024x - 2.104$	0.938
Truog		$y = 31.28x^{0.621}$	0.793		$y = 1.047x^2 + 3.061x - 3.019$	0.983		$y = 2.158x + 0.417$	0.926
ISFEI		$y = 0.005x^{2.847}$	0.777		$y = 0.412x^2 + 0.722x - 1.173$	0.974		$y = 0.023x^2 + 0.395x - 0.260$	0.899
citric acid		$y = 2.378x^{0.784}$	0.779		$y = 0.529x^{1.720}$	0.946		$y = 1.513x^{0.795}$	0.936
Olsen	J4	$y = 0.598x^2 - 1.439x + 11.71$	0.907	B4	$y = -1.398x^2 + 17.73x - 13.19$	0.941	F4	$y = -0.122x^2 + 5.010x - 21.45$	0.908
Bray 1		$y = 0.318x^2 + 4.454x - 8.855$	0.878		$y = 17.95\ln(x) + 2.040$	0.834		$y = -0.585x^2 + 8.082x + 0.053$	0.984
Truog		$y = 0.563x^2 + 2.876x + 15.61$	0.819		$y = -0.649x^2 + 18.91x - 14.34$	0.941		$y = 4.158x^{1.019}$	0.909
ISFEI		$y = 0.592x^2 - 2.278x + 8.735$	0.887		$y = 0.420x^2 + 2.591x - 1.407$	0.888		$y = 0.052x^2 + 0.429x - 2.806$	0.973
citric acid		$y = 0.135x^2 + 0.19x + 2.540$	0.899		$y = 5.126x - 3.996$	0.947		$y = 0.013x^2 + 1.229x - 1.697$	0.969

An almost similar range of r^2 values (0.69-0.98) was obtained for the individual Ficksburg soils as well as for the individual Bloemfontein soils. However, compared to the two sampling areas higher r^2 values (0.83-0.99) resulted for the individual Bloemfontein soils when their DPS_{ox} was related to P from the different agronomic tests.

These results proved that there are generally good relationships between the environmental and the agronomic tests. The strength of a relationship depends on the extractant used because they do not have similar abilities in extracting P in different soils. The closeness of a relationship also depends on the group of soils included, since the correlation was stronger when individual soils were analyzed separately than when soils from one sampling area were grouped together. As expected a weaker correlation manifested when all soils' extractable P data were regressed. This reflects the conclusion of other studies (Beauchemin & Simard, 1999; Sims *et al.* 1998; Lookman *et al.,* 1996; Pote *et al.,* 1996) which states that the correlation is usually strong when the studied soils are fairly homogenous in pH and texture, but weaker if soils with a wide range in properties are considered.

4.4 Estimated phosphorus threshold values for agronomic soil P tests

Either $CaCl_2$ extractable P or DPS_{ox} is often used in evaluating a soil's threat to water pollution with P. Some threshold values for $CaCl_2$ extractable P are given in Table 4.16. They range from 0.75 mg P kg^{-1} in China to 2.7 mg P kg^{-1} in Italy with an average of 1.485 mg P kg^{-1}. Threshold values of DPS_{ox} are displayed in Table 4.17. These values vary from 20% (Florida, USA) to 30% (Belgium, Germany and Delaware, USA) with an average of 26.07%. The average threshold values of $CaCl_2$ and DPS_{ox} were used in this study to estimate agronomic test P values that may be threatening for water pollution. In this estimation the regression equations presented in section 4.3.3 were applied.

Table 4.16 Threshold values for $CaCl_2$ extractable P (mg kg^{-1}) used in evaluating soil's threat to water pollution

Region	Threshold value	Reference
Italy	2.7	Indiati & Rossi (1999)
Delaware (USA)	0.9	Kleinman *et al*. (2000)
China	0.75	Zhao *et al.* (2007)
USA	1.59	Maguire & Sims (2002)

Average = 1.485 mg P kg^{-1}

Table 4.17 Threshold values for DPS_{ox} (%) used in evaluating soil's threat of water pollution

Region	Threshold value	Reference
Delaware (USA)	>25	Sims *et al.* (1998)
Netherlands	25	Breeuwsma *et al.* (1995)
Belgium	30	De Smet *et al.* (1996)
Germany	30	Leinweber *et al.* (1997)
Indiana (USA)	22.5	Provin (1996)
Florida (USA)	20	Nair *et al.* (2004)
Delaware (USA)	>30	Pautler & Sims (2000)

Average = 26.07%

4.4.1 Estimations from $CaCl_2$ extractable phosphorus

The phosphorus threshold values for agronomic tests that were estimated from an average $CaCl_2$ extractable P threshold are presented in Table 4.18 for the individual soils from Jacobsdal, Bloemfontein and Ficksburg. These values varied greatly between soils for a specific agronomic test. In the case of the Olsen test for example, the ranges are 3.4 to 32.9 mg P kg^{-1} for Jacobsdal soils, 18.8 to 69.2 mg P kg^{-1} for Bloemfontein soils, and 18.6 to 40.5 mg P kg^{-1} for Ficksburg soils. However, as expected when all soils of a site are considered smaller ranges were estimated (Table 4.19). The range for the Olsen test is now only from 24.4 mg P kg^{-1} for Bloemfontein soils to 32.2 mg P kg^{-1} for Ficksburg soils. Similar trends were observed for the Bray 1, Truog, ISFEI, and citric acid tests.

The estimated threshold values for all soils from the three sampling areas are 26.8, 25.5, 13.6, 20.6 and 11.5 mg P kg^{-1} for the Olsen, Bray 1, Truog, ISFEI, and citric acid tests, respectively (Table 4.19). Except for the Olsen test, the estimated threshold values for the other agronomic tests are lower than the optimum extractable P values used locally for fertilization recommendations to crops (Table 4.22). The implication is that when the extractable P status of cropped soils are maintained at optimum levels for Bray 1, Truog, ISFEI and citric acid they may be a threat to water pollution.

Table 4.18 Threshold values for agronomic tests (mg P kg^{-1}) estimated from $CaCl_2$ extractable P for the individual Jacobsdal, Bloemfontein and Ficksburg soils

Soil test	**J1**	**J2**	**J3**	**J4**
Olsen	32.85	3.39	28.97	22.98
Bray 1	32.01	28.10	25.18	28.40
Truog	31.76	54.96	194.08	48.05
ISFEI	8.80	9.99	22.54	15.23
citric acid	7.20	14.05	23.84	7.81
	B1	**B2**	**B3**	**B4**
Olsen	19.69	18.76	24.23	69.21
Bray 1	27.88	22.75	29.63	33.50
Truog	25.39	36.33	34.14	93.98
ISFEI	8.67	7.75	11.29	25.76
citric acid	10.80	8.68	7.57	29.52
	F1	**F2**	**F3**	**F4**
Olsen	40.50	36.94	26.03	18.58
Bray 1	53.59	44.95	33.36	13.34
Truog	50.94	48.33	38.47	48.36
ISFEI	20.15	26.58	14.52	7.20
citric acid	13.71	15.94	14.38	11.87

Table 4.19 Threshold values for agronomic tests (mg P kg^{-1}) estimated from $CaCl_2$ extractable P for the Jacobsdal, Bloemfontein, Ficksburg and all soils

Soil test	Jacobsdal	BLoemfontein	Ficksburg	All soils
Olsen	26.09	24.44	32.22	26.84
Bray 1	25.60	31.34	35.95	25.49
Truog	61.50	34.18	47.62	13.62
ISFEI	15.10	10.66	18.23	20.59
citric acid	10.71	10.68	14.25	11.53

4.4.2 Estimations from DPS_{ox}

The phosphorus threshold values for agronomic tests that were estimated from an average DPS_{ox} threshold are given in Table 4.20 for the individual soils from Jacobsdal, Bloemfontein, and Ficksburg. These values are generally larger than the values estimated from an average $CaCl_2$ extractable P threshold (Table 4.18) However, these values also varied greatly, similarly to $CaCl_2$-P, between soils for a specific agronomic test. In the case of the ISFEI test for example

the ranges were 52.7 to 351.7 mg P kg^{-1} for Jacobsdal soils, 31.3 to 351.6 mg P kg^{-1} for Bloemfontein soils, and 25.7 to 51.1 mg P kg^{-1} for Ficksburg soils. As expected when all soils of a site were considered, smaller ranges were estimated (Table 4.21). The range for the ISFEI test was now only from 11.3 mg P kg^{-1} for Ficksburg soils to 52.7 mg P kg^{-1} for Bloemfontein soils. Similar trends manifested for the other four agronomic tests, viz. Olsen, Bray 1, Truog and citric acid.

The estimated threshold values for all soils from the three sampling areas were 58.16, 51.6, 41.0, 191.0 and 62.5 mg P kg^{-1} for the Olsen, Bray 1, Truog, ISFEI and citric acid tests, respectively (Table 4.21). These estimated threshold values of all agronomic tests were much higher than the optimum extractable P values used locally for fertilization recommendations to crops (Table 4.22). The implication was that when the extractable P status of cropped soils is maintained at optimum levels they should not be a threat for water pollution. This was converse to the threshold phosphorus values estimated from $CaCl_2$ extractable P (Table 4.19).

Table 4.20 Threshold values for agronomic tests (mg P kg^{-1}) estimated from DPS_{ox} for the individual Jacobsdal, Bloemfontein and Ficksburg soils

Soil test	J1	J2	J3	J4
Olsen	148.16	192.98	77.65	380.62
Bray 1	146.73	180.33	62.00	323.39
Truog	133.88	751.60	236.97	105.27
ISFEI	195.06	52.66	53.79	351.70
citric acid	57.33	180.50	30.65	11.01
	B1	**B2**	**B3**	**B4**
Olsen	86.50	120.19	179.68	412.59
Bray 1	94.54	143.80	574.43	60.57
Truog	119.25	141.31	788.37	919.73
ISFEI	31.32	81.74	300.01	351.59
citric acid	102.43	39.33	144.28	129.64
	F1	**F2**	**F3**	**F4**
Olsen	227.08	629.31	33.65	26.24
Bray 1	20.55	553.27	50.66	45.03
Truog	196.5	195.44	56.68	115.33
ISFEI	51.14	38.62	25.67	43.72
citric acid	78.96	58.75	20.22	39.18

Table 4.21 Threshold values for agronomic tests (mg P kg^{-1}) estimated from DPS_{ox} for the Jacobsdal, Bloemfontein, Ficksburg and for all soils

Soil test	Jacobsdal	Bloemfontein	Ficksburg	All soils
Olsen	51.33	64.74	41.82	58.17
Bray 1	60.34	80.00	40.44	51.55
Truog	284.05	85.90	104.34	40.98
ISFEI	46.92	52.70	11.30	190.95
citric acid	29.58	35.34	14.54	62.51

Table 4.22 Optimum extractable phosphorus values (mg kg^{-1}) for cropped soils in South Africa

Agronomic test	Optimum values	Reference
Olsen	12	Eloff (1971)
Bray 1	35	FSSA (2003)
Truog	31	Botha & Meyer (2004)
ISFEI	30	FSSA (2003)
citric acid	35	Lambrechts (2012)

The results indicated that the estimated phosphorus threshold values for the agronomic tests vary depending on the test used and also on the soil. Some of the values were below and others above the optimum extractable P values used locally for fertilization recommendations to crops. Thus the use of agronomic tests for the environmental assessment of P in soils would require further investigation into the grouping of soils for an appropriate extraction method for setting threshold values from an environmental point of view. However, the general observation made from the study was that agronomic tests can be used in regulating application of P fertilizer, thus decreasing the risk of P accumulation and its subsequent loss to the environment while optimizing agricultural production.

CHAPTER FIVE

SUMMARY AND CONCLUSIONS

Most agricultural soils are P deficit and this makes P fertilization a vital practice in sustainable crop production systems. Phosphorus is applied in the form of either inorganic or organic fertilizers to maintain soil P levels sufficient for growing crops, thus increasing crop yields. However, freshwater eutrophication is often accelerated by increased P concentration in agricultural soil posing an environmental problem through non-point source pollution. The use of environmental threshold values is regarded as one of the ways by which P fertilizer application can be regulated. But because of the lack of knowledge in introducing the use of environmental soil P tests on a routine basis, agronomic soil P tests are considered as an option for environmental assessment of P. This, however, entails comparing agronomic soil P tests used in an area, and evaluating their suitability for use as alternative for environmental P tests. The objective of this study was therefore to review the current methods used to determine the agronomic and environmental P status of soils and to establish whether P extracted from a range of soils by various agronomic and or environmental P determination methods is related or not.

Soil samples from the orthic A horison were collected in three cropping areas in the Free State province, namely Jacobsdal, Bloemfontein, and Ficksburg. These samples were treated with K_2HPO_4 to induce different phosphorus concentration levels and then incubated at room temperature for three months. During incubation the samples were subjected to several wetting and drying cycles to ensure equilibration of the applied phosphorus. The samples were then analysed for P using the Olsen, Bray 1, Truog, ISFEI, and citric acid extractants commonly employed for routine analysis to establish the agronomic P status of soils. In order to establish the environmental P status of the soils, the samples were analysed using the $CaCl_2$ extraction and DPS_{ox}. Regression and correlation analysis was done to depict the relationships between P extracted by the different methods. Several regression models were fitted to the data and coefficients of determination for the relationship between P extractable with the soil tests were used for selecting the best model fitting to the data.

The regression and correlation analysis showed significant relationships among agronomic P tests when data of individual soils were analysed separately and when data of all soils from a sampling area were pooled. All the relationships were significant for the Ficksburg soils and for

the Bloemfontein soils, but not for the Jacobsdal soils. For the latter soils, the Truog-P correlations with Olsen-P, Bray 1-P, and ISFEI-P were not significant probably because they are calcareous.

Significant relationships were also established for P obtained by the environmental P tests when the correlation was done for each individual soil. However, when data of soils from a site were pooled significant relationships were obtained for the Bloemfontein soils and Ficksburg soils while the Jacobsdal soils showed an insignificant relationship. Pooling data of all the soils from the three sites also resulted in a lower correlation coefficient implying a poor relationship with the environmental P tests.

The correlation between P extracted by the agronomic tests and $CaCl_2$-P showed positive relationships except in a few instances. Truog-P and citric acid-P showed a poor correlation with $CaCl_2$-P when the Jacobsdal soils' data were pooled. Pooling of all soils' data also resulted in a poor correlation between $CaCl_2$-P and Truog-P. The DPS_{ox} correlated significantly with the extractable P of all agronomic tests when the individual soil's data were analysed separately. However, when data of all soils from a sampling area were pooled for regression analysis, all relationships were significant for the Bloemfontein soils, while Olsen-P, Bray 1-P and ISFEI-P for the Jacobsdal soils, and Bray 1-P and ISFEI-P for the Ficksburg soils were not significantly related to DPS_{ox}. Pooling data of all soils from the three sampling areas resulted with a better relationship between DPS_{ox} and the extractable P of all agronomic tests, except for ISFEI.

The regression equations for the relationships between environmental P tests and agronomic P tests were used to estimate threshold values for the agronomic P tests that may result in potential environmental pollution. These threshold values for all soils, when based on an average $CaCl_2$ extractable P threshold of 1.485 mg kg^{-1}, imply that if the extractable P status of cropped soils are maintained at optimum levels for Bray 1, Truog, ISFEI, and citric acid the soils may be a threat to water pollution. The opposite manifested with the estimated threshold values when based on an average DPS_{ox} threshold of 26.07%. It is essential to mention that the estimated threshold values for an agronomic test varied greatly between individual soils and even between the soils of a sampling area.

In general the results indicated that the estimated threshold values depend on the extractant used and the variation in soil properties. This implies therefore that grouping of soils that

respond similarly to P extraction is essential in areas where soils exhibit substantial variation in chemical and mineralogical properties if these agronomic tests are to be used for effective management of P pollution. Concerning the five agronomic P tests employed in this study, only the Olsen test showed the potential for developing a single threshold value for all soils. In general, it seems feasible that agronomic soil P tests, that are used on a routine basis for fertilization recommendations can also be appropriate tools for managing the risk of P pollution from cropped soils. However, before agronomic P tests could be considered for this purpose further studies are warranted to establish reliable threshold values. It is believed that reliable threshold values can be established only through field studies by relating the P in runoff to the P extracted from soil.

Future research should focus therefore on field studies in the study area characterizing the risk of P loss from a number of soils through either runoff or erosion to surface waters. In these studies the aim should be to establish which of the two environmental P tests or the five agronomic P tests is the best to apply for determining soils' potential for environmental pollution, and to develop threshold P values from an environmental point of view for the P test best suited for the task.

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Appendix 1 Chemical properties of bulk soils used in this study

Sampling area	Soil sample	Replicate	Organic C (%)	pH (H_2O)	Exchangeable cations (mg kg^{-1})				CEC ($cmol_c$ kg^{-1})
					Ca	Mg	K	Na	
Jacobsdal	J1	1	0.79	6.3	538	168	125	15	6.20
		2	0.80	6.3	495	155	118	13	5.76
		3	0.38	6.4	520	155	118	15	6.20
		mean	0.66	6.3	518	159	120	14	6.07
	J2	1	0.56	7.1	1040	365	253	17	10.76
		2	0.67	7.1	1052	383	260	17	10.54
		3	0.54	7.1	1060	380	258	20	11.52
		mean	0.59	7.1	1051	376	257	18	10.94
	J3	1	0.78	8.6	5075	575	505	70	20.98
		2	0.89	8.6	5925	675	530	70	21.41
		3	1.03	8.5	5775	625	522	72.5	21.09
		mean	0.90	8.6	5592	625	519	71	21.16
	J4	1	0.98	7.3	2523	550	298	22	16.74
		2	0.82	7.4	2320	500	295	22	16.30
		3	0.53	7.4	2396	500	300	25	16.52
		mean	0.78	7.4	2413	517	298	23	16.52
Bloemfontein	B1	1	0.44	6.2	467	150	148	23	7.17
		2	0.49	6.1	477	157.5	142	13	6.20
		3	0.49	6.2	465	150	142	15	6.30
		mean	0.47	6.2	470	153	144	17	6.56
	B2	1	0.45	6.5	504	170	240	15	5.97
		2	0.06	6.5	507	163	240	18	6.20
		3	0.44	6.5	517	178	250	18	6.30
		mean	0.32	6.5	509	170	243	17	6.16
	B3	1	0.76	6.2	580	180	235	15	7.39
		2	0.76	6.2	585	177	247	18	7.39
		3	0.76	6.2	583	177	225	13	7.28

		mean	0.76	6.2	583	178	236	15	7.36
	B4	1	0.87	6.1	842	385	297	58	12.61
		2	0.84	6.1	850	387.5	287	58	13.15
		3	0.89	6.1	777	352.5	270	55	12.28
		mean	0.87	6.1	823	375	285	57	12.68
Ficksburg	F1	1	0.95	5.4	360	85	95	13	5.76
		2	0.96	5.5	343	78	93	13	5.22
		3	0.94	5.4	353	78	90	13	5.54
		mean	0.95	5.5	352	80	93	13	5.51
	F2	1	1.39	6.0	505	125	338	20	7.39
		2	1.38	6.0	522	130	365	22.5	7.34
		3	1.46	6.0	512	128	335	20	2.83
		mean	1.41	6.0	513	128	346	21	6.05
	F3	1	1.19	6.0	490	95	110	13	6.20
		2	1.03	6.0	495	98	120	18	5.98
		3	1.02	6.0	485	95	110	15	5.98
		mean	108	6.0	490	96	133	15	6.05
	F4	1	1.83	6.2	1112	198	203	15	11.63
		2	2.03	6.1	1112	207	215	18	11.84
		3	1.59	6.2	1190	207	205	13	11.52
		mean	1.82	6.2	1138	204	208	15	11.67

Appendix 2 Extractable phosphorus contents (mg kg^{-1}) and DPS_{ox} (%) induced to the studied soils through application of K_2HPO_4 solution

Sampling area	Soil sample	P teatment (mg/kg)	Replicate	Agronomic tests					Environmental tests	
				Olsen	Bray 1	Troug	ISFEI	Citric acid	CaCl2	DPS (%)
Jacobsdal	J1	0	1	3.25	2.37	3.50	0.50	0.50	0.25	1.81
			2	2.00	2.26	4.50	0.50	0.50	0.25	2.35
			3	3.25	1.94	3.50	0.00	0.50	0.25	1.41
			mean	2.8	2.19	3.83	0.33	0.50	0.25	1.78
	J1	5	1	6.50	4.57	6.00	2.00	1.00	0.25	2.32
			2	6.50	3.78	6.00	2.00	1.00	0.25	2.29
			3	6.50	3.81	4.50	2.50	1.00	0.25	2.57
			mean	6.50	4.06	5.50	2.17	1.00	0.25	2.39
	J1	13	1	12.00	6.32	8.50	2.50	1.50	0.25	2.89
			2	9.00	8.25	8.50	2.50	1.50	0.25	3.31
			3	10.00	7.29	10.00	2.50	1.50	0.25	3.18
			mean	10.33	7.29	9.00	2.50	1.50	0.25	3.13
	J1	25	1	12.00	12.48	14.00	4.50	1.75	0.50	4.86
			2	12.50	12.95	16.00	4.50	1.75	0.50	4.60
			3	12.50	12.91	14.00	4.50	1.75	0.50	4.44
			mean	12.33	12.78	14.67	4.50	1.75	0.50	4.63
	J1	42	1	16.50	22.56	28.00	8.00	4.50	1.25	5.03
			2	20.00	22.26	28.00	8.50	6.00	1.25	6.18
			3	10.50	22.19	26.00	8.50	5.50	1.25	5.77
			mean	16.67	22.34	27.33	8.33	5.33	1.25	5.62
	J1	65	1	56.25	39.58	38.00	14.00	9.00	3.25	8.85
			2	50.00	39.73	42.00	16.00	8.00	3.00	9.98
			3	50.00	39.58	42.00	14.00	12.50	2.50	7.80
			mean	52.08	39.63	40.67	14.67	9.83	2.92	8.84
	J1	95	1	56.25	61.47	55.00	30.50	13.50	6.25	11.41
			2	60.00	59.97	55.00	40.00	13.50	6.50	12.16
			3	56.25	64.47	55.00	38.00	13.50	6.00	10.20
			mean	57.50	61.97	55.00	36.17	13.50	6.25	11.24

J2	0	1	14.25	14.39	44.00	6.50	10.00	0.50	5.41
		2	16.00	15.29	50.00	5.00	10.00	0.50	6.68
		3	18.50	17.47	47.00	6.00	11.00	0.50	7.26
		mean	16.25	15.72	47.00	5.83	10.33	0.50	6.46
J2	5	1	15.50	18.89	47.00	7.00	11.50	0.75	7.76
		2	19.00	23.09	47.00	6.00	11.50	0.75	8.17
		3	19.00	18.29	47.00	7.00	11.50	0.75	8.07
		mean	17.83	20.09	47.00	6.67	11.50	0.75	7.99
J2	13	1	19.00	23.09	47.00	8.00	13.50	1.00	13.75
		2	19.00	18.29	53.50	8.00	13.50	1.00	8.21
		3	19.00	22.49	56.00	8.00	13.50	1.00	8.75
		mean	19.00	21.29	52.17	8.00	13.50	1.00	9.78
J2	25	1	25.00	31.18	60.00	12.00	14.50	1.75	10.70
		2	25.00	28.79	60.00	10.50	14.00	1.75	9.76
		3	25.00	31.18	60.00	12.00	14.50	1.75	10.20
		mean	25.00	30.38	60.00	11.50	14.33	1.75	10.22
J2	42	1	28.50	40.78	69.00	18.00	17.50	3.25	11.99
		2	32.00	41.53	69.00	18.50	16.00	2.75	11.23
		3	30.00	43.93	69.00	18.00	16.00	3.00	11.98
		mean	30.17	42.08	69.00	18.17	16.50	3.00	11.73
J2	65	1	50.00	61.47	80.00	24.50	21.00	5.88	13.85
		2	56.25	59.97	80.00	24.50	20.00	5.50	17.19
		3	24.00	64.47	84.00	24.50	22.50	6.25	14.93
		mean	43.42	61.97	81.33	24.50	21.17	5.88	15.24
J2	95	1	62.50	80.96	120.00	48.50	23.50	10.75	16.13
		2	60.00	82.46	125.00	48.50	23.50	10.75	15.89
		3	25.00	80.96	120.00	48.50	26.00	10.50	15.93
		mean	49.17	81.46	121.67	48.50	24.33	10.67	15.99
J3	0	1	10.50	7.75	150.00	8.00	16.00	0.25	11.17
		2	12.50	8.72	150.00	8.00	17.50	0.25	13.58
		3	8.50	9.07	150.00	8.00	17.50	0.25	12.93
		mean	10.50	8.51	150.00	8.00	17.00	0.25	12.56

J3	5	1	10.00	10.40	160.00	10.00	18.50	0.25	14.83
		2	15.00	11.17	160.00	10.00	18.50	0.25	14.09
		3	14.50	11.21	160.00	8.50	18.50	0.25	13.08
		mean	13.17	10.93	160.00	9.50	18.50	0.25	14.00
J3	13	1	15.50	11.79	165.00	12.00	20.00	0.50	15.17
		2	19.25	12.88	165.00	12.00	20.00	0.25	15.29
		3	15.50	14.75	167.50	14.00	20.00	0.50	15.73
		mean	16.75	13.14	165.83	12.67	20.00	0.50	15.39
J3	25	1	30.00	19.79	175.00	16.50	21.00	0.75	17.79
		2	19.00	19.79	175.00	16.50	21.00	0.75	16.64
		3	18.00	20.99	175.00	16.50	22.00	0.75	17.31
		mean	22.33	20.19	175.00	1650	21.33	0.75	17.24
J3	42	1	30.00	28.79	190.00	22.00	23.50	1.25	17.69
		2	31.00	29.54	190.00	22.00	23.00	1.50	18.56
		3	30.00	28.79	190.00	22.00	23.50	1.50	17.73
		mean	30.33	29.04	190.00	22.00	23.33	1.42	17.97
J3	65	1	45.00	35.98	205.00	34.50	27.50	2.50	18.29
		2	50.00	39.58	205.00	30.50	25.00	3.00	24.37
		3	35.00	36.58	205.00	26.00	23.50	2.50	22.85
		mean	43.33	37.38	205.00	30.33	25.33	2.67	21.57
J3	95	1	77.50	55.85	235.00	54.50	29.00	4.63	18.94
		2	66.25	67.84	235.00	68.00	31.25	5.50	24.55
		3	71.25	61.47	235.00	68.00	30.25	5.13	21.76
		mean	71.67	61.72	235.00	63.50	30.17	5.08	21.70
J4	0	1	12.00	8.69	32.00	8.00	4.00	0.25	2.46
		2	13.00	8.80	30.00	7.00	4.00	0.25	3.23
		3	13.00	8.17	30.00	8.00	4.50	0.25	3.62
		mean	12.67	8.55	30.67	7.67	4.17	0.25	3.08
J4	5	1	16.50	11.76	32.00	8.00	4.50	0.25	5.28
		2	12.50	10.92	33.00	9.00	5.25	0.25	3.58
		3	11.50	10.92	33.00	9.00	5.25	0.25	5.09
		mean	13.50	11.20	32.67	8.67	5.00	0.25	4.59

	J4	13	1	19.50	15.18	38.00	10.00	6.25	0.50	5.11
			2	13.75	13.94	38.00	11.00	7.00	0.50	5.89
			3	15.50	15.55	38.00	11.00	5.25	0.50	3.16
			mean	16.25	14.89	38.00	10.67	6.17	0.50	4.71
	J4	25	1	28.50	23.46	50.00	12.00	8.00	1.00	4.54
			2	20.00	21.59	47.00	12.50	8.00	1.00	4.50
			3	20.00	23.46	44.00	12.50	8.00	1.00	5.20
			mean	22.83	22.84	47.00	12.33	8.00	1.00	4.74
	J4	42	1	28.50	35.98	56.00	14.00	10.00	2.00	6.49
			2	27.50	32.38	46.00	18.00	9.00	1.75	6.20
			3	28.50	34.93	52.00	18.00	10.00	2.00	7.52
			mean	28.17	34.43	51.33	16.67	9.67	1.95	6.72
	J4	65	1	41.25	50.97	87.50	28.00	12.50	4.00	7.26
			2	41.25	58.47	87.50	32.50	12.50	5.13	8.69
			3	37.50	50.97	80.00	30.50	11.25	3.75	7.10
			mean	40.00	53.47	85.00	30.33	12.08	4.29	7.64
	J4	95	1	52.50	70.46	115.00	52.00	20.00	7.50	9.11
			2	66.25	71.96	105.00	48.50	20.00	7.50	10.49
			3	66.25	71.96	105.00	52.00	20.00	7.50	11.21
			mean	61.67	71.46	108.33	50.83	20.00	7.50	10.24
Bloemfontein	B1	0	1	2.00	2.77	1.33	0.00	0.50	0.00	1.06
			2	2.00	2.71	1.33	0.00	0.50	0.00	1.31
			3	1.20	2.78	1.33	0.00	0.50	0.00	1.44
			mean	1.73	2.76	1.33	0.00	0.50	0.00	1.26
	B1	5	1	2.50	4.94	2.00	0.00	0.50	0.25	1.53
			2	4.00	5.40	3.50	0.00	0.50	0.25	1.62
			3	3.50	4.84	2.00	0.00	0.50	0.25	1.56
			mean	3.33	5.06	2.50	0.00	0.50	0.25	1.57
	B1	13	1	7.00	7.98	4.50	2.00	1.00	0.25	2.24
			2	6.50	8.43	6.00	0.50	1.00	0.25	2.45
			3	7.50	8.99	6.00	2.00	1.00	0.25	2.61
			mean	7.00	8.46	5.50	1.50	1.00	0.25	2.44

B1	25	1	10.00	15.10	7.00	2.00	2.00	0.25	2.93
		2	10.00	16.49	10.00	2.50	2.00	0.25	3.41
		3	12.00	15.64	11.00	2.50	2.00	0.25	3.39
		mean	10.67	15.74	9.33	2.33	2.00	0.25	3.24
B1	42	1	14.25	24.29	21.00	6.00	10.00	0.50	5.63
		2	14.25	26.09	21.00	5.00	9.00	0.50	5.60
		3	14.25	28.79	21.00	5.00	10.00	0.50	6.00
		mean	14.25	26.39	21.00	5.33	9.67	0.50	5.72
B1	65	1	26.50	34.33	35.00	12.00	17.25	1.50	7.11
		2	26.50	37.78	35.00	12.50	17.25	2.00	8.99
		3	25.00	34.93	32.00	11.00	17.25	1.75	8.34
		mean	26.00	35.68	34.00	11.83	17.25	1.75	8.15
B1	95	1	45.00	58.47	60.00	23.50	25.00	4.00	13.50
		2	41.25	60.34	60.00	22.50	24.00	4.00	14.23
		3	45.00	60.34	60.00	22.50	26.00	4.50	13.02
		mean	43.75	59.72	60.00	22.83	25.00	4.17	13.58
B2	0	1	5.75	6.24	4.50	0.00	1.00	0.25	1.57
		2	5.75	6.49	3.50	0.50	1.00	0.25	1.85
		3	6.50	5.91	4.50	0.50	1.00	0.25	1.85
		mean	6.00	6.21	4.17	0.33	1.00	0.25	1.76
B2	5	1	7.00	7.27	6.00	0.50	2.00	0.25	2.58
		2	7.00	7.99	6.00	0.50	1.00	0.25	2.78
		3	12.50	7.40	6.00	0.50	1.00	0.25	2.50
		mean	8.83	7.55	6.00	0.50	1.00	0.25	2.61
B2	13	1	8.25	11.52	8.50	2.00	2.00	0.25	3.29
		2	9.50	10.90	8.50	2.50	2.00	0.25	3.52
		3	10.00	10.53	10.00	2.50	2.00	0.25	3.33
		mean	9.25	10.98	9.00	2.33	2.00	0.25	3.38
B2	25	1	14.25	16.01	14.00	4.00	3.00	0.25	4.39
		2	14.75	15.82	14.00	4.00	3.00	0.50	4.58
		3	13.00	15.15	16.00	4.00	4.00	0.50	4.70
		mean	14.00	15.66	14.67	4.00	3.33	0.50	4.55

B2	42	1	16.50	26.09	26.00	6.50	5.50	1.00	6.41
		2	18.00	26.76	28.00	6.50	5.50	1.00	6.85
		3	27.50	25.49	32.00	8.50	5.50	1.00	7.99
		mean	20.67	26.11	28.67	7.17	5.50	1.00	7.05
B2	65	1	16.50	22.19	38.00	12.00	10.00	2.50	9.47
		2	27.50	34.93	38.00	12.50	9.00	2.25	9.76
		3	28.50	35.98	38.00	12.50	10.00	2.25	9.68
		mean	24.17	31.03	38.00	12.33	9.67	2.33	9.64
B2	95	1	41.25	57.57	64.00	24.50	16.00	5.50	13.88
		2	50.00	59.97	64.00	28.00	16.00	5.75	14.19
		3	47.50	57.57	64.00	26.00	15.00	5.50	14.44
		mean	46.25	58.37	64.00	26.17	15.67	5.58	14.17
B3	0	1	2.75	2.14	1.00	0.00	0.50	0.00	0.93
		2	2.75	2.39	2.00	0.00	0.50	0.00	0.97
		3	2.75	2.50	1.00	0.00	0.50	0.00	1.10
		mean	2.75	2.35	1.33	0.00	0.50	0.00	I.00
B3	5	1	4.50	2.85	2.00	0.50	0.50	0.00	1.36
		2	4.50	3.15	3.50	0.50	1.00	0.00	1.40
		3	4.50	2.86	2.00	0.50	1.00	0.00	1.38
		mean	4.50	2.96	2.50	0.50	0.83	0.00	1.38
B3	13	1	4.50	4.91	4.50	0.50	2.00	0.00	1.68
		2	6.50	5.15	4.50	2.00	1.00	0.00	1.78
		3	7.00	4.81	6.00	2.00	2.00	0.00	1.72
		mean	6.00	4.95	5.00	1.50	1.67	0.00	1.72
B3	25	1	12.50	7.54	10.00	2.50	2.25	0.25	2.32
		2	12.50	8.09	8.50	2.50	2.25	0.25	2.21
		3	12.50	7.55	10.00	2.50	2.25	0.25	2.42
		mean	12.50	7.72	9.50	2.50	2.25	0.25	2.32
B3	42	1	16.00	14.39	17.50	4.50	4.00	0.25	2.87
		2	14.75	14.99	16.00	4.50	4.00	0.50	2.87
		3	13.00	14.77	17.50	4.50	4.00	0.50	2.97
		mean	14.58	14.72	17.00	4.50	4.00	0.42	2.90

B3	65	1	25.00	28.79	32.00	12.00	6.25	1.00	4.90
		2	27.50	30.58	35.00	12.00	6.25	1.25	4.83
		3	25.00	28.79	32.00	10.00	6.25	1.00	4.83
		mean	25.83	29.39	33.00	11.33	6.25	1.08	4.85
B3	95	1	33.00	43.78	48.00	18.00	11.25	2.50	5.36
		2	34.00	42.73	52.00	16.50	11.25	2.50	5.73
		3	31.00	43.93	52.00	16.50	12.25	2.50	5.98
		mean	32.67	43.48	50.67	17.00	11.58	2.50	5.69
B4	0	1	4.50	2.53	6.00	0.50	1.00	0.00	0.84
		2	3.25	2.31	4.50	2.00	1.00	0.00	1.15
		3	4.00	2.34	4.50	2.00	1.00	0.00	1.13
		mean	3.92	2.39	5.00	1.50	1.00	0.00	1.04
B4	5	1	4.50	2.78	6.00	2.00	2.00	0.00	1.22
		2	5.25	2.95	6.00	2.00	2.00	0.00	1.15
		3	5.25	3.56	6.00	2.00	2.00	0.00	1.20
		mean	5.00	3.10	6.00	2.00	2.00	0.00	1.19
B4	13	1	5.75	5.76	7.00	2.50	2.25	0.00	1.29
		2	6.50	5.36	7.00	2.50	2.25	0.00	1.43
		3	7.00	4.83	8.50	2.50	3.00	0.00	1.31
		mean	6.42	5.32	7.50	2.50	2.50	0.00	1.35
B4	25	1	13.00	10.30	11.00	4.00	3.00	0.00	1.47
		2	7.50	8.35	14.00	4.00	4.25	0.00	1.42
		3	13.00	8.93	11.00	4.00	4.00	0.00	1.36
		mean	11.17	9.19	12.00	4.00	3.75	0.00	1.42
B4	42	1	11.50	14.99	17.50	4.50	5.50	0.00	1.64
		2	12.00	17.17	17.50	4.50	5.50	0.00	1.72
		3	12.50	16.19	17.50	4.50	4.25	0.00	1.60
		mean	12.00	16.12	17.50	4.50	5.08	0.00	1.65
B4	65	1	24.00	16.19	30.00	6.00	8.00	0.25	2.37
		2	23.00	15.59	28.00	6.50	8.00	0.25	2.45
		3	24.00	14.54	26.00	6.00	8.00	0.25	2.71
		mean	23.67	15.44	28.00	6.17	8.00	0.25	2.50

	B4	95	1	26.00	22.94	35.00	10.00	11.25	0.50	3.00
			2	25.00	21.59	35.00	12.00	11.25	0.50	2.85
			3	27.50	23.39	39.00	10.50	12.25	0.50	2.91
			mean	26.17	22.64	36.33	10.83	11.58	0.50	2.92
Ficksburg	F1	0	1	2.00	1.27	2.00	2.00	1.00	0.00	0.48
			2	2.75	1.40	2.00	2.50	1.00	0.00	1.14
			3	3.25	1.15	2.00	2.50	1.00	0.00	1.06
			mean	2.67	1.27	2.00	2.33	1.00	0.00	0.88
	F1	5	1	3.25	2.78	4.50	2.50	1.00	0.00	1.15
			2	3.25	2.72	4.50	2.50	2.00	0.00	1.00
			3	3.25	2.16	4.50	2.50	2.00	0.00	1.42
			mean	3.25	2.55	4.50	2.50	1.67	0.00	1.18
	F1	13	1	6.50	5.54	7.50	4.00	2.25	0.00	1.40
			2	5.75	5.24	8.50	4.00	3.00	0.25	1.54
			3	7.00	6.00	8.50	2.50	3.00	0.25	1.20
			mean	6.42	5.59	8.17	3.50	2.75	0.17	1.38
	F1	25	1	10.00	8.27	14.00	4.50	4.25	0.25	2.13
			2	10.00	9.98	14.00	6.00	4.25	0.25	2.10
			3	10.00	10.66	14.00	4.50	4.00	0.25	2.21
			mean	10.00	9.64	14.00	5.00	4.17	0.25	2.14
	F1	42	1	12.50	20.69	25.50	8.00	8.00	0.25	2.74
			2	14.25	21.29	28.00	8.50	6.00	0.50	2.34
			3	13.75	20.99	30.00	10.00	8.00	0.50	2.91
			mean	13.50	20.99	27.83	8.83	7.33	0.42	2.64
	F1	65	1	45.00	50.97	51.00	18.50	12.25	1.00	5.26
			2	47.50	46.18	47.00	6.50	11.25	1.00	5.39
			3	32.50	48.73	47.00	20.00	12.25	1.00	6.28
			mean	41.67	48.63	48.33	15.00	11.92	1.00	5.67
	F1	95	1	52.50	70.76	60.00	8.80	17.25	2.00	8.86
			2	56.50	69.57	60.00	38.00	17.25	2.00	8.28
			3	41.25	66.57	66.00	38.00	17.25	2.25	9.65
			mean	50.08	68.97	62.00	26.60	17.25	2.08	8.90

F2	0	1	3.25	2.84	7.00	2.00	4.00	0.25	1.80
		2	6.50	2.84	7.00	2.50	4.25	0.25	1.91
		3	7.00	2.53	8.50	2.50	4.25	0.25	1.96
		mean	5.58	2.73	7.50	2.33	4.17	0.25	1.89
F2	5	1	9.00	4.46	10.00	2.50	5.50	0.25	3.18
		2	9.50	4.35	10.00	2.50	4.25	0.25	3.04
		3	10.00	4.23	10.00	2.50	5.50	0.25	3.13
		mean	9.50	4.35	10.00	2.50	5.08	0.25	3.12
F2	13	1	10.50	6.45	14.00	6.00	6.25	0.25	2.15
		2	7.00	7.26	12.50	4.50	6.25	0.25	4.04
		3	12.00	7.34	14.00	4.50	7.00	0.25	4.05
		mean	9.83	7.02	13.50	5.00	6.50	0.25	3.39
F2	25	1	14.25	12.73	21.00	6.50	7.25	0.50	4.79
		2	13.75	12.76	21.00	6.50	9.00	0.50	4.76
		3	10.75	13.52	21.00	6.50	8.00	0.50	4.84
		mean	12.92	13.00	21.00	6.50	8.08	0.50	4.80
F2	42	1	14.75	20.99	33.00	12.00	11.25	0.50	5.61
		2	15.50	22.56	33.00	10.50	11.25	0.75	4.92
		3	14.75	37.78	33.00	12.50	12.25	0.75	6.33
		mean	15.00	27.11	33.00	11.67	11.58	0.67	5.58
F2	65	1	32.50	40.78	47.00	22.00	13.25	1.50	6.24
		2	45.00	42.73	47.00	22.00	17.00	1.50	6.65
		3	35.00	42.73	47.00	22.50	15.00	1.50	6.38
		mean	37.50	42.08	47.00	22.17	15.08	1.50	6.42
F2	95	1	71.30	61.47	60.00	46.00	20.00	2.50	10.03
		2	66.25	59.97	60.00	52.00	20.00	2.50	8.88
		3	47.50	61.47	64.00	49.00	20.00	2.50	7.93
		mean	61.68	60.97	61.33	49.00	20.00	2.50	8.89
F3	0	1	4.00	1.29	3.50	0.00	2.00	0.00	1.76
		2	4.00	0.72	3.50	0.00	2.00	0.00	1.94
		3	2.75	1.92	3.50	0.00	2.00	0.00	1.85
		mean	3.58	1.31	3.50	0.00	2.00	0.00	1.85

F3	5	1	5.25	2.34	4.50	0.50	4.00	0.00	2.97
		2	5.75	2.30	6.00	0.50	3.00	0.00	2.20
		3	6.50	2.28	6.00	0.50	3.00	0.00	2.42
		mean	5.88	2.31	5.50	0.50	3.33	0.00	2.52
F3	13	1	9.00	3.56	7.00	2.00	5.50	0.25	7.50
		2	9.00	4.10	7.00	2.00	4.25	0.25	3.01
		3	9.00	4.37	7.00	2.00	4.25	0.25	3.97
		mean	9.00	4.01	7.00	2.00	4.67	0.25	4.18
F3	25	1	11.25	8.86	11.00	2.50	6.25	0.25	4.66
		2	12.00	7.46	12.00	2.50	6.25	0.25	4.97
		3	11.25	8.35	12.00	2.50	6.25	0.25	4.22
		mean	11.50	8.22	11.67	2.50	6.25	0.25	4.60
F3	42	1	12.24	16.49	19.50	5.00	8.00	0.50	7.77
		2	16.50	16.27	21.00	5.00	8.00	0.50	6.46
		3	15.00	17.17	21.00	5.00	9.00	0.50	7.15
		mean	14.58	16.64	20.50	5.00	8.33	0.50	7.13
F3	65	1	24.00	28.26	32.00	10.00	12.25	1.00	17.01
		2	24.00	28.79	32.00	10.00	12.25	1.00	16.11
		3	24.00	26.46	30.00	9.00	11.25	0.75	16.31
		mean	24.00	27.84	31.33	9.67	11.92	0.92	16.47
F3	95	1	30.00	41.38	47.00	18.00	16.00	2.00	21.72
		2	30.00	41.38	47.00	20.00	17.00	2.00	20.32
		3	30.00	39.73	47.00	20.00	18.25	2.00	17.46
		mean	30.00	40.83	47.00	19.33	17.08	2.00	19.69
F4	0	1	4.50	1.48	25.50	2.0	5.50	0.25	5.83
		2	4.00	1.67	25.50	2.0	6.25	0.25	5.58
		3	5.75	1.46	25.50	2.0	6.25	0.25	5.54
		mean	4.75	1.53	25.50	2.0	6.00	0.25	5.65
F4	5	1	5.75	2.26	28.00	2.0	7.25	0.25	6.97
		2	7.50	2.39	28.00	2.5	8.00	0.25	7.40
		3	5.75	2.32	30.00	2.5	7.25	0.25	6.84
		mean	6.33	2.32	28.67	2.3	7.50	0.25	7.06

F4	13	1	9.00	2.95	30.00	2.50	8.00	0.25	6.74
		2	7.50	3.18	30.00	2.50	8.00	0.25	8.21
		3	7.50	3.14	32.00	2.50	8.00	0.50	7.10
		Mean	8.00	3.09	30.67	2.50	8.00	0.33	7.30
F4	25	1	11.25	5.04	35.00	5.00	9.00	0.75	8.66
		2	13.75	5.21	35.00	5.00	9.00	0.75	9.05
		3	12.50	5.12	35.00	5.00	9.00	0.75	8.57
		mean	12.50	5.12	35.00	5.00	9.00	0.75	8.75
F4	42	1	13.25	10.19	41.00	6.00	12.25	1.00	10.15
		2	14.25	9.90	44.00	6.50	11.25	1.50	10.33
		3	13.25	10.19	44.00	6.50	12.25	1.50	9.55
		mean	13.58	10.09	43.00	6.30	11.92	1.33	10.00
F4	65	1	25.00	17.09	64.00	10.50	16.00	2.50	10.80
		2	26.50	16.49	64.00	12.00	17.00	2.50	13.57
		3	25.00	15.59	64.00	10.50	16.00	2.50	12.08
		mean	25.50	16.39	64.00	11.00	16.33	2.50	12.11
F4	95	1	27.50	25.49	70.00	18.00	21.00	4.00	15.33
		2	27.50	23.69	70.00	18.50	22.25	4.50	16.86
		3	27.50	25.49	70.00	22.00	25.00	5.13	18.18
		mean	27.50	24.89	70.00	19.50	22.75	4.50	16.78