Factors Affecting Phosphorus Requirements for the Soils of South African Sugar Industry

by

Lwazi Z. Poswa

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School of Agricultural, Earth and Environmental Sciences

University of KwaZulu-Natal

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Professor P. Muchaonyerwa (Supervisor)

Signed:………………………………………...Date:…………………………………

Dr N. Miles (Co-supervisor)

Signed:………………………………………...Date:…………………………………

Dr A. Manson (Co-supervisor)

ABSTRACT

Management of phosphorus (P) for crop production requires the following considerations to be taken into account: (1) in their undisturbed state, soils on the eastern seaboard of South Africa are severely deficient in phosphorus; (2) P availability to crops is reduced through chemical immobilization (fixation); (3) P is the most costly of the macronutrients; and (4) 'overloading' of soil with P has environmental risks. In this study, the objective was to identify the primary factors controlling P solubility in industry soils.

Of crucial importance in extending advice on P fertilisation is knowledge of the amount of P required under field conditions for unit increase in P soil test. The aims of this study were to (a) to determine (i) P sorption characteristics and (ii) phosphorus requirement factor (PRF) values of representative soils of the sugar industry, and (b) to evaluate the use of mid-infrared spectroscopy for the routine prediction of PRF values. Laboratory incubations were used for quantifying the fertiliser P requirement factors (PRFs) of 39 soil (0 – 20 cm) samples taken from fields of the South African sugar industry. Soils from each site were treated with three levels of P and taken through wetting and drying cycles over a six-week period. Three P-test methods (Truog, Mehlich-3 and Resin) were included, and the reciprocals of isotherm slopes used to establish PRFs of the soils. The strong correlation between PRF and Al_{ox} which is routinely measured by mid infrared spectroscopy (MIR), was used to calibrate the MIR to estimate PRF.

Soil properties known to influence P retention varied widely with pH (H_2O) 4.05 - 7.55, 7 to 70% clay (mean = 27%), and 0.44 to 9.72% organic carbon (OC) (mean = 2.27). Soil P desorption index, P sorption index and isotherm slope for 0.2 mg P L^{-1} ranged from 0.05 - 1.54 (mean = 056), 2.64 - 403.93 L/kg soil (mean = 48.56) and 23.88 - 919.55 mg P L^{-1} soil (mean = 222.69), respectively. The ranges (and mean) of PRF values for the Truog, Mehlich-3 and Resin extractants were2.26-22.52 (5.84), 1.89-27.17 (7.13) and 4.39-39.68 (11.31) kg P ha^{-1} per unit soil test, respectively.Soil properties known to affect P-sorption were correlated with PRF values for all three extractants for (i) combined data for all soil systems and (ii) for each soil system (more detailed correlations).All soil systems, except the Hinterland system, showed strong correlation (r^2 = 0.42 to 0.98) (combined correlation) between PRF and clay content, for the three extractants. The coefficients of determination (r^2) showed a strong positive relationship relating PRF with PSI (0.71 to 0.87), OC (0.67 to 0.87), Al_{ox}(0.69 to 0.92), Fe_{ox} (0.75 to 0.93) and isotherm slope at 0.2mg P/L (0.66 to 0.87), while an inverse relationship was found between sample density (volume weight) (0.69 to 0.78)and PDI (0.65 to 0.70).

The use of MIR to predict PRF was successfully calibrated, using the strong correlation of Alox with PRF.The findings of this study confirm that soils of the sugar industry vary widely in P sorption characteristics and PRF values and imply that this parameter (i.e., PRF) can be reliably predicted using MIR spectroscopy, which improves the efficiency of routine P fertiliser recommendations.

ACKNOWLEDGEMENTS

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LIST OF ABBREVIATIONS AND ACRONYMS

Al_{ox} oxalate extractable Al

ECEC   effective cation exchange capacity

EPR   external phosphate requirement

Fe_{ox} oxalate extractable Fe

FTIR   Fourier transform infrared

MIR   mid infrared reflectance spectroscopy

Pi   inorganic P in soil

Po   organic P in soil

PCA   principal component analysis

PDI   phosphorus desorption index

PLS   partial least square

PR   Phosphate rock

PRF   phosphorus requirement factor

PRF_{Truog} P requirement factors extracted by the Truog extractant from the incubated soils

$PRF_{Mehlich}$ P requirement factors extracted by the Mehlich-3 extractant from the incubated soils

PRF_{Resin} P requirement factors extracted by exchange Resins from the incubated soils

PSI   phosphorus sorption index

RMSEEc   root mean square error of estimation for MIR calibration

RMSECV   root mean square error of cross validation for MIR

RPDc   residual prediction deviation for MIR data calibration

RPDv   residual prediction deviation for MIR data validation

SOC   soil organic carbon

CHAPTER 1: General Introduction

Fertiliser management for sugarcane production is characterised by large inputs of nitrogen (N), phosphorus (P) and potassium (K) as commercial inorganic fertilisers or as organic manures, which may comprise of up to 30% of farm production costs (Anon, 1998; Singles, 2015). Phosphorus is the second major macronutrient for sugarcane production as it is involved in the transformation of solar energy into chemical energy during photosynthesis and is essential for the development of a healthy root system (Foth, 1984; Marschner, 1995; Schachtman *et al*., 1998; Meyer *et al*., 2011). It is therefore an integral part of many soil fertility programmes and hence applied to agricultural land as either manure or inorganic fertiliser to meet crop requirements.

However, managing P supplies to the sugarcane crop present particular challenges for agronomists, since not only is P the most expensive of the macro-nutrients per unit price, but wide variations in soil properties greatly complicate the process of accurately estimating fertiliser P requirements (Miles *et al.*, 2013). In acid soils, the predominance of oxides of iron and aluminium (both crystalline and amorphous) strongly reduce the solubility of soil inorganic P by fixation on positively charged surfaces and by forming insoluble Al and Fe precipitates (Warren, 1994; Hinsinger, 2001; Gichangi *et al*., 2007; Meyer *et al*., 2011). In alkaline soils, phosphorus readily reacts with calcium to form sparingly soluble calcium phosphates. These reactions may result in a very high proportion of applied fertiliser P becoming chemically bound and only a small proportion of soil P is present in the soil solution and available for plant uptake (Johnston *et al*., 1991; Gichangi *et al*., 2008).

Studies have also shown that, at the same pH, soils with higher clay content have higher P fixing capacity compared with sandier soils (Johnson *et al*, 1991; Warren, 1994; Bainbridge *et al*., 1995) and that organic matter (humus-aluminium complexes) does contribute to P availability in soil (Haynes, 1984; Owusu-Bennoah and Acquaye, 1989). Owusu-Bennoah and Acquaye (1989) studied the phosphate sorption characteristics of some Ghanaian soils and found that sorption maxima were highly correlated with the soil properties in the order: $Al_2O_3 >$ clay content $>$ free $Fe_2O_3 >$ organic carbon. Similarly, a study conducted to evaluate the phosphate fixing capacity of soils by the isotopic exchange techniques in north-east France found that there was a significant correlation between amount of phosphorus fixed, pH, exchangeable cations, clay content and soluble phosphate (Morel *et al*., 1989). High risks of P deficiency in the sugarcane industry are expected on highly weathered and leached soils,

particularly the red Oxisols (or Ferralsols) that are common throughout the tropical and subtropical cane producing areas of South Africa (Meyer, 1974; Johnston *et al.*, 1991).

Soil tests for plant available P are used worldwide to determine the current P status of soils so as to estimate fertiliser P requirements for specific yield goals. The normal approach for managing soil P is to (i) determine the actual soil 'available' P level using a specific soil test extractant, and (ii) compute the soil P deficit from the difference between a known critical level applicable to that particular crop (established through field trial calibration studies) against the actual available P level obtained from soil P-test. This deficit is converted into a mass of nutrient required per unit area by multiplying it by a conversion factor reflecting soil properties responsible for P sorption as well as the depth of incorporation of the fertiliser (i.e., the P requirement factor (PRF)). Thus:

Field P requirement (kg/ha) = (optimum soil P – measured soil P) x PRF   (*eqn. 1.1*)

The PRF is, therefore, defined as a soil specific factor which represents the amount of P required per ha for unit increase in P level for a particular soil test and allows for the effect of P fixation on the recovery of added P (Johnston *et al.*, 1991; Henry and Smith, 2004). For a given soil P-test, PRF has been shown to vary widely across different soils due to differences in the ability of different soils to sorb P (Henry and Smith, 2004). Determination of the PRF for a particular soil is laborious as it involves (i) a six weeks incubation experiment (with alternated cycles of wetting and drying designed to stimulate the fate of added P under field conditions) of soils with additional P in incremental rates to induce P fixation, followed by (ii) the extraction of P (using approved extraction methods) from the soil solution, and (iii) plotting the amount of P recovered in the extraction solution versus added P (Johnston *et al.*, 1991; Henry and Smith, 2004). This relationship generally gives a linear regression function, the inverse of the slope of which is the PRF for the particular soil.

For a given soil P-test, PRF has been shown to be a characteristic that varies widely across different soils. Johnston *et al.* (1991), conducted studies of PRF values over a wide range of soils of varying P fixing capacity representative of the KwaZulu-Natal Province. Using three different extractants (i.e., Truog-P (Truog, 1930), Bray-1 (Bray & Kurtz, 1945) and Ambic-2 (Van der Merwe, *et al.*, 1984)), they found that the range in PRF values varied amongst soils and extraction methods; 2.3-30.3, 2.0-17.7 and 2.5-37.9 kg/ha per mg P L^{-1} soil, for there three extractants, respectively. They also reported that the level of P sorption was strongly related to clay content and the presence of 2:1 mineral clays.

The current multiple point approach and incubations to measure PRF is too tedious to for routine laboratory analysis, therefore, there is a need for a quicker, reliable and cost-effective approach to measure the P requirement factors of the soils of the sugar industry. For approach to be successful, a good relationship must first be shown to exist between PRF values and selected soil properties or P sorption characteristics, which are already measured routinely or which can be readily added to the range of routine tests conducted by soil testing laboratories (White, 1980; Henry and Smith, 2004). Due to advances in technology, spectroscopic techniques provide a good alternative that may be used to enhance or replace conventional methods of soil analysis, as they overcome some of their limitations (Reeves *et al.*, 2001; Jahn *et al.*, 2006; Linker, 2011).

Compared with conventional methods, Near Infrared (NIR) and Mid-Infrared (MIR) spectroscopy techniques are time- and cost-efficient, non-destructive, and do not require any reagents for analysis (Xie *et al.*, 2011). Numerous studies have demonstrated the effectiveness of MIR in performing quantitative analysis of soil parameters (e.g. Janik *et al*, 1995: Janik and Skjemstad, 1995; McCarty *et al.*, 2002: Forouzangohar *et al.*, 2008). In South Africa, MIR spectroscopy is used routinely by the Fertiliser Advisory Services (FAS) of SASRI and Cedara to predict ammonium-oxalate extractable Al and Fe, clay content, organic carbon and sample density among other soil properties. The feasibility of MIR to predict PRF in soil should be investigated due to strong correlations found between P sorption and ammonium-oxalate extractable Al (Al_{ox}), and satisfactory prediction of Al_{ox} by MIR.

The objectives of this study were to (a) determine (i) P sorption characteristics and (ii) PRF values of representative soils of the sugar industry, and (b) evaluate the use of mid-infrared spectroscopy for the routine prediction of PRF values.

CHAPTER 2: LITERATURE REVIEW

2.1. Introduction

Phosphorus (P) is a naturally occurring, essential macronutrient required by plants for photosynthesis, respiration, seed production, root growth and other critical plant functions (Foth, 1984; Gichangi *et al*., 2008). Adequate P results in improved crop quality, greater stalk strength, increased root growth, and earlier crop maturity (Anon, 1998; Brady and Weil, 2008; Meyer *et al*., 2011). Thus, P deficiency can impede numerous developmental processes, resulting in reduced plant growth, delayed maturity and a reduction in the quality and quantity of crop yield (Gichangi *et al*., 2008).

Phosphorus is unique among anions in that it has low mobility and the least available nutrient to plants due to its strong reactivity with both the solid and solution phases of the soil. Thus, P can be a major limiting factor for plant growth since plants can only extract P that is in the soil solution. As a consequence of reduced bioavailability of P in soils, external supplies through chemical P fertilizers and animal manures have been proved necessary to maintain adequate supplies of P for crop growth. Whilst the benefits of adding P to the soil are clear, 'over-applications' can have severe impacts on water quality of the catchments receiving P lost from the agricultural soil through runoff and/or erosion.

Important components of the P cycle in sugarcane production include uptake by sugarcane, recycling through the breakdown and biological turnover of trash and the return of mineralized P, solubilisation of mineral phosphates of calcium (Ca-P), aluminium (Al-P) and iron (Fe-P) by microorganisms, fixation of soluble forms of P through precipitation by soluble forms of Al, Fe or Ca and adsorption by sesquioxic clay colloids (Meyer *et al*., 2011). In this review the focus will be on forms and concentrations of P in soil and the factors controlling its retention and release to the soil solution. Phosphorus status of South African soils and the methods used to assess its availability will be reviewed later.

2.2. Phosphorus concentrations and forms in soil

Soils in their undisturbed state are severely deficient in phosphorus and most cropping systems require supplemental phosphorus to maximize their yield potential. Low availability of phosphorus (P) is the most widespread and economically important nutrient deficiency for agricultural production in most South African soils, particularly in the high-rainfall eastern seaboard of the country. The total soil phosphorus content usually ranges from 50 to 3000 mg

kg^{-1} (existing in organic and inorganic forms), however, only a small proportion of the total P is available for plant uptake due to chemical immobilization (fixation/sorption) when P is added to the soil solution (Harrison, 1987; Troeh and Thompson, 2005). Phosphorus in the soil solution of most agricultural soils ranges from <0.01 to 1 ppm (Brady and Weil, 2002), however, an equilibrium soil solution P concentration of 0.2 mg P L^{-1} has been shown to be a threshold for many crops, beyond which no response to added P is observed (Gichangi *et al.*, 2008). Studies have shown that this value may vary depending on plant species and agronomic and nutritional factors (Raven and Hossner, 1994). In the South African sugarcane industry, for example, Meyer (1980b) found that the minimum concentration of P required in soil solution for a healthy sugarcane plant was 0.10 mg P L^{-1} whilst Henry and Smith (2006) showed that 0.11 mg P L^{-1} was suitable for low to moderately P fixing soils of the tobacco growing areas of KwaZulu-Natal.

Soil solution is the key to plant nutrition since plants can only absorb phosphorus that is dissolved in the soil water. Phosphorus almost always occurs as the oxyanion (PO_4^{3-}), however, the forms of dissolved phosphorus in the soil solution depend on soil pH conditions. At circumneutral soil pH (6.5-7.5), both HPO_4^{2-} and $H_2PO_4^-$ are important anions, with HPO_4^{2-} being more prevalent in slightly alkaline conditions and H_2PO^{4-} dominating in slightly acidic environment (Fig 1.)
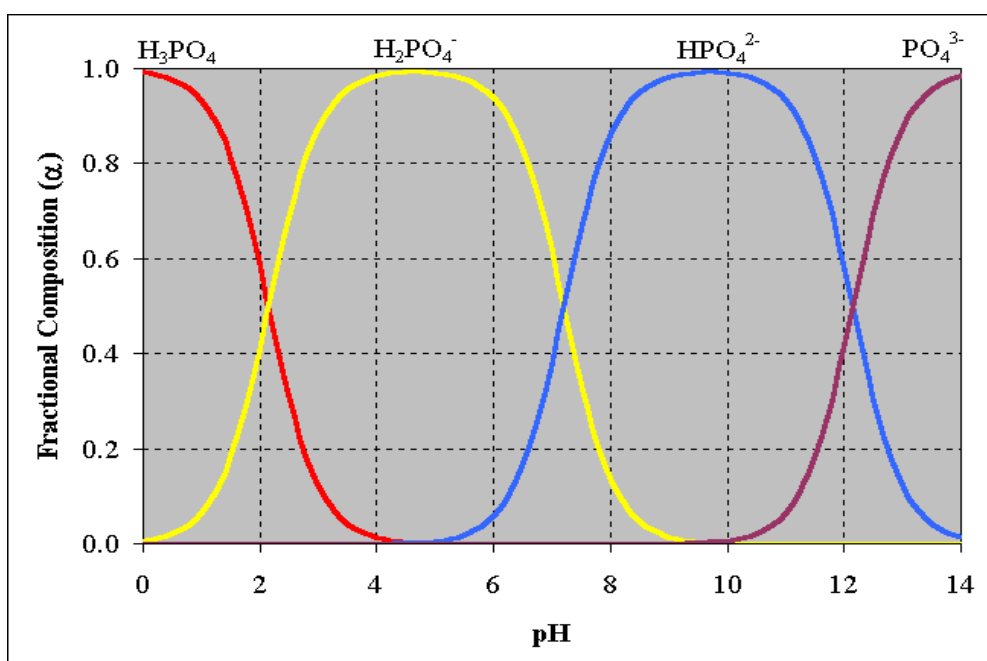
Figure 2.1: Speciation of orthophosphate as a function of soil pH.

Plant roots absorb inorganic forms of P as either monovalent ($H_2PO_4^-$) ions or divalent (HPO_4^{2-}) ions. However, these ions can be adsorbed on clay minerals or precipitate forming complex minerals with a wide variety of elements depending on soil pH. In acidic soils (pH <5), P react with aluminium (Al) and iron (Fe) to forminsoluble compounds whereas calcium binds to P at high pH (alkaline soils) and reduce its availability to the plants. These reactions will be discussed in the following sections.

2.3. Soil P reserves and fertility inputs

The most commonly used P sources in crop production are either of inorganic or of organic nature. These inorganic and organic P sources continuously undergo transformations in the soil with a consequent effect on P availability to the plants. The ultimate source of phosphorus (P) to the biosphere is the weathering of residual minerals such as apatite and from P additions in the form of commercial fertilizers, plant residues, agricultural wastes, and/or biosolids. Weathering of geologic materials (igneous, sedimentary and metamorphic rocks) is the primary source of phosphorus in the agricultural systems, however, the amount of phosphorus released is a small fraction of that required for optimum crop production. Anthropogenic processes however, play an important role in improving soil P fertility and crop production through supplementary applications of water-soluble-chemical fertilisers, animal manures and/or composts. Decomposing organic residues also play a vital role in the addition of P to the soil system by releasing P through mineralisation processes, however, this process is generally slow to meet the current crop demands of P. The availability of P to the soil solution is therefore, dependant on the source of P used and the ability of the soil to quickly replenish P into the soil solution (to be discussed later) as the plants remove it. The next section will detail different sources of P in agricultural systems.

2.3.1.   Mineral P sources

Phosphate mineral deposits are widespread throughout the world. Phosphate rocks have widely differing mineralogical, chemical and textural characteristics depending upon their origin and the weathering conditions that have prevailed (Stewart *et al.*, 2005). Several common soil phosphate minerals controlling P in soils and sediments include apatite, hydroxyapatite, fluorapatite, octocalcium phosphate, strengite, vivianite, variscite, and wavellite (Reddy *et al*., 1999; Brady and Weil, 2002).

Mineral soils contain 50 to 70% of their total P in inorganic forms, mostly as compounds of calcium (Ca), aluminium (Al) and iron (Fe), depending on the soil pH and the stage of

weathering (Pierzynski *et al.*, 2005). In less or moderately weathered calcareous soil different forms of apatite (Ca-PO_4) minerals are found whereas in highly weathered acidic soils variscite (Al-PO_4) and strengite (Fe-PO_4) are the most common phosphate minerals because Ca and other basic minerals get leached, resulting in Fe and Al dissolving as the pH decreases (Holford, 1997; Pierzynski *et al.,* 2005; Hariprasad & Niranjana, 2008) (Table 2.1).

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

<u>*Acid soils*</u>	<u>**Chemical composition**</u>
Variscite	$AlPO_4.2H_2O$
Strengite	$FePO_4.2H_2O$
<u>*Neutral and calcareous soils*</u>	
Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4.2H_2O$
Dicalcium phosphate (DCP)	$CaHPO_4$
Octacalcium phosphate (OCP)	$Ca_4H(PO_4)_3.2.5H_2O$
β-tricalcium phosphate (βTCP)	$Ca_3(PO_4)_2$
Hydroxyapatite	$Ca_5(PO_4)_3OH$
Fluorapatite	$Ca_5(PO_4)_3F$

In neutral and calcareous soils, calcium phosphates are present as films or discrete particles while inorganic P is either precipitated as iron and aluminium phosphate secondary minerals and/or is adsorbed to surfaces of Fe/Al oxides and clay or silt surfaces in acid soils (Sanchez, 1976; Havlin *et al.*, 2005a). Heck (1934) as cited by Meyer *et al*. (2011) has divided mineral soil phosphorus reserves into three fractions according to their availability to the plant:

(i) Readily available - water soluble $(H_2PO_4)^-$ and $(HPO_4)^{2-}$ anions from $Ca(H_2PO_4)^-_2.H_2O$;

(ii) Slowly available ($AlPO_4$); and

(iii) Very slowly available reserves $Ca_3(PO_4)_2$ and $FePO_4$

2.3.2.   Chemical fertiliser P sources

Native phosphorus contents in soils are generally low, however, most agricultural systems make use of commercially manufactured P fertilisers to raise soil P levels to desired concentrations for optimum crop production. Almost all P fertilizers are produced by mining phosphate rock (PR) and subjecting it to physical and chemical processes. Depending upon their origin and the weathering conditions that have prevailed, phosphate rocks have widely differing mineralogical, chemical and textural characteristics (Stewart *et al.*, 2005). South Africa obtains most of its PR from a large deposit near Phalaborwa which is of volcanic origin and consists of fairly low grade rock.

The South African sugarcane industry uses about 9 500 tons P annually at R30 per unit P currently, which makes it the most expensive major nutrient (Anon, 1998). The most commonly used inorganic P sources include single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP), diammonium phosphate (DAP), potassium phosphate (MKP) and compound fertilizer NPK such as 2.3.2 or 2.3.4 (10-13% P) (Troeh & Thompson, 2005; Meyer *et al.*, 2011) (Table 2.2). Inorganic P fertilisers are often applied in the furrow at planting to ensure healthy root development for newly established cane. The choice of P-carrier will depend on the cost of per unit P of the carrier, and also on the purposes of fertilisation. For this reason, most sugar producing areas favour the use of ammonium phosphates (MAP and DAP) or blends, since they simultaneously supply P with N and/or K and the price per unit of P is much lower than that of most other P fertilisers (Meyer *et al*., 2011). Furthermore, the benefits of using ammonium phosphate fertilisers in the furrow to supply N is that it enables quicker canopy cover and better weed control and also from the fact that the presence of ammonium (NH_4^+) ions has a stimulating effect on P absorption by roots (Havlin *et al.*, 2005a; Meyer *et al*., 2011). However, care should be exercised for long-term use of ammonium phosphates and ammoniated superphosphates under intense agriculture due to the acidification effects as a result of NH_4^+ ions they contain (Sharpley, 2001).

Most of inorganic P fertilisers are water soluble, and are chosen for situations where intensive crop based agriculture is taking place, and a rapid growing cycle is required and harvest is soon followed by resowing (Meyer *et al*., 2011). A high percentage of water solubility is vital for short-season, fast-growing crops, crops with a restricted root system, crops receiving a starter fertilizer application, and crops grown in a low phosphorus soil where less than optimum rates of phosphorus are applied (Sharpley, 2001). However, studies have shown that

when soluble P fertiliser is added to the soil solution it is rapidly converted to less soluble forms, depending on soil pH, soil water content, and soil temperature (Ratchaneeporn, 2009). As a result, it has been reported that plants generally utilize less than 20% of applied P during the first year of application mainly due to reactions in soil that form 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 (Haygarth and Jarvis, 1999; Hiradate *et al.*, 2007).

Table 2.2: Commonly used inorganic phosphate fertilisers in the sugarcane industry (van Antwerpen *et al.*, 2013)

P source	Chemical Composition	P (%)	Other nutrients
Single superphosphate	$Ca(H_2PO_4)_6.XCaCO_3$	7-10	Ca, S (8-10%)
Triple superphosphate	$Ca(H_2PO_4)_2$	19-23	Ca
Monoammonium phosphate (MAP)	$NH_4H_2PO_4$	22	N (12%)
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	20	N (21%)
Ammonium polyphosphate (liquids)	$(NH_4)_3HP_2O_7$	15	N (11%)
2:3:2 (22)	–	9.4	N (6.3%), K (6.3%)
2:3:4 (30)	–	10.0	N (6.7%), K (13.3%)
2:3:4 (40)	–	13.3	N (8.9%), K (17.8%)

Phosphate rocks (PRs) can be used either as raw materials in the industrial manufacture of water soluble phosphate (WSP) fertilizers or as P sources for direct application in agriculture. When fertilising for permanent pastures and/or soils where P levels are already high, a slow P releasing P source such as phosphate rock can be applied. Research has shown that finely ground sedimentary phosphate rocks are suitable for direct application because they consist of fairly open, loosely consolidated aggregates of microcrystals with a relatively large specific surface area (Zapata and Roy, 2004; Havlin *et al.*, 2005). Direct application of phosphate rock (PR) has been shown to be a valuable source of nutrients depending on the rock type, soil properties, climatic conditions, crops/cropping systems, and nutrient management practices (Rajan and Upsdell, 1981).

However, the rate at which the PRs dissolve is very slow, and modification of PR by appropriate chemical, physical, and biological technologies has also has been suggested effective direct application of PR (Rajan and Chien, 2001). Meyer *et al*. (2011) stated that PRs generally work well when applied as a broadcast treatment to acid soils and has good residual P effects that often last into the fourth and fifth ratoon crops, but should initially be supplemented with an in-furrow application of about 30 kg/ha P as MAP. Another common agricultural practical means of speeding this up is by the addition of organic matter (Brady, 1974). It has been proposed that upon decomposition, the organic matter produces organic acids which help dissolve the insoluble rock phosphate (Troeh and Thompson, 1993).

Although low-cost direct application of phosphate rock has been used commercially in only a few countries, e.g., Malaysia, Indonesia, Brazil, Colombia, and New Zealand among others, and despite hundreds of published research papers and several national/international conferences, information on the direct application of PRs is limited and conflicting results are still being reported (Rajan and Chien, 2001).

2.3.3. Organic P sources

Soil organic P generally accounts for 15% to 80% of the total P in soils (Harrison, 1987; Havlin *et al.*, 2005). The high variability in organic P contents maybe due to different factors that affect organic matter in soil which include climate, vegetation, soil texture, land use pattern, fertiliser practices, drainage, and irrigation (Prasad and Power, 1997). Organic P sources, which are products added to the soil as alternative sources of nutrients and which are derived from living organisms, are a valuable source of nutrients. Other than being a source of nutrients, organic amendments have a positive effect on the physical properties of the soil and are generally cheaper than commercial WSP fertilisers since they derived from waste products. The most commonly used organic sources in agriculture include animal manure, sewage sludge and plant residues. In comparison to the water soluble P fertilisers, a considerable fraction of the P in the organic matter is in organic forms (e.g. inositol phosphates, phospholipids and nucleic acids), and hence can only contribute to the P nutrition of plants after being mineralised to the orthophosphate ($H_2PO_4^-$ and HPO_4^{2-}) ions (Sims, 2000; Pierzynski *et al.,* 2005).

Phosphorus in the organic sources can only be released through mineralization processes mediated by soil organisms and plant roots in association with phosphatase secretion (Dalal, 1977; Shen *et al*., 2011). Soil microbial activity, in turn, is influenced by prevailing environmental and soil conditions which include soil moisture, temperature, surface physical-

chemical properties, soil pH and Eh (for redox potential) (Shen *et al*., 2011). Not only do micro-organisms mineralise organic P, but some groups (*Aspergillus*, *Arthrobacter*, *Pseudomonas* and *Achromobacter*) secrete organic acids, such as α-ketogluconic acid, which attach insoluble Ca phosphates and release the phosphate (White, 2006). In addition to microbial mineralisation, organic sources vary in their rates of decomposition, which affect the ease with which nutrients are mineralised for plant use. The organic carbon:organic phosphorus (C:P) ratio of a particular organic source play a vital role in determining whether there is net mineralization or net immobilization of P. Menzies (2009) divided the C:P ratios into three categories based on the likelihood of whether organic P will be mineralisation or immobilisation once returned to the soil:

- When the C:P ratio is less than 200:1, net mineralization prevails.

- When the C:P ration is between 200:1 and 300:1, immobilization and mineralization rates are fairly equal.

- When the C:P ratio is greater than 300:1, net immobilization occurs. During immobilization there is not enough P to sustain both plants and microorganisms; and so, microorganisms scavenge the soil for P.

Therefore, knowing the C:P ratio of organic amendments is very useful when deciding which organic amendment to use. Moreover, the rate at which plant available P is released from the organic matter depends on the form of organic P source used. Pierzynski *et al*. (2005) indicated 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.

A number of these products are routinely used in the South African sugar industry, however, their P content and chemical composition of different organic P sources vary (Table 2.3). However good the averages of a given organic amendment are, the P content on individual farms or organic sources may vary considerably from the average, and the true value can only be known through laboratory analyses. It is also important to bear in mind that the same source of organic P may vary from batch to batch (van Antwerpen, 2011), as the content of P maybe be affected by handling-techniques, storage and the age of the organic source. As mentioned before, organic source are less water-soluble than commercial fertiliser, therefore, organic amendments cannot be used to substitute water-soluble-P fertiliser as a starter fertiliser due to slow release of P through mineralisation. In the sugarcane producing areas,

filtercake (a by-product in the sugar reefing process) has traditionally been used as a source of P, however, the high moisture content (± 50%) when taken from the mill have a profound effect on the transportation cost to the extent that usage is normally restricted to within 15 km of the mill (van Antwerpen *et al*., 2013).

Table 2.3: Some of the organic amendments used in the SA sugar industry, along with their typical P (%) and estimated moisture contents (van Antwerpen *et al*., 2013).

Organic amendment	P (%)	Moisture (%)
Bagasse	0.27	> 50
Compost	0.09	± 55
Condensed molasses stillage (CMS)	0.16	± 45
Filtercake	0.5 to 2.5	± 50
Green manure (legume)	0.25	35 to 70
Kraal (farmyard) manure	0.86	± 14
Molasses	0.12	± 75
Pith	-	± 40
Poultry litter	1.6	20
Poultry manure	1.5	40
Sawdust	0.11	< 20
Sugarcane tops	0.18	60
Sugarcane trash	0.11	15
Vinasse	0.09	85 to 95

Studies have shown that long-term use of organic amendments has both positive and negative effects in soil. The positive effects are that organic amendments increase 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 (Motavalli and Miles, 2002: Nthenjane, 2012). The humic acids from organic amendments contain large numbers of negative charges, carboxyl and hydroxyl groups, which strongly compete for the adsorption sites with adsorbed inorganic P (Shen *et al*., 2011). On the other hand, prolonged use without proper monitoring of soil P levels can have a negative impact on the environment as high concentrations of P (> 41 mg P kg^{-1}, a value empirically selected to indicate high levels) can lead to eutrophication on the water bodies, thereafter becomes a hazard to the environment.

2.4. Phosphate retention and release in soils

Predicting phosphorus requirements for plants in most agricultural soils had long been recognised as complex and difficult since not only soils are severely deficient in P but plant

availability of applied P tends to be rapidly affected due to reactions with soil components. Several reactions that controls the transformation of phosphorus in soils have been documented, which subsequently result in the retention or release of P in soil systems. The retention of P by soil occurs largely as adsorption and precipitation reactions of P with Fe and Al oxides, clay minerals, and calcium carbonate ($CaCO_3$) which are mainly controlled by changes in soil pH. On the other hand, P is released into the soil solution through (i) 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 (already discussed in section 2.3.3).

Although precipitation-dissolution reactions are of interest, sorption-desorption reactions usually provide a better description of the retention and release of P by soils (Syers and Curtin, 1989). Therefore, the availability of P to 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 and Sparks, 2007).

2.4.1. Sorption and precipitation reactions

Phosphate retention in soils involves both adsorption and precipitation reactions; but the adsorption is considered to be the most important process controlling P availability in soils over a short period (Gichangi *et al*., 2008). By definition, P sorption is the removal of labile P from the soil solution, due to the adsorption on, and absorption into the solid phases of the soil, mainly on to surfaces of more crystalline clay compounds, oxyhydroxides, or carbonates and/or magnesium (Holford and Mattingly, 1975). Phosphate precipitation is a process in which phosphorus reacts with another substance to form insoluble P compounds (a solid mineral) (Gichangi *et al*., 2008). As successive increments of soil are contacted by the moving front of the fertilizer solution, dissolving increasing amounts of Fe, Al, Mn, Ca, Mg, and soil derived cations, the solution becomes supersaturated relative to a variety of P compounds (Sample *et al.,* 1980), resulting in the precipitation of P minerals.

When soluble phosphatic fertilisers are applied to soils, they initially dissolve causing an immediate rise in the concentration of soil solution P, which then participates primarily in adsorption and precipitation processes (Prasad and Power, 1997). The reactions that occur are mainly pH depend. In acidic soils, predominance of positive charges on Al- and Fe-oxides and hydroxides facilitates the attraction of negatively charged orthophosphate $H_2PO_4^-$ and HPO_4^{2-}

ions to form insoluble compounds (Havlin *et al.*, 2005). Specific adsorption (ligand-exchange) occurs when P anions replace the hydroxyl groups on the surface of Al and Fe oxides and hydrous oxides (Haynes and Mokolobate, 2001). The solubility of these phosphates increases with increase in soil pH.
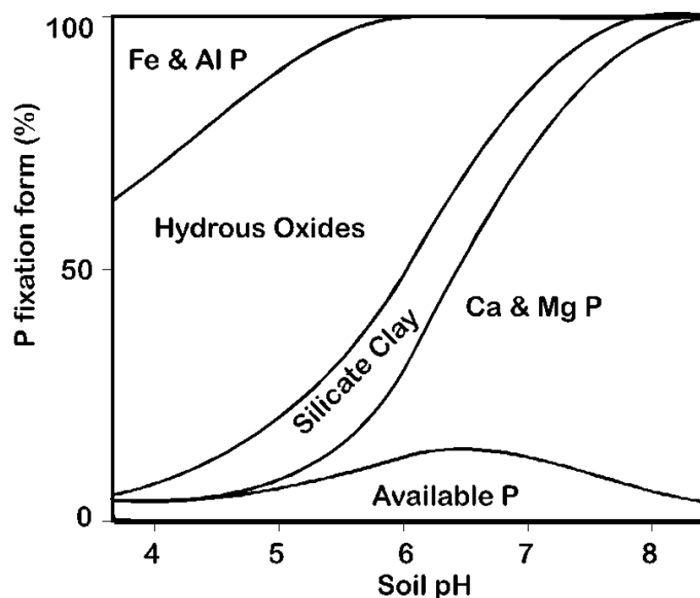
Figure 2.2: Relationship between soil pH and different forms of P fixation.

In calcareous soils, the presence of $CaCO_3$ with large surface area also shows a high adsorption and a rapid precipitation of Ca-P minerals (Havlin *et al.*, 2005). Phosphate precipitates with Ca, generating dicalcium phosphate (DCP) that is available to plants, however with time, this ultimately transforms into more stable forms such as octocalcium phosphate and hydroxyapatite (HAP), which are less available to plants at alkaline pH (Arai and Sparks, 2007). The solubility of these phosphates increases with decreasing soil pH. Therefore, P is most available in the pH range of 6.5 to 7.0 (Troeh & Thompson, 2005) and any 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.

Phosphorus retention reactions (adsorption and precipitation) are also affected by the type of mineral surfaces in contact with P in the soil solution (Havlin *et al.*, 2005a). Havlin et al. (2005a) explained that P is adsorbed most extensively by Al and Fe oxides and to a greater extent by 1:1 clays (such as kaolinite) as compared to 2:1 clays (e.g. montmorillonite) due to the presence of higher Fe/Al oxides content in the 1:1 clay minerals. The amount of clay present in a soil profile also has a profound influence on the degree of P retention with P

retention being higher in soils with high clay content compared to sandy textured soils (Kamprath, 1973; Pierzynski *et al.*, 2000).

2.4.2. Desorption and dissolution reactions

As mentioned earlier, P can be released into the soil solution through minerals dissolution, desorption of adsorbed P from soil constituents and through organic matter mineralisation processes into plant available forms. Desorption is the reverse reaction of sorption and describes the release of sorbed P from clays, oxides, and minerals into solution via diffusion arising from a concentration gradient (Pierzynski *et al.*, 1994; Mengesha, 2008). This occurs when plant P uptake depletes soluble P concentrations to very low levels creating a concentration gradient which thereby result into the slow release of adsorbed P from soil constituents in order to maintain solution equilibrium (replenish the soil solution). This slow release can sustain plant growth in many natural systems, but is usually not rapid enough to maintain adequate phosphorus availability in intensively managed cropping systems without some supplemental phosphorus in the form of fertilizer, manure, or crop residues (Sharpley, 1985; Mengesha, 2008). Although soil P sorption has been studies intensively, relatively less has been done on the P desorption in soils and sediments.

Dissolution of phosphate minerals occurs when the mineral dissolves and releases phosphorus. Dissolution of soil minerals require a source of H^+ ion which can originate from the soils itself or from roots or microbes, and sinks for Ca and P (Frossard *et al.*, 1995). Applications of organic materials have been shown to influence P availability due to its effects on P fixation. The role played by organic amendments in controlling P availability is two-fold; not only does organic matter decomposes to release P, but P adsorption to soil particles can be greatly reduced through applying organic substances.

Decomposing organic matter release P more quickly in warm humid climates with well-aeration and much slower in cool dry climates and on saturated wet (anaerobic) soils. The humic acids from organic matter contain large numbers of negative charges, carboxyl and hydroxyl groups, which strongly compete for the adsorption sites with inorganic P (Nthenjane, 2012). Organic material can form a protective cover by coating sesquioxides or forming stable complexes between organic anion (citrate, tartrate, oxalate, malate and malonate) arising from the decomposition of organic matter with iron and aluminum, thus preventing their reaction with phosphorus. Furthermore, small molecular organic acids from mineralisation of humic substances in manure can dissolve Ca phosphate, and especially for

citrate, it can efficiently weaken the nanoparticle stability of hydroxyapatite (HAP), by controlling the free Ca availability and thereby the nucleation rate (Martins et al., 2008). However, mechanisms of manure-induced P transformation processes between inorganic P and organic P in soil still need further investigation (Shen *et al*., 2011).

2.5. Phosphorus status in soils of the South African sugar industry

Most sugarcane producing areas are situated on the eastern seaboard of South Africa which receives high rainfall than the majority of the country and P deficiency is an important soil fertility problem in undisturbed soils or in small scale-growers compared to older and more established sugarcane areas. In new (virgin) land, P reserves in soils are invariably unavailable for plant uptake, being held in organic, inorganic or sorbed forms. In contrast, for many of the older more established sugarcane areas, P has built up over many years in the soil due to long-term use of fertilisers and history of recycling P rich filter press mud back to sugarcane lands (Meyer *et al*., 2011).

Although previous studies outside the sugarcane industry have shown that most of the agricultural soils in the eastern part of South Africa are deficient in P due to high sorption capacities, surveys by Meyer *et al*. (1998) and van der Laan and Miles (2010) indicated that soil test data from the fertiliser advisory service (FAS) generally showed a fairly low incidence of P deficiency throughout the industry. Meyer *et al*. (1998) found that, on an industry wide basis only 12% of the soil samples appeared to be deficient in P based on the 13 ppm critical value used for ratoon cane. van der Laan and Miles (2010) also found that the regions with the highest percentage of soil samples deficient with P at planting were the Zululand North, North Coast and Lower South Coast (Table 2.4) and these regions are said to be dominated by small scale growers with limited resource-inputs (low usage of inorganic and/or organic fertilisers) compared to large-scale and more established growers. This information was obtained from surveys conducted to monitor long-term trends from soil analytical data captured by the South African Sugarcane Research Institute's FAS between the periods of 1980-1997 (Meyer *et al*., 1998) and 2007-2009 (van der Laan and Miles, 2010). Of major concern though, van der Laan and Miles (2010) found that a high number of surveyed soils had soil P test values well in excess of crop requirements (>41 mg P kg) (Table 2.4) which implies an increased potential for P pollution through export to fresh waterways via runoff and leaching losses, especially in sandy soils. However, Meyer *et al*. (2011) cautioned that a risk of P deficiency is particularly high for sugarcane growing on the red Oxisols that

are common throughout tropical and subtropical cane producing areas, due mainly to their inherent capacity to strongly fix applied P.

Table 2.4: A summary of soil P concentrations (means), percentage of soil samples deficient in P and percentage of soil samples with P levels above 41 mgkg^{-1} for each extension region in the SA sugar industry for the 2007-09 period (van der Laan and Miles, 2010).

| Extension region | Soil P averages | | | | Soil samples with P levels (>41 mg kg^{-1}) |
| | P* (mg kg^{-1}) | | P** (mgkg^{-1}) | | |
	Mean	Deficiency (%)	Mean	Deficiency (%)	%
Mpumalanga (*i*)	58	13	40	5	68
Swaziland (*i*)	40	11	40	1	40
Pongola (*i*)	38	11	39	5	42
Umfolozi (*i*)	44	11	38	4	58
Komatipoort (*i*)	40	18	36	5	41
Zululand North	27	40	27	5	22
Zululand Central	38	19	33	3	41
Zululand South	32	20	35	1	23
North Coast	33	27	34	5	28
Durban North Coast	37	18	36	1	34
Midlands North	41	15	41	4	43
Midlands South	33	23	32	4	28
South Coast	33	22	37	2	26
Lower South Coast	30	25	33	3	23
Threshold criteria	<31		<13		>41

*- at planting; ** - ratoon; *i* – production predominantly under irrigation

From an advisory viewpoint in the South Africa sugar industry, sufficient P is recommended at planting to raise the soil P level to 40 mg P kg^{-1} soil (based on Truog-P test) in accordance with the amounts of P extracted from the soil. The amount of P needed for 40 mg Pkg^{-1} soil is sufficient to meet the P requirements of at least the plant crop and the first ratoon (Anon, 1998; Meyer *et al*., 2011). For the whole crop cycle, a threshold Truog value of 31 mg kg^{-1} has been used by the fertiliser advisory service at SASRI to meet the P requirement of the plant and first ratoon crop but for single ratoon crop advice a threshold value of 13mg kg^{-1} has been shown to be adequate (Meyer *et al*., 2011).

2.6. Methods for assessing phosphorus availability and requirements in soils

2.6.1. Soil tests for available P

Availability of phosphorus (P) for plant utilization is not a function of its concentration in the soil, but rather on the rate of its release from the soil surfaces into the soil solution. This is estimated by soil testing, which is an essential and integrated part of soil management in present-day agricultural systems (Fageria *et al.*, 1997). Crop response is poorly related to the total amount of P in a soil and therefore a successful soil test should provide some index of P availability (Sanchez, 2007). The fundamental goal of soil P testing has always been to identify the "optimum" soil test P concentration required for plant growth. The need for additional fertilisation or manuring, and the economic return on an investment in fertilizer P, may then be predicted. Agronomic soil tests to indicate available P have been designed such that (i) they are suitable for routine application, (ii) they extract sufficient P to be easily measurable, (iii) they extract sufficient P to represent a significant portion of the soil P potentially available for plant uptake and (iv) they do not extract significant amounts of P that are not available to plants (Tiessen and Moir, 1993).

Extraction methods used in evaluating P status of soils include extraction with water, weak acids, bases, salts and anion exchange resin. The most commonly used tests in South African laboratories are the Bray 1, Ambic, Truog and Olsen tests, with the P-tests used in the South African sugar industry being the Truog and resin methods. The following sections provide an overview of the three soil test P methods used in this study: Truog (traditionally used by the advisory service at SASRI), Mehlich-3 (a multiple element extraction method that is currently proposed by the Fertiliser Society of South Africa to be used standard P extractant for all South African laboratories), and resin extractant (gives the best estimate of available P).

I. Truog method

The Truog method ($0.02N$ H_2SO_4) (Truog, 1930) is the most widely used for advisory purposes in sugar industries in countries such as Mauritius, Brazil, the Philippines, Hawaii, Australia and South Africa. In South Africa the Truog extractant has been carefully calibrated for sugarcane over many years under a wide range of bioclimatic and soil conditions, by correlating soil analysis data with yield responses to P treatment in 31 exploratory 3Nx3Px3K factorial trials and 53 4Nx2Px3K regional fertilizer trials (Meyer *et al*., 2011). Of the many methods that have been tested, the modified Truog extractant gave the best correlation between soil P levels and response to applied P fertilizer (Du Toit *et al*., 1962). It is a dilute

acid extraction (0.002 N H$_2$SO$_4$ at pH 3.0). The Truog method suffers from the limitation of all acid extractants, i.e., a tendency to over-estimate plant available P (under-estimating fertiliser P requirements) in neutral and alkaline soils typical of the northern irrigated areas of the SA sugarcane industry (Miles *et al.*, 2013).

II.   Mehlich-3 method

Mehlich-3 extractant(0.2N HOAc+0.25N NH$_4$NO$_3$+0.015N NH$_4$F+0.013N HNO$_3$+0.001M EDTA at pH 2.5) (Mehlich, 1984) is a multi-nutrient extraction method, determining P, K, Ca, Mg, Na, Cu, Zn, Mn, B, Al, and Fe, and is considered to be suitable for a vast range of soils varying in their physicochemical properties (Frank *et al.*, 1998; Sims, 2000). This method uses an acetic acid solution to extract P, promoting the dissolution of Ca-phosphates. The fluorides in the solution enhance the extraction of Al-phosphate through complexation reactions. This extractant has been found to be strongly correlated to Bray-1 P on acid soils (r^2 = 0.97) and to Olsen on alkaline soils (r^2 = 0.92) (Alvey, 2013). In countries such as USA, Canada and Czech Republic, Mehlich-3 extraction is employed as a standard method for phosphorus extraction and is also widely used in routine soil testing. This method is also being investigated for routine use by all South African laboratories for advisory purposes.

III.   Resin method

Methodologies for resin-P extraction were detailed in Sibbesen (1978), Schoenau and Huang (1991), Chardon *et al.* (1996) and Myers *et al.* (2005). Resin extraction methods have been favourably employed to estimate plant-available P for soils with large variations in physical and chemical properties and are reliable over all soil types (Myers *et al.,* 2005). This 'ion sink' P testing method has an advantage over conventional chemical extractants such as Truog (Truog, 1930) and Mehlich-3 (Mehlich, 1984) because it functions similarly to a plant root surface, adsorbing available P ions from the *in situ* labile P pools in the soil (Myers *et al.,* 2005).

The procedure typically involves the use of chloride-saturated resin at a 1:1 resin-to-soil ratio in 10 to 100 mL of water or weak electrolyte for 16 to 24 hrs (Amer *et al.*, 1955; Olsen and Sommers, 1982).Anion exchange resin in aqueous suspension with soil simulates plant roots by removing the dissolved phosphate from the soil solution via surface adsorption. The solution P concentration, quantity of sorbed P, and temperature all affect the quantity of P extracted by the resin. The rate of P adsorption by the resin is controlled by diffusion, which is a function of solution P concentration (Amer *et al.*, 1955; Dobermann *et al.*, 1994). The

resin maintains the solution P concentration at a low level to facilitate continued P desorption from the soil. The quantity and the rate of P sorption by the resin correspond to the quantity and the rate of P desorption from the soil (Sparks *et al*., 1996).

2.6.2. Phosphorus requirement factor

Most soil testing laboratories are faced with the difficulty of dealing with soil types that vary not only in texture, but also in clay mineralogy. Establishing P requirements of sugarcane in southern Africa presents particular challenges for agronomists, since not only is P the most expensive of the macro-nutrients, but wide variations in soil properties imply variable availability of applied P for crop uptake. Of crucial importance in extending advice on P fertilisation is knowledge of the amount of P required under field conditions for unit increase in P soil test. The quantity of P fertiliser that must be applied per hectare to raise the soil test value by one unit, is termed P requirement factor (PRF). A low value of PRF indicates low capacity of the soil for P sorption (Henry and Smith, 2004). The reality of a possible range in P requirement factors when establishing P requirements (as shown in *equation 1.1*) is very often not given adequate attention (Johnston *et al*., 1991).

Recap:

P requirement (kg/ha) = (optimum soil P − measured soil P) x PRF   (*eqn. 1.1*)

The multiple-point approach and incubation experiments involved in measuring PRF values for a particular soil has proved to be tedious to be adopted by soil testing laboratories for routine purposes. Thus, a simpler approach is required to estimate the PRF values from soil properties or P sorption indices that are already measured routinely or which can be readily added to the range of routine tests conducted by soil testing laboratories (Johnston *et al*., 1991; Henry and Smith, 2004). The success of this approach relies upon a good relationship between PRF values and selected soil properties or P characteristics (White, 1980). Functions of best fit describing the relationship between the variables must then be established as an aid to converting test values into estimates of the sorption parameters. Several authors have attempted to relate soil characteristics to P sorption parameters in soil (Fox and Kamprath, 1970; Bainbridge *et al*., 1995; Moazed *et al*, 2010).

The Cedara advisory service of the KwaZulu-Natal Department of Agriculture and Rural Development make use of soil sample density to determine the PRF based on the principle that clay soils (low sample density) require more P to increase soil P test by 1 mg L^{-1} than

sandy soils (high sample density) and this approach has been found to provide a reliable estimate of the PRF for crops such as maize, potatoes and cabbages (Manson *et al*., 2012). For the sugarcane industry, the fertiliser advisory service (FAS) of SASRI use a rapid phosphorus desorption index (PDI) (a method based on the P9+ adsorption isotherm principle) proposed by Reeve and Sumner (1970) to predict the fate of applied P fertiliser in terms of P fixation since conventional extractants for predicting P fixation cannot be used routinely (Meyer and Wood, 1989). Depending on whether the soil is weakly (PDI more than 0.40), moderately (PDI between 0.20-0.40) or strongly (PDI values less than 0.20) P-fixing, the furrow application is increased to 90, 100 or 120, kg P ha^{-1}, respectively.

South African sugarcane growers have placed great reliance on the value of soil analyses conducted by the Fertiliser Advisory Service of SASRI for not only diagnosing and correcting nutrient deficiencies but also providing cost effective fertiliser recommendations. Therefore, there is a need for a reliable and direct method to quickly measure the P requirement factors of the soils of the sugar industry at very little analytical costs. Since the six-week method for determining PRF values in soils does not lend itself for routine use, a simplified and more direct measure of PRF values for accurate fertiliser recommendation purposes by the FAS is required.

2.6.3. Use of mid-infrared (MIR) spectroscopy to predict P requirement factors

There is a need for the development of more time- and cost-effective methodologies for soil analysis as there is great demand for larger amounts of good quality, inexpensive soil data to be used in environmental monitoring, modelling and precision agriculture. Due to advances in spectrometer hardware, computing and statistical software, spectroscopic techniques provide a good alternative that may be used to enhance or replace conventional methods of soil analysis, (Reeves *et al.* 2001; Jahn *et al*., 2006; Linker, 2011). Mid-infrared reflectance (MIR) spectra of soil samples in combination with chemometrics have potential for rapid, timely, less expensive analyses, which require minimal sample preparation (Shepherd and Walsh, 2002; Christy, 2008). No fractionation is required, hazardous chemical reagents and wastes are avoided, and simultaneous characterisation of various soil properties can be predicted from a single spectrum (Siebielec *et al*., 2004).

Numerous studies have demonstrated the effectiveness of MIR in performing quantitative analysis of soils. The MIR wavelength region (2500-25000 nm) has been used to predict soil properties such as pH, EC, clay, organic carbon, inorganic carbon, total nitrogen, carbonate,

and major compositions of soil samples including SiO_2, Al_2O_3, Fe_2O_3, TiO_2, MgO, and CaO, P buffering capacity and sorption coefficient of pesticides in soil (Janik *et al*. 1995; Janik and Skjemstad, 1995; McCarty *et al*. 2002; Forouzangohar *et al*., 2008).

The application of MIR spectroscopy to soil is derived from the fact that spectra hold information on the soil's fundamental composition such as its organic matter, minerals, the amount of water present, and colour (Janik and Skjemstad, 1995; Pirie *et al*., 2005; Niazi, 2011). The qualitative information in the MIR spectra of soils is characterised by strong stretching and bending vibrations of specific bonds (e.g. Fe-O, Al-O, Si-O and -OH) and of organic matter functional groups such as alkyl, carboxylic (protonated and nonprotonated), carbohydrates, amide, amine, and most importantly aromatic functional groups (Van der Marel and Beutelspacher, 1976; Skjemstad and Dalal, 1987; Theng and Tate, 1989; Janik and Skjemstad, 1995; Wander and Traina, 1996; Janik *et al*., 1998). Soil properties are predicted either by direct absorption of the light associated with functional groups (e.g. organic C, total N, or clay composition) or by correlation to such properties and the mineral composition of the soil (e.g. CEC and soil texture) (Van der Marel and Beutelspacher, 1976).

When the MIR radiation is focused onto a soil sample, the molecules in the sample will increase their vibration energy by absorbing energy at specific frequencies depending on the molecular geometry, bond strengths and atomic masses (Yang *et al*., 2012). The resulting radiation is thus modified, resulting in a spectrum or "signature" of the molecular composition with peaks at the adsorbing frequencies (Yang *et al*., 2012). The combined contributions from the various soil components can result in a very complex spectrum that is difficult to quantitatively interpret, but multivariate computer models (particularly partial least-squares [PLS] regression) can be used to derive accurate qualitative and quantitative relationships or models between the spectral signatures and many chemical and physical soil properties. For predictions of soil properties, MIR spectra, and the corresponding analytical data are transformed into a smaller set of orthogonal PLS loadings and loading scaling terms (scores), thus combining the spectral and concentration data into a multivariate calibration model (Haaland and Thomas, 1988). This calibration model can then be used for predictions of property values from spectra of unknown samples.

There are three main requirements for the successful development of MIR calibrations: i) the samples should be representative of the geographic region in which it is to be used; ii) they should be carefully prepared and scanned; and iii) the reference data used for calibration

should be obtained with reliable analytical methods. New samples can only be predicted if they fall within the property range of the calibration set (Naes *et al.*, 2002).

The calibration of the MIR-based approach to predict PRF in soil could provide a cheaper and time-effective method compared to conventional chemical procedures, especially where large numbers of samples need to be analysed routinely as the case in fertiliser advisory services. Infrared spectroscopy has been used to delineate the adsorption mechanisms of arsenic (As) on the surface of Fe/Al oxides and clay minerals in soils (Goldberg and Johnston, 2001; Jia *et al.*, 2007; Carabante *et al.*, 2010; Niazi *et al.*, 2011) and to predict P buffering index in Australian soils (CSIRO). In South Africa, the advisory services of SASRI and Cedara make use of MIR to predict ammonium-oxalate extractable Al and Fe, clay content, organic carbon and sample density among other soil properties. Due to strong correlation between P sorption and ammonium-oxalate extractable Al (Al_{ox}), and satisfactory prediction of Al_{ox} by MIR, the feasibility of MIR to predict PRF in soil should also be investigated.

2.7. Conclusion

From this literature review, it is evident that the prediction and recommendations of required phosphorus (P) in soils is a complex issue due to variations in soil properties. The discussion indicates that chemical, physical and biological processes influence the fate of P fertilizer added to soils. 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. To calculate P requirements, it is necessary to know how much of that nutrient must be applied to overcome any buffering effects (i.e., PRF) to raise the test value to a desired level. However, the soil P tests currently used for determining PRF values are laborious incubation methods that detract from the timeous transfer of P fertiliser recommendations to the growers. However, with new technologies being released every day, the potential of MIR to predict PRF values would be of great value in routine soil testing.

CHAPTER 3: MATERIALS AND METHODS

3.1. Soil sampling and preparation

The soils used in this study were selected from bucket-soil samples that were collected over time by SASRI's soil science department from various locations of the South African sugarcane industry (i.e., KwaZulu-Natal and Mpumalanga) (Figure 3.1). The 39 topsoil samples (0-20 cm) used in this study were selected to cover a whole range of different soil properties and differing P levels based on preliminary analyses of the samples. These soil were also selected to range of soils from major bioclimatic regions under which sugarcane production is produced in South Africa: six samples were collected from the hinterland (H) soil system, 9 samples from dry lowveld (DL) system, 7 samples from coastal sands (CS) system, 10 soil samples from the coastal lowlands (CL) system and 7 samples from the mistbelt (M) system. The main features of these soils systems (i.e., climate, altitude and soil physical properties) are outlined in Appendix 1. For the purposes of this thesis, sample numbers from different soil systems are denoted by a prefix letter that represent the system of origin as indicated above.

The soil samples were oven dried for three days at 40°C, ground to pass through a 1 mm sieve (standard sieve-diameter used at FAS) and kept in labelled plastic containers for chemical and physical characterisation

3.2. Soil characterisation

All the analyses were done in replicates of 3 per sample. Sample density (g cm^{-1}) was determined by recording the mass of a 10 cm^3 scoop of the dried and ground soils (Johnston *et al*., 1987). Soil pH was measured at a 1:2.5 soil: solution ratio by scooping 10 mL of soil into a beaker and adding 0.01 *M* $CaCl_2$ and was shaken for 5 min at 150 rpm. The soil pH was measured using a pH meter with a glass and reference calomel electrode (Beckman ϕ 310 pH meter), after the suspensions was allowed to stand for 30 min.

Total carbon (C) was determined by dry combustion using a LECO TruSpec C/N auto-analyser (LECO Corporation, 2003). Exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+ were extracted with the Ambic multi-nutrient extractant (van der Merwe *et al*., 1984) and determined by atomic absorption spectrophotometry. Exchangeable acidity ($Al^{3+} + H^+$) was determined by extraction with 1.0 *M* KCl and titration with 0.05*M* NaOH (Farina and Channon, 1991).
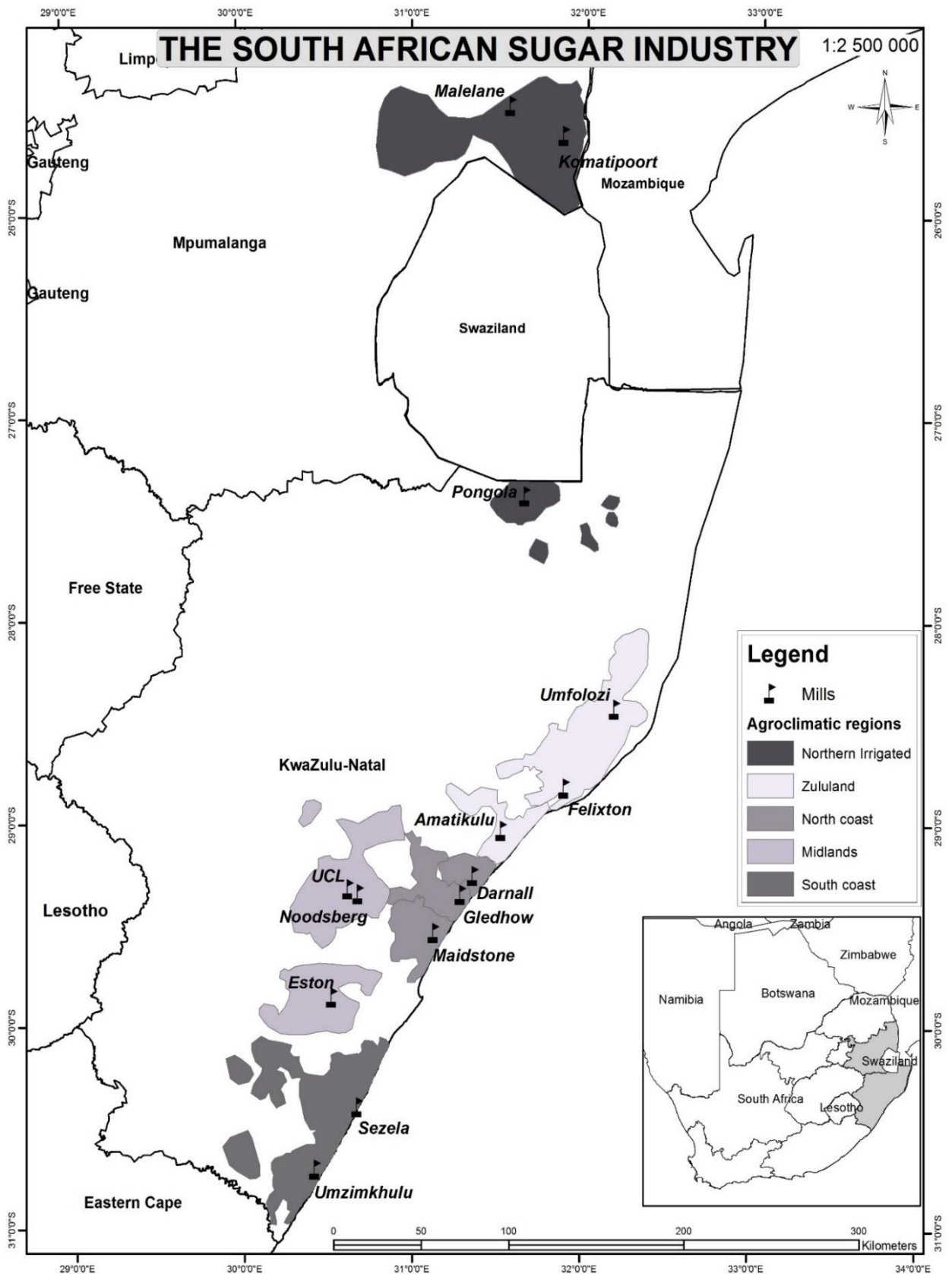
Figure 3.1: A map representing different agro-climatic regions of the South African sugarcane industry.

Effective cation exchange capacity (ECEC) was estimated by the summation of exchangeable cations and exchangeable acidity. Phosphorus was determined using Troug (Truog, 1930) and resin (Myers *et al*., 2005) extractants. It must be said that Mehlich-3 P tests (Mehlich, 1984) were not done during the preliminary measurements, hence, the data in not available. Particle size distribution of the soils was determined using a Bouyoucos hydrometer method after dispersion of the soil with sodium hexametaphosphate (Calgon solution) (Bouyoucos, 1962), based on Stoke's Law.

Amorphous Al and Fe (Al_{ox} and Fe_{ox}) were determined in a 0.2 *M* acidified ammonium oxalate solution, which was adjusted to pH 3 with oxalic acid (McKeague *et al*., 1971). One-gram of soil was treated with 50 mL of Tamm reagent (690 mL of 0.2 *M* oxalic acid + 900 mL of ammonium oxalate). The sample was shaken for 4 hrs at 150 rpm on an end-to-end shaker in the dark. The concentrations for Al_{ox} and Fe_{ox} were measured using the inductively coupled plasma optical emission spectroscopy (ICP-OES).

3.3. Phosphate sorption studies

3.3.1. Phosphate Sorption

The method described by Pierzynski (2000) was used in the P sorption study. Soil samples (1-g) were equilibrated with 25 mL of varying concentrations of P in 0.01 $CaCl_2$ solution in 50 mL centrifuge tubes. The initial concentrations of the solutions were 0, 0.05, 0.50, 1.00, 5.00 and 10 mg P L^{-1} as KH_2PO_4. The tubes were then closed and shaken for 24 hrs on an end-to-end shaker at a room temperature ($25 \pm 1 °C$) at 150 oscillations per minute. The samples were centrifuged for 15 min at 3000 rev min^{-1} and the supernatant was filtered through a Whatman no.42 membrane filter. The P in solution was determined using the ascorbic acid-molybdenum blue method (Murphy and Riley, 1962) at a wavelength of 880 nm. The amount of P sorbed was calculated as the difference between the amount of P added and that remaining in solution (Fox and Kamprath, 1970). Sorption isotherms were compiled by plotting the P sorbed (mg P kg^{-1} soil), on a linear y axis, against solution P concentration (mg L^{-1}) on a logarithmic x axis, and approximately straight-line curves were obtained. The slope of the curve gives information about the phosphate buffering capacity (Ozanne and Shaw, 1968), whilst the intercept at zero phosphate sorption is an estimate of phosphate in the soil solution, a value which is reported to be related to plant growth (Wild, 1967). The amount of P required to maintain equilibrium P concentration of 0.2 mg L^{-1} (referred to as the standard P requirement

for most plants) was obtained by dividing the slope of the function by 0.2, the units of which are mg P L^{-1}.

3.3.2. Phosphate Sorption Index (PSI)

The method described by Bache and Williams (1971) was used to determine the phosphorus sorption index (PSI) of the soils and all samples were replicated 3 times. This involved an 18 hrs equilibration with 75 mg P L^{-1} in 0.01 M CaCl$_2$. Following equilibration, the soil suspensions were centrifuged at 3000 rev min^{-1} for 10 minutes and filtered through Whatman no. 42 filter paper to obtain a clear solution. Phosphorus in the supernatant was then determined by the method of Murphy and Riley (1962). The phosphorus sorption index (PSI) was calculated using equation 3.1 below.

Calculation:

$$\text{PSI (L kg}^{-1}) = \frac{X}{\log C} \qquad \qquad \textit{Equation 3.1}$$

where,

$$X = \text{P sorbed (mg P kg}^{-1})$$

$$C = \text{P conc. at equilibrium (mg P L}^{-1})$$

3.3.3. Phosphate Desorption Index (PDI)

Phosphorus desorption index (PDI) was determined by the Reeve and Sumner (1970) method. Duplicate 5gsoil samples (A and B) were weighed, and 5 mL of deionised water was added to sample **A** and 5 mL of 200mg P L^{-1} of P solution was added in sample **B** and left overnight. Twenty millilitres of Bray 2 solution (2.22 g NH$_4$F, makeup to 2 L with 0.1N HCl) was added to both soil A and B and shaken for 1 min (small batches to accommodate time). The solutions were filtered and P was analysed using UV VIS spectrophotometer (Murphy and Riley, 1962).

Calculation:

$$PDI = (Conc.\textbf{\textit{B}} - Conc.\textbf{\textit{A}}) \times \frac{25}{1000} \qquad \qquad \textit{Equation 3.2}$$

The PDI value is the amount of P recovered expressed as a fraction of the amount added in solution (Meyer, 1974). Thus the higher the PDI value, the less the P immobilization (greater desorption).

3.4. Determination of P requirement factors

Samples of each soil (<1 mm sieved) were incubated with three incremental levels of P fertiliser. A solution of potassium dihydrogen phosphate (KH_2PO_4) containing 0, 50 and 100 mg P L^{-1} soil was thoroughly mixed with 1.5 L samples of each soil by stirring with a laboratory spatula. Soils were brought to 'field capacity' (50% pore space) by adding distilled water. Treated soils were left open in plastic container and the temperature was maintained at 25 $^\circ$C $\pm$ 0.5 $^\circ$C. The samples were subjected to three drying cycles by wetting by adding water to 'field capacity' every fortnight. After six weeks, the samples were air-dried and ground to pass through a 1 mm sieve before analysis. Phosphorus was determined using three different extractants (Troug, Mehlich-3 and resin).

The relationship between P measured in mg L^{-1} and P added in kg ha^{-1} (assuming an incorporation depth of 200 mm) was found to be near linear, so that linear regression functions could be fitted to each soil. The inverse of the slope of this function reflects the P requirement factor (PRF), the units of which are kg P ha^{-1} per mg P L^{-1}. It represents the quantity of P fertiliser that must be applied per hectare to raise the soil test value by one unit and provides an index of P sorption, which in this study is also used to establish regression relationships with other soil properties (Johnston *et al*., 1991).This was done with a view to possibly predicting P sorption from readily-measured parameters such as sample density, effective CEC and clay content (Johnston *et al*., 1991; Bainbridge *et al*., 1995; Henry and Smith, 2004).

3.5. Mid-infrared spectroscopy calibrations to predict P requirement factors in soil

The potential of mid-infrared (MIR) spectroscopy in combination with multivariate chemometric techniques was investigated to predict the soil PRF of the studied soils from KwaZulu-Natal and Mpumalanga Provinces. Approximately 0.3 g of these soil samples were scooped into 2mm (depth) x 6mm (diameter) wells on a 96-well metal sample micro-plate with a spatula and levelled without compressing the soil whilst simultaneously ensuring the soil is as smooth as possible. The plates were run on the Bruker Tensor II MIR instrument (Bruker Alpha Drift; Ettlingen, Germany) with a High-throughput Screening Accessory (HTS-XT) to obtain raw spectra between the wave numbers of 3997.2 cm^{-1}- 600 cm^{-1}.

Using the OPUS Version 7.5 Build 7, 5, 18-software, a PLS regression was created with the best calibration being automatically selected by the software. A cross validation was also performed by the software which removes a single sample and reads it as an unknown against

the calibration, then plots the result versus the true value. The software does this repeatedly until each sample has had a chance to be read as an unknown and a cross validation graph is created.

3.6. Statistical analysis

Correlation and regression analyses were performed to relate P requirement factors (PRF) for the three extractants (i.e., Truog, Mehlich-III and Resin) with selected soil properties using Microsoft Excel 2010. Probability tests were also performed at two levels of significance ($p = 0.01$ and $p = 0.05$).

The following quick statistic tools were used to examine the validity of the calibration prior to a proper method validation:

Root mean square error of estimation (RMSEE):

It was calculated from the Sum of Squared Errors (SSE). The residual is the difference between the true and fitted value. SSE is the quadratic summation of these values. The RMSEE predicts the amount of error on the regression.

$$RSEE = \sqrt{\frac{1}{M-R-1}} \; SSE$$

where:

      M – the number of standards

      R – the rank (the number of factors that taken into consideration

      SSE – the Sum of Squared Errors

Root Mean Square Error of Cross Validation (RMSECV):

For cross validation (performed on all calibrations), the RMSECV value can be taken as a criterion to judge the quality of the method.

$$RMSECV = \sqrt{\frac{1}{M} \cdot \sum_{i=1}^{M} (Differ)^2} = \sqrt{\frac{1}{M} \cdot PRESS}$$

where:

      M – the number of standards

PRESS – (Predictive Residual Error Sum of Squares) is the sum of all squared differences between true and predicted concentration.

Differ – is the difference between the true concentration of a sample i (as determined by another method) and the predicted concentration expressed by

$$Differ = Y_i^{true} - Y_i^{pred}$$

<u>Residual Prediction Deviation (RPD)</u>:

This is the ratio of Standard Deviation to Standard Error of Prediction.

CHAPTER 4: RESULTS

4.1. Physical soil characteristics

The soils differed vastly in their physical and chemical characteristics that are expected to affect P retention and release (Tables 4.1 to 4.5). The particle size distribution and textural class for each of the 39 soils under study are presented in Tables 4.1 to 4.3. Their textures vary from fine sandy loam to clay having a wide range of clay content with the lowest being 6% and highest having 76% clay. However, the soil system which appeared to have the least clay contents was the Hinterland and the highest bulk density (majority of the soils with more than 1.2 g mL^{-1}) compared to other soil systems.

4.2. Chemical soil characteristics

The chemical characteristics determined in the 39 soils under study are summarised in Table 4.4 to 4.6. On the whole, the soils in the South African sugarcane industry are acidic to near neutral with pH (CaCl$_2$) range of between 3.47 and 6.65. The soils varied widely in total carbon contents (measured on LECO) with the lowest value of 0.44% (DL4) on Namib soils of the Dry Land system and highest of 9.72% (M4) from humic soils in Eston (Mistbelt system). Soils from the Mistbelt system had a fairly high total carbon than the rest of the soil systems. Amorphous aluminium (Al$_{ox}$) ranged from 416 to 1636 mg L^{-1} (mean = 968 mg L^{-1}) whilst amorphous iron (Fe$_{ox}$) ranged from 481 to 5256 mg L^{-1} (mean = 1978). The soils varied greatly in the amounts of oxalate Al and Fe, and exchangeable bases within the same soil system.

4.3. Phosphorus status and sorption indices

The soils differed in their P status and characteristics expected to affect P retention and release (Table 4.7 to 4.9). This study revealed the very diverse sorption properties occurring in the South Africa sugarcane industry. Extractable P was shown to be adequate for ratoon cane (> 13 mg P L^{-1}) while only few soils showed deficiency for plant cane for Truog P (>31 mg L^{-1}). The majority of the soils studied soil fell under low sorbing soils (PDI > 0.40) according to description used by Meyer and Wood (1989). Values of P sorbed at 0.2 mg P L^{-1} (used in this study as amount of P required to maintain a soil solution P of 0.2 mg P L^{-1}) ranged from very low (23.9 mg kg^{-1} soil) and to high (919.6 mg kg^{-1} soil).

The raw coefficients of determination (r^2) values for individual soils for soil test P measured in mg L^{-1} and P added in kg ha^{-1} (assuming an incorporation depth of 200 mm) ranged from 0.921-1, 0.784-0.999 and 0.899-1 for Truog, Mehlich III and Resin, respectively. Values of P requirement factor (PRF) (Tables 4.7 to 4.9) and were found to vary widely, underlining the magnitude of sorption capacities and their effect in accurately predicting P requirements in the soils of the South African sugarcane industry. The ranges (and mean) of PRF values for the Truog, Mehlich-3 and Resin extractants were 2.26-22.52 (5.84), 1.89-27.17 (7.13) and 4.39-39.68 (11.31) kg P ha^{-1} per unit soil test, respectively.

Table 4.1: Physical properties and textural classes of the studied soils, their soil forms and locations from the *Hinterland* and *Dry Lowveld*.

Sample number	Soil Location	Soil form	Sample density (g mL⁻¹)	Clay %	Silt %	Sand %	Textural Class
				Particle size distribution			
				Clay %	Silt %	Sand %	
			HINTERLAND				
H1	Midlands South (Stony Hill)	Cartref	1.34	10	7	83	Loamy sand
H2	Midlands South (Ukulinga)	Westleigh	1.18	35	24	41	Clay loam
H3	Oribi Flats	Cartref	1.49	9	4	87	Loamy sand
H4	Wartburg	Glenrosa	1.23	14	7	79	Loamy sand
H5	Wartburg	Shortlands	1.27	30	9	67	Sandy clay loam
H6	Wartburg	Westleigh	1.41	16	11	73	Sandy loam
			DRY LOWLANDS				
DL1	Komatipoort	Shortlands	1.18	35	30	35	Clay Loam
DL2	Malelane	Oakleaf	1.14	67	24	9	Clay
DL3	Malelane	Shortlands	1.14	59	24	17	Clay
DL4	Malelane	Namib	1.36	6	6	88	Loamy sand
DL5	Muden	Oakleaf	1.27	22	5	73	Sandy clay loam
DL6	Pongola	Westleigh	1.31	32	16	52	Sandy clay loam
DL7	Pongola	--	1.26	21	8	71	Sandy clay loam
DL8	Pongola	--	1.15	23	8	69	Sandy clay loam
DL9	Tugela	Oakleaf	1.45	8	3	89	Loamy sand

Table 4.2: Physical properties and textural classes of the studied soils, their soil forms and locations from the *Coastal Sands* and *Lowlands*.

Sample number	Soil Location	Soil form	Sample density (g mL^1)	Particle size distribution Clay %	Silt %	Sand %	Textural Class
			COASTAL SANDS				
CS1	Port Shepstone	Katspruit	1.39	15	19	67	Sandy clay loam
CS2	Port Shepstone	Tukulu	1.36	15	12	73	Sandy loam
CS3	Port Shepstone	Mayo	1.08	35	14	51	Sandy clay loam
CS4	Tugela Mouth	Oakleaf	1.23	25	20	55	Sandy clay loam
CS5	Umfolozi	Rensburg	1.18	76	19	5	Clay
CS6	Umfolozi	Oakleaf	1.15	40	19	41	Clay loam
CS7	Umfolozi	Oakleaf	1.15	46	21	33	Clay
			COASTAL LOWLANDS				
CL1	Doornkop	Glenrosa	1.27	21	8	71	Sandy clay loam
CL2	Doornkop	Sweetwater	1.14	28	7	65	Sandy clay loam
CL3	Empangeni	--	1.34	20	3	77	Sandy clay loam
CL4	Empangeni	Glenrosa	1.16	38	13	49	Sandy clay loam
CL5	Gingindlovu	Glenrosa	1.16	19	12	69	Sandy loam
CL6	Gingindlovu	Swartland	1.12	36	20	44	Clay loam
CL7	Mount Edgecombe	Arcadia	1.11	46	14	41	Clay
CL8	Mount Edgecombe	Cartref	1.11	13	4	83	Loamy sand
CL9	Sekela	Cartref	1.35	14	7	79	Loamy sand
CL10	Stanger	Cartref	1.34	8	4	88	Loamy sand

Table 4.3: Physical properties and textural classes of the studied soils, their soil forms and locations from the *Mistbelt* system.

Sample number	Soil Location	Soil form	Sample density (g ml^{-1})	Particle size distribution			Textural Class
				Clay %	Silt %	Sand %	
			MISTBELT				
M2	Eshowe	Inanda	1.25	11	5	85	Loamy sand
M3	Eshowe	Inanda	1.08	8	3	89	Loamy sand
M4	Eston	Nomanci	0.79	23	32	45	Loam
M5	Eston	Kranskop	0.93	31	26	43	Clay loam
M6	Eston	Inanda	1.18	45	24	31	Clay
M7	Inanda	Inanda	1.03	38	35	26	Clay loam

Table 4.4: Selected chemical properties of the soils used in this study: *Hinterland* and *Dry Lowveld*.

Sample number	Soil Location	Soil form	pH 0.01 CaCl$_2$	Total carbon (%)	Ammonium-oxalate extractable (mg L^{-1})		Exchangeable cations (mg L^{-1})				Exch. Acidity (Al+H) (cmol$_c$/L)	Total Cations (cmol$_c$/L)
					Al	Fe	Ca	Mg	K	Na		
				HINTERLAND								
H1	Midlands South (Stony Hill)	Cartref	4.39	0.69	416	481	302	49	70	14	0.26	2.29
H2	Midlands South (Ukulinga)	Westleigh	6.52	1.96	1545	5256	2417	298	126	27	0.12	13.11
H3	Oribi Flats	Cartref	4.19	0.84	825	711	271	62	45	11	0.64	2.63
H4	Wartburg	Glenrosa	5.39	1.29	721	809	425	121	196	12	0.40	3.74
H5	Wartburg	Shortlands	4.43	1.29	1636	2718	686	185	223	12	0.46	5.62
H6	Wartburg	Westleigh	4.81	0.69	664	1895	627	129	205	12	0.13	3.91
				DRY LOWLANDS								
DL1	Komatipoort	Shortlands	6.44	1.93	1875	3901	3375	754	161	481	0.00	23.25
DL2	Malelane/Komati	Oakleaf	6.51	1.88	1964	6067	2281	849	131	167	0.01	16.68
DL3	Malelane/Komati	Shortlands	6.65	1.85	1914	7500	2516	699	186	174	0.01	9.46
DL4	Malelane/Komati	Namib	5.55	0.44	360	574	453	94	49	17	0.01	3.14
DL5	Muden	Oakleaf	4.99	0.69	305		924	226	93	23	0.01	6.83
DL6	Pongola	Westleigh	5.19	0.92	1458	3361	1232	366	106	27	0.04	8.22
DL7	Pongola	--	6.13	0.99	705	2690	2235	510	80	59	0.08	11.68
DL8	Pongola	--	6.14	1.60	1260	2225	1231	346	64	28	0.06	7.38
DL9	Tugela	Oakleaf	3.47	0.76	639	1136	54	11	43	7	1.60	2.11

Table 4.5: Selected chemical properties of the soils used in this study: *Coastal Sand* and *Coastal Lowlands*.

Sample number	Soil Location	Soil form	pH 0.01 CaCl$_2$	Total carbon (%)	Ammonium-oxalate extractable (mg L^{-1}) Al	Fe	Exchangeable cations (mg L^{-1}) Ca	Mg	K	Na	Exch. Acidity (Al+H) (cmol$_c$/L)	Total Cations (cmol$_c$/L)
					COASTAL SANDS							
CS1	Port Shepstone	Katspruit	4.25	0.90	973	2747	588	113	98	24	0.59	4.30
CS2	Port Shepstone	Tukulu	3.79	1.15	1029	1067	140	29	48	8	0.87	2.54
CS3	Port Shepstone	Mayo	5.14	4.49	4775	2101	2441	163	78	19	0.07	14.05
CS4	Tugela Mouth	Oakleaf	5.45	1.37	1106	5243	2290	653	175	60	0.03	13.24
CS5	Umfolozi	Rensburg	5.60	1.60	2346	15776	4116	1607	203	250	0.10	37.24
CS6	Umfolozi	Oakleaf	5.31	1.39	1784	--	2795	930	145	89	0.01	22.41
CS7	Umfolozi	Oakleaf	5.25	1.50	1442	--	2953	977	118	120	0.01	23.63
					COASTAL LOWLANDS							
CL1	Doornkop	Glenrosa	3.92	1.80	1470	2691	355	82	49	17	1.97	5.40
CL2	Doornkop	Sweetwater	4.73	2.17	3966	--	874	94	51	15	0.21	5.54
CL3	Empangeni	--	4.08	1.10	1306	2507	328	90	105	24	0.87	3.24
CL4	Empangeni	Glenrosa	5.11	2.24	1616	--	1816	255	97	24	0.01	11.54
CL5	Gingindlovu	Glenrosa	5.04	2.09	2300	2768	650	147	59	22	0.49	5.56
CL6	Gingindlovu	Swartland	6.20	3.35	2151	5869	2703	286	197	38	0.06	13.93
CL7	Mount Edgecombe	Arcadia	4.86	4.05	2658	5807	3661	254	120	56	0.09	16.90
CL8	Mount Edgecombe	Cartref	3.84	3.76	17	--	754	27	133	13	0.05	3.58
CL9	Sekela	Cartref	4.33	1.19	950	806	360	83	65	11	0.48	3.13
CL10	Stanger	Cartref	4.22	1.14	1055	1078	289	57	43	17	0.81	2.67

Table 4.6: Selected chemical properties of the soils used in this study: *Mistbelt* system.

Sample number	Soil Location	Soil form	pH 0.01 CaCl$_2$	Total carbon (%)	Ammonium-oxalate extractable (mg L^{-1}) Al	Fe	Exchangeable cations (mg L^{-1}) Ca	Mg	K	Na	Exch. Acidity (Al+H) (cmol$_c$/L)	Total Cations (cmol$_c$/L)
M1	Eshowe	Inanda	5.45	3.78	8173	4333	820	224	123	8	0.49	6.30
M2	Eshowe	Inanda	5.67	1.86	3373	3058	1588	204	128	13	0.05	9.01
M3	Eshowe	Inanda	4.29	3.86	8317	6201	402	77	45	18	2.11	4.40
M4	Eston	Nomanci	5.03	9.72	22115	16358	1431	143	213	13	0.16	7.07
M5	Eston	Kranskop	4.82	6.20	14227	12190	909	115	386	14	0.28	6.33
M6	Eston	Inanda	4.37	3.23	3629	6503	1038	244	263	16	0.78	6.10
M7	Inanda	Inanda	4.45	6.47	13627	8591	906	96	202	13	2.37	9.55

Table 4.7: Exchangeable phosphorus and soil sorption indices for the studied soils: *Hinterland* and *Dry Lowveld* systems

Sample number	Soil Location	Soil form	Extractable P (mg P L^{-1}) resin P	Truog P	PSI	PDI	P Sorp. Slope 0.2 (mg P L^{-1})	P requirement factor (kg P ha^{-1} per unit soil test value Truog	Mehlich-3	Resin
					HINTERLAND					
H1	Midlands South (Stony Hill)	Cartref	16.9	21.7	8.54	0.94	40.28	3.18	2.15	7.08
H2	Midlands South (Ukulinga)	Westleigh	14.9	22.9	29.00	0.40	186.45	7.40	9.44	12.71
H3	Oribi Flats	Cartref	13.2	16.5	14.4	0.85	67.60	2.99	2.15	6.78
H4	Wartburg	Glenrosa	10.1	8.5	14.03	0.84	48.25	4.86	4.34	11.09
H5	Wartburg	Shortlands	47.6	59.1	24.36	0.68	139.42	3.86	2.78	7.76
H6	Wartburg	Westleigh	105.6	168.1	11.69	1.54	33.20	3.07	6.38	9.26
					DRY LOWLANDS					
DL1	Komatipoort	Shortlands	21.3	44.7	34.69	0.45	173.80	4.35	6.64	6.89
DL2	Malelane/Komati	Oakleaf	9.8	15.6	38.29	0.27	206.49	6.43	10.10	12.21
DL3	Malelane/Komati	Shortlands	23.9	40.6	40.74	0.29	242.07	6.47	11.78	11.03
DL4	Malelane/Komati	Namib	10.1	20.5	3.13	0.88	23.88	2.74	2.15	4.39
DL5	Muden	Oakleaf	52.7	69.6	15.15	0.59	93.68	3.41	2.55	7.79
DL6	Pongola	Westleigh	15.7	17.2	25.41	0.49	116.28	5.55	7.32	7.82
DL7	Pongola	--	5.3	13.6	13.99	0.58	96.81	4.33	5.91	9.78
DL8	Pongola	--	7.7	11.8	18.51	0.61	127.69	5.06	5.48	10.30
DL9	Tugela	Oakleaf	65.2	87.9	9.18	0.98	74.77	2.78	1.90	5.16

Table 4.8: Exchangeable phosphorus and soil sorption indices for the studied soils: *Coastal Sands* and *Coastal Lowlands* systems

Sample number	Soil Location	Soil form	Extractable P (mg P L^{-1}) resin P	Truog P	PSI	PDI	P Sorp. Slope 0.2 (mg P L^{-1})	P requirement factor (kg P ha^{-1} per unit soil test value) Truog	Mehlich-3	Resin
			COASTAL SANDS							
CS1	Port Shepstone	Katspruit	17.4	28.1	19.63	0.68	90.13	3.62	3.38	11.31
CS2	Port Shepstone	Tukulu	30.4	43.4	18.34	0.81	117.32	3.86	1.89	6.87
CS3	Port Shepstone	Mayo	9.8	10.1	60.17	0.33	372.19	5.75	6.20	15.63
CS4	Tugela Mouth	Oakleaf	19.1	78.4	18.68	0.57	89.65	4.08	5.17	9.11
CS5	Umfolozi	Rensburg	5.5	17.1	49.13	0.17	222.14	7.75	25.77	12.66
CS6	Umfolozi	Oakleaf	8.3	32.2	21.7	0.44	115.14	5.69	10.36	9.78
CS7	Umfolozi	Oakleaf	7.5	29.5	17.98	0.51	132.28	5.94	10.89	9.12
			COASTAL LOWLANDS							
CL1	Doornkop	Glenrosa	19.9	30.8	24.45	0.73	165.15	4.13	2.53	8.13
CL2	Doornkop	Sweetwater	32.2	34.5	61.22	0.42	355.36	4.17	3.33	11.44
CL3	Empangeni	--	18.8	25.9	14.42	0.76	144.23	4.46	2.80	7.85
CL4	Empangeni	Glenrosa	18.8	15.3	2.64	0.36	253.49	6.60	7.99	14.86
CL5	Gingindlovu	Glenrosa	6.0	11.0	28.88	0.65	173.73	5.55	3.38	13.12
CL6	Gingindlovu	Swartland	74.3	222.0	20.67	0.53	223.11	3.78	4.21	9.29
CL7	Mount Edgecombe	Arcadia	18.4	16.5	42.13	0.28	200.84	10.24	15.17	13.51
CL8	Mt Edgecombe	Cartref	6.7	24.4	0.00	0.80	27.58	2.26	2.45	4.52
CL9	Sekela	Cartref	26.5	44.9	16.48	0.78	78.86	2.59	2.05	6.37
CL10	Stanger	Cartref	21.4	30.6	9.68	0.82	99.31	2.65	2.09	6.65

Table 4.9: Exchangeable phosphorus and soil sorption indices for the studied soils: *Mistbelt* system

Sample number	Soil Location	Soil form	Extractable P (mg P L^{-1})		PSI	PDI	P Sorp. Slope 0.2 (mg P L^{-1})	P requirement factor (kg P ha^{-1} per unit soil test value)		
			resin P	Truog P				Truog	Mehlich-3	Resin
					MISTBELT					
M1	Eshowe	Inanda	22.3	28.7	81.32	0.19	626.2	7.47	7.72	18.52
M2	Eshowe	Inanda	33.0	60.3	31.07	0.58	163.98	4.42	3.84	14.08
M3	Eshowe	Inanda	20.0	27.6	93.75	0.28	574.55	6.34	7.73	13.61
M4	Eston	Nomanci	23.3	39.6	403.93	0.05	919.55	22.52	27.17	39.68
M5	Eston	Kranskop	44.6	76.4	184.01	0.09	762.50	20.08	16.67	23.58
M6	Eston	Inanda	20.6	22.2	54.15	0.33	265.37	6.68	8.88	12.72
M7	Inanda	Inanda	31.7	45.5	350.23	0.16	875.60	8.67	18.42	20.70

4.4. Relationship between P requirement factors with soil properties

Table 4.10 presents the combined linear correlation-coefficients (r) between P requirement factors and soil parameters for the five systems included in this study. Phosphorus requirement factors for the different extractants were highly correlated to each other, and were also strongly correlated ($p = 0.01$) with other indices that affect soil P sorption: inversely correlated with PDI (r = -0.65 to -0.70), positively correlated PSI (r = 0.71 to 0.87) and isotherm slope at 0.2 mg P L^{-1} (r = 0.66 to 0.87). Furthermore, strong relationships existed between PRFs and ammonium oxalate extractable aluminium (r = 0.69 to 0.92) and iron (r = 0.75 to 0.93). Values of PRF were also highly significantly ($p = 0.01$) related to soil carbon content (r = 0.67 to 0.87) and inversely related to sample density (r = -0.69 to -0.78).

Linear correlation coefficients per soil system between P requirement factors and soil parameters are shown in Table 4.11-4.15. This was done to test if the above mentioned parameters behave the same throughout the different soil systems. Contrary, the Hinterland soils fairly correlated with PSI having a correlation coefficient (r) ranging from 0.53 to 0.77, inversely correlated with PDI (r = -0.16 to -0.70), positively correlated with organic carbon (OC) (r = 0.66 to 0.95) and clay (r = 0.56 to 0.75). In contrast to the Hinterland system, the PRF values from all other soils systems (i.e. Dry Lowlands, Coastal Sands and Lowlands, and Mistbelt) strongly correlated with PDI (Tables 4.12 to 4.15). Strangely, PRF values for all the extractants poorly correlated with clay % for the Mistbelt soils. Organic carbon (OC) correlated relatively poorer to PRF in soils from the Coastal Sands and Coastal Lowlands systems. Amorphous aluminium (Al_{ox}) poorly correlated with PRF values for three soils systems (i.e., Hinterland, Coastal Sands and Coastal Lowlands) while strongly correlated with PRF values for the Dry Lowlands and the Mistbelt soil systems. Amorphous iron (Feox) strongly correlated with all the extractants across the soils systems. Surprisingly, PRF values for three soils systems (i.e., Hinterland [except for PRF_{Truog}], Coastal Sands [except PRF_{Resin}] and Coastal Lowlands [except PRF_{Resin}]) correlated poorly with the standard P requirements (P-Sorption$_{Slope\ 0.2}$).

Table 4.10: Linear correlation coefficients describing relationships of P sorption parameters with selected soil variables for all the studied soils (*n=39*)

Parameters	Sample density	Carbon	Clay	Al_{ox}	Fe_{ox}	PDI	PSI	Slope 0.2	PRF_{Truog}	$PRF_{Mehlich\ III}$
Carbon	-0.86^{**}									
Clay	-0.51^{**}	$0.26^{n.s}$								
Al_{ox}	-0.76^{**}	0.92^{**}	$0.13^{n.s}$							
Fe_{ox}	-0.76^{**}	0.71^{**}	0.64^{**}	0.72^{**}						
PDI	0.80^{**}	-0.65^{**}	-0.69^{**}	-0.62^{**}	-0.75^{**}					
PSI	-0.68^{**}	0.87^{**}	$0.14^{n.s}$	0.95^{**}	0.69^{**}	-0.56^{**}				
Slope 0.2	-0.78^{**}	0.89^{**}	$0.27^{n.s}$	0.95^{**}	0.70^{**}	-0.72^{**}	0.90^{**}			
PRF_{Truog}	-0.78^{**}	0.82^{**}	0.31^{*}	0.86^{**}	0.81^{**}	-0.66^{**}	0.78^{**}	0.79^{**}		
$PRF_{Mehlich\ III}$	-0.69^{**}	0.67^{**}	0.63^{**}	0.69^{**}	0.93^{**}	-0.70^{**}	0.71^{**}	0.66^{**}	0.79^{**}	
PRF_{Resin}	-0.78^{**}	0.87^{**}	$0.22^{n.s}$	0.92^{**}	0.75^{**}	-0.65^{**}	0.87^{**}	0.87^{**}	0.89^{**}	0.75^{**}

**significant at $p = 0.01$; *significant at $p = 0.05$; n.s. = not significant; Al_{ox} = ammonium-oxalate extractable aluminium; Fe_{ox} = ammonium-oxalate extractable iron; Slope 0.2 = sorption slope at 0.2 mg P L^{-1}.

Table 4.11: Linear correlation coefficients describing relationships of P sorption parameters with selected soil variables from the *Hinterland* soil system

Parameters	Sample density	Carbon	Clay	Al_{ox}	Fe_{ox}	PSI	PDI	Slope 0.2	PRF_{Truog}	$PRF_{Mehlich\ III}$
Carbon	-0.83									
Clay	-0.71	0.85								
Al_{ox}	-0.53	0.78	0.93							
Fe_{ox}	-0.61	0.83	0.94	0.81						
PDI	-0.62	0.90	0.95	0.97	0.90					
PSI	0.62	-0.80	-0.62	-0.67	-0.52	-0.74				
Slope 0.2	-0.61	0.87	0.94	0.94	0.90	0.98	-0.80			
PRF_{Truog}	-0.82	0.95	0.75	0.59	0.81	0.77	-0.70	0.76		
$PRF_{Mehlich\ III}$	-0.52	0.66	0.62	0.39	0.81	0.55	-0.16	0.51	0.78	
PRF_{Resin}	-0.75	0.78	0.56	0.35	0.67	0.53	-0.33	0.46	0.89	0.88

Table 4.12: Linear correlation coefficients describing relationships of P sorption parameters with selected soil variables from the *Dry Lowlands* soil system

Parameters	Sample density	Carbon	Clay	Al_{ox}	Fe_{ox}	PSI	PDI	Slope 0.2	PRF_{Truog}	$PRF_{Mehlich\ III}$
Carbon	-0.86									
Clay	-0.79	0.86								
Al_{ox}	-0.72	0.91	0.93							
Fe_{ox}	-0.74	0.79	0.90	0.87						
PDI	-0.77	0.89	0.98	0.94	0.94					
PSI	0.86	-0.78	-0.94	-0.80	-0.92	-0.92				
Slope 0.2	-0.81	0.91	0.92	0.90	0.96	0.97	-0.88			
PRF_{Truog}	-0.78	0.76	0.85	0.85	0.89	0.87	-0.90	0.87		
$PRF_{Mehlich\ III}$	-0.76	0.80	0.90	0.89	0.98	0.91	-0.91	0.92	0.96	
PRF_{Resin}	-0.83	0.69	0.66	0.61	0.76	0.68	-0.82	0.76	0.87	0.80

Table 4.13: Linear correlation coefficients describing relationships of P sorption parameters with selected soil variables from the *Coastal Sands* soil system

Parameters	Sample density	Carbon	Clay	Al_{ox}	Fe_{ox}	PSI	PDI	Slope 0.2	PRF_{Truog}	$PRF_{Mehlich\ III}$
Carbon	-0.67									
Clay	-0.67	0.20								
Al_{ox}	-0.72	0.97	0.39							
Fe_{ox}	-0.33	-0.16	0.91	0.04						
PDI	-0.58	0.82	0.56	0.92	0.37					
PSI	0.78	-0.49	-0.92	-0.65	-0.75	-0.77				
Slope 0.2	-0.64	0.94	0.42	0.98	0.11	0.95	-0.64			
PRF_{Truog}	-0.72	0.31	0.98	0.49	0.83	0.62	-0.91	0.52		
$PRF_{Mehlich\ III}$	-0.45	-0.01	0.96	0.20	0.97	0.45	-0.83	0.26	0.92	
PRF_{Resin}	-0.53	0.78	0.42	0.86	0.24	0.89	-0.72	0.84	0.48	0.32

Table 4.14: Linear correlation coefficients describing relationships of P sorption parameters with selected soil variables from the *Coastal Lowlands* system

Parameters	Vol. Weight	Carbon	Clay	Al_{ox}	Fe_{ox}	PSI	PDI	Slope 0.2	PRF_{Truog}	$PRF_{Mehlich\ III}$
Carbon	-0.88									
Clay	-0.67	0.68								
Al_{ox}	-0.40	0.14	0.44							
Fe_{ox}	-0.89	0.94	0.97	0.86						
PDI	-0.23	0.07	0.23	0.93	0.68					
PSI	0.66	-0.52	-0.89	-0.72	-0.89	-0.53				
Slope 0.2	-0.42	0.10	0.55	0.91	0.94	0.72	-0.78			
PRF_{Truog}	-0.43	0.44	0.78	0.49	0.67	0.40	-0.80	0.44		
$PRF_{Mehlich\ III}$	-0.49	0.60	0.84	0.36	0.71	0.28	-0.81	0.32	0.94	
PRF_{Resin}	-0.49	0.22	0.69	0.69	0.66	0.47	-0.85	0.74	0.81	0.66

Table 4.15: Linear correlation coefficients describing relationships of P sorption parameters with selected soil variables from the *Mistbelt* soil system

Parameters	Vol. Weight	Carbon	Clay	Al$_{ox}$	Fe$_{ox}$	PSI	PDI	Slope 0.2	PRF$_{Truog}$	PRF$_{Mehlich III}$
Carbon	-0.96									
Clay	0.23	-0.14								
Al$_{ox}$	-0.98	0.98	-0.27							
Fe$_{ox}$	-0.94	0.95	-0.16	0.92						
PDI	-0.83	0.94	-0.07	0.92	0.82					
PSI	0.90	-0.85	-0.15	-0.84	-0.79	-0.73				
Slope 0.2	-0.89	0.88	-0.03	0.91	0.75	0.87	-0.92			
PRF$_{Truog}$	-0.92	0.87	-0.26	0.88	0.95	0.69	-0.77	0.70		
PRF$_{Mehlich III}$	-0.92	0.99	-0.07	0.96	0.95	0.95	-0.81	0.84	0.86	
PRF$_{Resin}$	-0.92	0.93	-0.37	0.94	0.90	0.84	-0.71	0.74	0.89	0.92

Al$_{ox}$ = ammonium-oxalate extractable aluminium; Fe$_{ox}$ = ammonium-oxalate extractable iron; Slope 0.2 = sorption slope at 0.2 mg P L^{-1}.

4.5. Prediction of P requirement factors using mid-infrared (MIR) spectroscopy

The relationship between the actual values for PRF obtained during laboratory incubations (*x-axis*), and the corresponding values predicted by the mid infra-red spectroscopy method (*y-axis* are shown in Figures 4.1 to 4.3. The predictions of PRF using infrared spectra were statistically sound, with highest coefficient of determination (r^2_c = 0.99) and residual prediction deviation (RPD_c = 8.87) and lowest root mean square error of estimation ($RMSEE_c$ = 0.73) values for PRF_{Resin} with the calibration dataset (Fig. 4.1a). Calibration of PRF_{Truog} and $PRF_{Mehlich-III}$ resulted in very similar results but with lower precision than PRF_{Resin}. For test-set validation, predictions were good for PRF_{Truog} and $PRF_{Mehlich-III}$ with PRF_{Resin} having a better prediction than the other two extractants.

Fit vs True / Truog PRF [kg/ha] / Calibration

Predicted values (kg/ha)

$y = 0.864x + 0.447$

Rank: 8   R² = 86.78   RMSEE = 1.52   RPD: 2.75

Actual values (kg/ha)

Prediction vs True / Truog PRF [kg/ha] / Cross Validation

Predicted Value (kg/ha)

$y = 0.823x + 0.567$

Rank: 8   R² = 80.83   RMSECV = 1.76   Bias: 0.041   RPD: 2.28

Actual value (kg/ha)
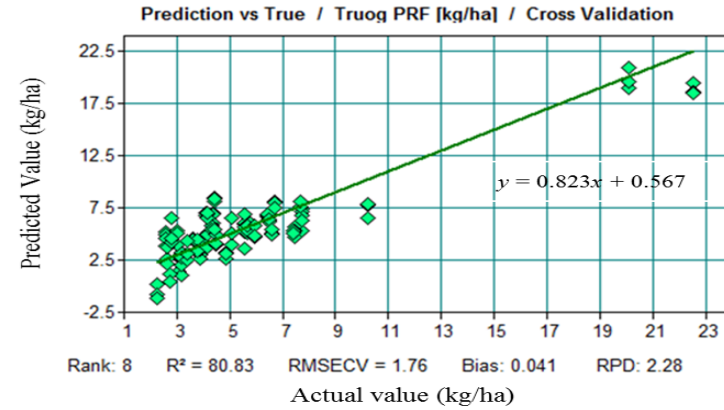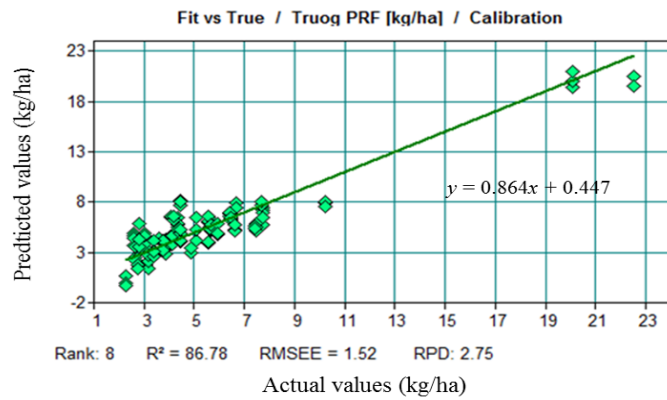
Figure 4.1 Illustration of the calibrations (**a**) and cross validations (**b**) of PRF for the Truog-extractant using MIR; actual PRF (kg P ha^{-1}) (*x-axis*) versus predicted PRF (kg P ha^{-1})(*y-axis*).

Fit vs True / Mehlich P [kg/ha] / Calibration

Predicted value (kg/ha)

$y = 0.865x + 0.458$

Rank: 11   R² = 91.63   RMSEE = 1.97   RPD: 3.46

Actual value (kg/ha)

Prediction vs True / Mehlich P [kg/ha] / Cross Validation

Predicted value (kg/ha)

$y = 0.805x + 0.657$

Rank: 11   R² = 80.19   RMSECV = 2.87   Bias: -0.0157   RPD: 2.25

Actual value (kg/ha)
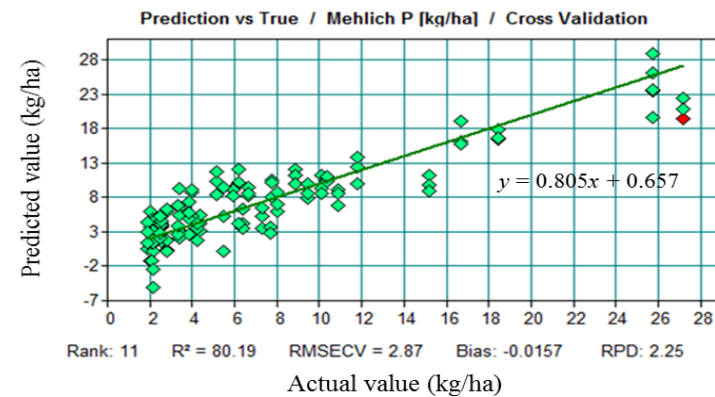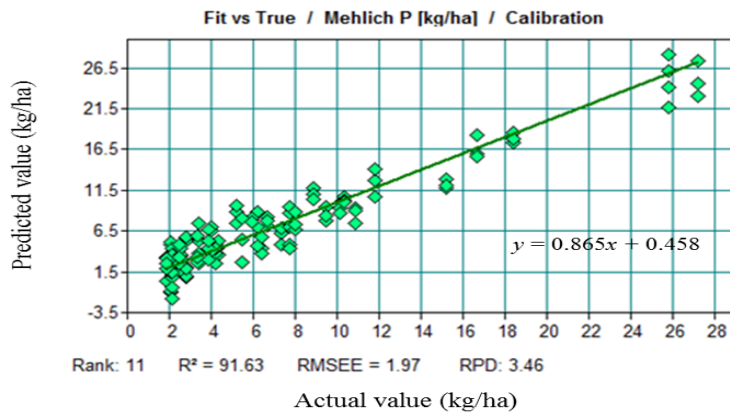
Figure 4.2 Illustration of the calibrations (**a**) and cross validations (**b**) of PRF for the Mehlich-III-extractant using MIR; actual PRF (kg P ha^{-1}) (*x-axis*) versus predicted PRF (kg P ha^{-1})(*y-axis*).

Fit vs True / Resin P [kg/ha] / Calibration

$y = 0.920x + 0.414$

Rank: 16　　R² = 98.73　　RMSEE = 0.73　　RPD: 8.87

Actual value (kg/ha)

(a)

Prediction vs True / Resin P [kg/ha] / Cross Validation

$y = 0.848x + 0.776$

Rank: 16　　R² = 84.71　　RMSECV = 2.35　　Bias: 0.117　　RPD: 2.56
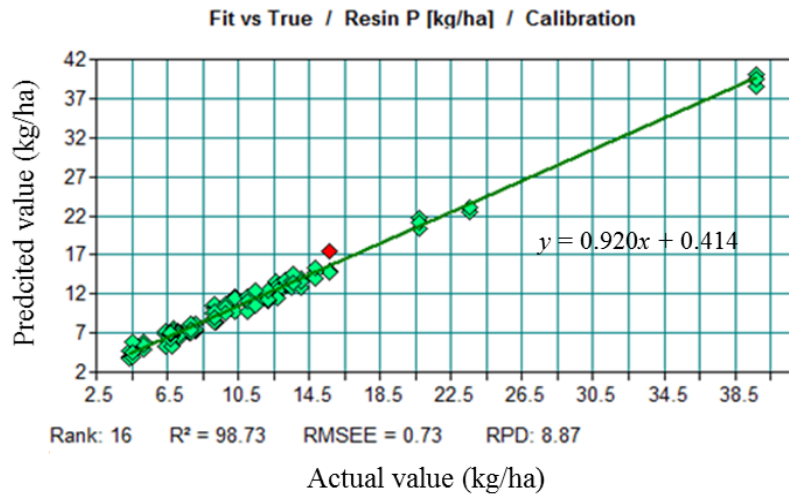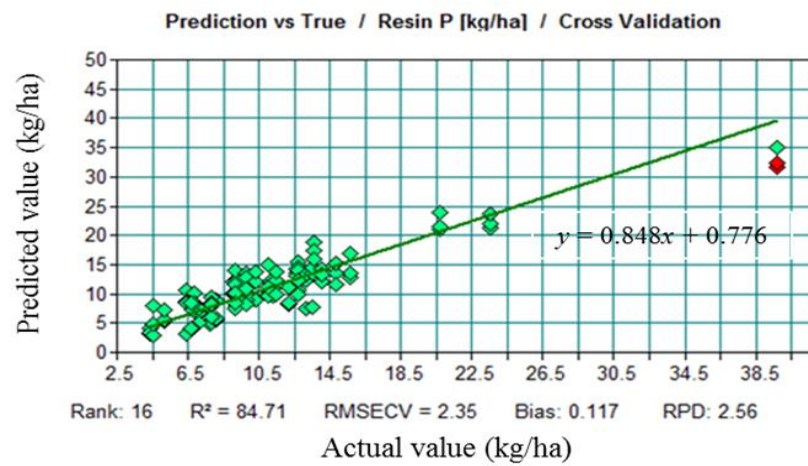
Actual value (kg/ha)

(b)

Figure 4.3 Illustration of the calibrations (**a**) and cross validations of PRF for the Resin-extractant using MIR (**b**); actual PRF (kg P ha^{-1}) (*x-axis*) versus predicted PRF (kg P ha^{-1})(*y-axis*)

CHAPTER 5: DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

DISCUSSION

Managing phosphorus (P) supplies to the sugarcane crop presents particular challenges for agronomists, since not only is P the most expensive of the macro-nutrients, but the reviewed literature showed that wide variations in soil properties greatly complicate the process of accurately estimating fertiliser P requirements.

The acidic to neutral soil pH values (Tables 4.1-4.3) observed in the studied soils confirm earlier reports on data from the KwaZulu-Natal Province that showed a high number of soils were in this pH range (Johnston *et al*., 1991; Bainbridge *et al*., 1995; Henry and Smith, 2006; van der Laan and Miles, 2010). It did not come as a surprise that most soils from the *Dry Lowlands* had the highest pH values due to their geo-climatic conditions with some natural lime in them (Appendix 1). The effective cation exchange capacity (ECEC) of the studied soils was low and similar to the values reported by Johnston *et al*. (1991). These low ECEC values could mainly be attributed to higher rainfall (and irrigation) and warm temperatures that are normally experienced in the eastern parts of South Africa which lead to intense leaching of bases and accumulation of exchangeable Al in these soils (Gichangi *et al*., 2008). Furthermore, the low ECEC values could be attributed to the low clay content observed across the studied regions (Appendix 2), in which only 31% of the soil samples having clay content $\geq 35\%$. However, use of lime and/or gypsum and organic amendments in the sugar industry can drastically improve the ECEC of these soils.

Soil organic carbon (OC) contents varied widely from low to high, with the range being 0.44 to 9.72%. Soils with humic A horizon, such as Inanda, Kranskop, Nomanci (SCWG, 1991), have the highest soil organic carbon than other soil forms. Soil OC concentrations are often cited as major indicators of soil quality. Sixty-seven percent of these soils had soil OC values below 2%, which is the threshold value below which most soils are prone to aggregate destabilisation and reduced crop yields (Janzen *et al*., 1992; Howard and Howard, 1990; Nthenjane, 2012). However, soils from the Coastal Lowlands and Mistbelt systems have the the highest percentage of soil samples with adequate-to-high soil organic carbon compared to other regions, with >64% percent of the samples having a soil organic carbon content above 2%.

Sixty-two percent of studied soils from the sugarcane industry were deficient in P for the plant-cane crop (threshold value <31 mg P l^{-1}, Truog P), but only 8% of the samples were deficient in P for the ratoon crop P-requirements (threshold <13 mg P L^{-1}) (Tables 4.7-4.9). Deficient levels of P are infrequent in ratoon crops (van der Laan and Miles, 2010). Of major concern, is that, 31% of these soils had extractable P levels above 41 mg P l^{-1} (Truog), a value empirically selected to indicate high levels and pose some environmental threat.

Phosphorus adsorption measurements and glasshouse studies by other researchers have indicated that soils with the same extractable P levels do not necessarily have similar P requirements. Differences in P requirements are mainly attributed to the need to overcome the effects of P retention arising from the sorption of phosphate ions by the sesquioxides and organic matter. The range (and mean for all the soil systems) for the PRF values for the Truog, Mehlich III and Resin extractants was 2.26-22.52 (5.84), 1.89-27.17 (7.13) and 4.39-39.68 (11.31) kg P ha^{-1} per mg P L^{-1}, respectively (Table 4.7 to 4.9). The amounts P fertiliser required to increase a soil P-test by 1mg P l^{-1} in solution were in the range found by other authors for the KwaZulu-Natal soils (Johnston *et al*., 1991; Henry and Smith, 2004). Johnston *et al*. (1991), for example, using three different P-extractants (i.e. Ambic, Bray 1 and Truog) reported values ranging from 2.5-37.9 (13.4), 2.0-17.7 (7.0) and 2.3-30.3 (9.9), respectively.

The findings of this study have also confirmed the extensive literature that soils with the same or similar extractable Resin P levels (DL1, DL3, M1, M4, M6 and CL10) would not necessarily have the same P requirements due to sorption effects (Appendix 5). It is interesting to note that, of the 39 soil samples collected across the sugarcane industry, only 5.13% have PRF$_{Truog}$ above 10 kg P ha^{-1} per mg P L^{-1}, 15.40 % for PRF$_{Mehlich}$ while 46.15% have PRF$_{Resin}$ concentration above 10 kg P ha^{-1} per mg P L^{-1}.The PRF values for Troug extractant were consistently lower than those of Resin extractant for all the studies soils. This may be ascribed to the pH status of these soils and confirm the findings made by Miles *et al*. (2013) that at pH values >5 (most of the study soils have pH > 5), Truog-extractable P tends to overestimate plant available P on high pH soils due probably to the solubilisation of plant-unavailable calcium phosphate, thus underestimating the sorption effects of a particular soil (Meyer and Wood, 1989).

Sorption categories developed by Meyer and Wood (1989) in their twenty-eight 3N x 3P x 3K factorial experiments, using the Reeve and Sumner (1970) phosphorus desorption index (PDI), were applied to the soils used in this study. Soils with PDI < 0.2, 0.20-0.40 and > 0.40

are classified as high, moderate, and low P-fixing soils, respectively. A majority (69%) of the soils in the sugarcane industry was classed as low P-fixing soils, 18% as moderate P-fixing soils while the remaining 13% were classed as strong P-fixing soils (Appendix 6). The low number of strongly P-fixing soils in the South African sugarcane industry could be a result of saturation of fixation sites through large quantities of animal manures used (mainly chicken manure and filtercake) in combination with relatively high average pH values (pH>5.0 for all the regions), which could lead to limited sorption sites and have limited solubility of Al and Fe. Moreover, with sugarcane being a ratooning crop (minimum soil disturbance for a number of years), accumulation and saturation of adsorption sites should be expected at the very surface where fertiliser P is applied over the ratooning cycles. These results clearly concur with the findings by Meyer (1980) on the relationship between PDI and P sorption in soils. It has been observed that higher PRF values were associated with strongly P-fixing soils (PDI <0.2) while the lowest PRF values were associated with high PDI (>0.40) values. Indeed, PDI and PRF were closely and inversely correlated with the coefficient of correlation (r) ranging from -0.65 to -0.70 (Table 4.10).

It has been established from the PRF values obtained in this study (Appendix 6) that, on average, an application of 13.30 kg P ha^{-1}, 19.15 kg P ha^{-1} and 23.03 kg P ha^{-1} is required to raise the Truog P, Mehlich P and Resin P levels (respectively) by 1 mg P L^{-1} in the plough layer of strongly P-fixing soils (PDI<0.20), while about half this rate is sufficient for moderately P-fixing soils (PDI 0.20-0.40).For the low P-fixing soils (PDI>0.40), four-times less fertiliser P is required to raise the soil P-test by 1mg P L^{-1} compared to the high P-fixing soils (PDI<0.20) for the respective P-extractants. It is important to keep in mind that PRF (derived from isotherm slope) is a relatively permanent characteristics and provides a reliable reflection of a soil's sorption characteristics (Bache and Williams, 1971).While this may be permanent for "virgin" soils, P management could affect PRF if, for example, large quantities of manures, rich in P, are added to the soil, saturating sorption sites.

Soils with a humic A-horizon such as M4 (Nomanci soil form), M5 (Kranskop soil form) and M7 (Inanda soil form) (SCWG, 1991) and high oxalate-extracted (amorphous) aluminium contents (above 10 000 mg L^{-1}) (Tables 4.4 to 4.6) were found to be the highest P sorbing and would require high amounts of fertiliser (or manure) P to increase their soil test by 1mg/L. This finding concurs with the finding by other authors on the South African soils (Bainbridge *et al*., 1995; Gichangi *et al*., 2008). Haynes and Swift (1989) in their study on the effect of pH and drying on adsorption of phosphate by aluminium-organic matter associations

suggested that this could be caused by an active participation of organic matter in P sorption through Al-organo complexes by providing additional sites for sorption. In contrast, soils with high sand fractions have the lowest PRF values. This is no surprise as it have been well established that sandy soils have lower P-sorbing capacity than clayey soils, as sand is a relatively inert material.

Various soil properties known to be responsible for P-sorption in soils were correlated with PRF values for the three extractants. While the correlations among the three extractants were significant at the 99% significance level (p = 0.01), PRF values for the three extractants were also strongly correlated with other soil properties that are known to be responsible for P-sorption (Tables 4.10 to 4.15). The correlation coefficients (r) for the correlations presented in Table 4.10 are understandably lower for the combined correlations compared to correlations given in Tables 4.11-4.15 for the individual soil systems in the sugarcane industry. In Table 4.11, the P requirement factors for the three extractants inversely and significantly correlated with PDI (r = 0.65 to 0.70), positively correlated to PSI (r = 0.71 to 0.87) and isotherm slope at 0.2 mg P L^{-1} (r = 0.66 to 0.87). Isotherm slope and PSI are soil indices which express the soil's ability to sorb P and the buffering capacity of the soil with respect to phosphorus, which is mainly governed by crystalline clay compounds, oxyhydroxides, or carbonates (Holford and Mattingly, 1975). Therefore, the higher the ability for the soil to sorb P the more fertiliser will be required to raise soil test P by 1 mg P L^{-1}. The index derived by Reeve and Sumner (1970), PDI, measures the ability of the soil to release sorbed P into solution. The more the soil releases P into the soil solution (PDI > 0.40) the lower the fertiliser P will be required to raise a soil test by 1 mg P L^{-1}, hence the inverse correlation between PDI and PRF. These sorption indices (i.e., PSI, PDI) directly control the retention and release of soil P by soil constituents into soil solution.

Although four of the studied soil systems show a very strong relationship between soil clay content and P-sorption (Table 4.11 to 4.15), it is interesting to note that for the Mistbelt soil system a poor correlation existed between clay content and PSI (r = -0.15), PDI (r = -0.07), sorption at slope 0.2 mg/L (r = -0.03), PRF$_{Truog}$ (r = -0.26), PRF$_{Mehlich}$ (r = -0.07) and PRF$_{Resin}$ (r = -0.37). These findings are in contrary to the many research articles in the literature, which showed a strong relationship between clay content and P soil sorption. These results concur with the findings by many authors who found strong correlations between organic carbon, Al$_{ox}$ and soil texture on P sorption (Johnston *et al*., 1991; Bainbridge *et al*., 1995; Gichangi *et al*., 2008). As mentioned earlier, soils with high aluminium and iron oxides and

high organic carbon tend to have more affinity to sorb P by providing more adsorption sites to applied P, hence the strong positive correlation with PRF values. Sample density has been shown to provide a reasonable estimate of clay content in the soil (the higher the sample density, the more sandier the soil is, and vice versa) (Manson *et al*., 2012). The inverse relationship between volume weight and PRF values showed that the lower the soil density (high clay content), the higher the PRF value of the particular soil.

Oxalate-extractable aluminium (Al_{ox}) has been widely reported to be a reliable indicator of P fixation in soils. In this respect it is noteworthy that the Fertiliser Advisory Services of SASRI and Cedara were able to successfully estimate Al_{ox} using mid-infrared reflectance (MIR) spectroscopy for routine soil analyses. Because of the strong correlation between PRF values and Al_{ox} and since the method of determining PRF is time consuming and laborious, the use of MIR to predict PRF values was evaluated. With the six-week laboratory incubations being laborious for accurate measurements of soil PRF values, the strong correlation between PRF and routinely measured soil parameters could be used to predict PRF. Encouragingly, fairly robust calibrations were developed for all three extractants. The PRF_{Truog}, $PRF_{Mehlich}$ and PRF_{Resin} calibrations and validations are shown in Figures 4.1 to 4.3. The r^2 values of 0.87, 0.92, and 0.99 and a residual prediction deviation (RPD) of 2.75, 3.46, and 8.87 were obtained for PRF_{Truog}, $PRF_{Mehlich}$ and PRF_{Resin}, respectively (Table 4.17). The cross validation of the use of MIR to predict PRF in soils gave an r^2 of 0.81, 0.80 and 0.85 and a residual prediction deviation (RPD) of 1.76, 2.87 and 2.35 for PRF_{Truog}, $PRF_{Mehlich}$ and PRF_{Resin}, respectively. The more RPD approaches 3.0, the better is the model of prediction for a certain soil property (Janik and Skjemstad, 1995; OPUS Spectroscopy Software User Manual, version 6, 2006). This is a particularly exciting development in terms of the prediction of PRF in routine soil testing, since now PRF can easily be estimated within a matter of seconds using MIR. It is noteworthy that the $PRF_{Mehlich}$ provided the highest RPD followed by PRF_{Resin} for MIR calibration, however, the Mehlich-3 method has not been employed yet for routine analysis by FAS.

CONCLUSIONS

Establishing the phosphorus (P) requirements of sugarcane in southern Africa presents particular challenges for agronomists, since not only is P the most expensive of the macro-nutrients, but wide variations in soil properties imply variable availability of applied P for crop uptake. This dissertation was concerned with the basic (mainly chemical) analysis of 39 topsoils from areas of the South African sugar belt and measurements of their phosphate sorption and desorption characteristics with a view to estimate their phosphorus requirement factors (PRF). In addition, mid-infrared (MIR) spectroscopy was investigated as a predictive tool for quicker and more cost-effective means of obtaining PRFs.

Thirty-nine topsoils from irrigated and rainfed areas were subjected to detailed chemical analyses. Phosphorus immobilization was determined using sorption isotherms, single point immobilization indices and glasshouse incubations. Phosphorus sorption was poorly related to clay contents, and reasonably well-related to soil sample density and oxalate extractable aluminium and iron (Fe); however, an outstanding feature of the results was the evidence of the major role of oxalate-extractable aluminium (Al) in controlling P sorption in all soils, regardless of their origin and properties. Phosphorus sorption in soils with >3% C was found to be four- to six-fold higher than in soils with lower C levels. The findings presented contribute to an understanding of P fixation mechanisms in industry soils, and provide an explanation for the recurring P requirement observed on higher organic matter soils.

Recommendations for future research

Further studies should:

- Collect more soil samples with varying PRF values, including those from other parts of South Africa (non-sugarcane regions), for inclusion in MIR calibrations in order to improve the models' reliability.

CHAPTER 6: REFERENCES

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APPENDICES

Appendix 1: Soil Systems in the Sugar Belt (SASRI Soils bulletin no. 19, 1999)

The distribution of soils in the sugar industry is not related to soil parent materials alone but also to other factors. A soil system refers to an association of soils that coincide with geographical areas of similar climate, topography and age of the land surface. Five systems describe the studied soils.

Coastal Sands System

- Includes all Recent Sands and soil derived from Cretaceous sediments raised above sea level two million years ago.
- Associated with a young land surface, which is wide in the north, and narrow and discontinuous in the south.
- Occurs at low altitude in a maritime climate.
- Many soils derived from wind-blown coastal dunes are less than 4 000 years old.

Coastal Lowlands System (formerly Umzinto Coast Lowlands)

- Area inland from coastal sands to ±300 metres altitude.
- Has strong maritime influence and mainly frost free.
- Soils shallow and less than 18 000 years old showing great variability as geologically complex.
- Strong pattern of ancient termitaria (iziduli) on lighter textured soils.

Hinterland System (formerly Umzinto Midlands)

- Areas mainly between 300 to 950 metres altitude, with topography undulating to fairly steep.
- Occurs on an older land surface than the Coastal Lowlands System.
- Soils usually deeper but variable with strong iziduli pattern.
- Frost occurs in the west and at higher altitudes.

**Mistbelt System** (formerly Nottingham System)

- Soils very old and associated with the ancient African land surface.
- Climate cool and moist with mist and topography gentle.
- Soils uniform, even when associated with different parent materials.
- Many soils with thick or thin humic topsoil while subsoil often deeply weathered with apedal structure.

Dry Lowveld System (formerly Komatipoort System)

- Soils occur in low rainfall areas where evaporation exceeds precipitation and require irrigation to produce economic crops.
- On young land surfaces mainly below 380 m altitude.
- Soils mostly shallow, often stony, strongly structured and contain free lime.
- Occur on the same land surface as Coastal Lowlands System.

Note: All areas within the cane belt have been mapped on small scale maps. These maps are designed to give only an approximate distribution of the main Systems but, if topography and soil types are both observed carefully in the field, the accuracy and detail of the System Map can be greatly improved. Systems mapping is useful to describe a large group of soils that all developed under similar circumstances even though they may differ in parent materials and other characteristics.

Appendix 2: Phosphorus requirement factors (PRF$_{Resin}$) (kg P ha^{-1} per unit soil test) for a range of selected soils with similar exchangeable Resin P levels (*n = 6*).
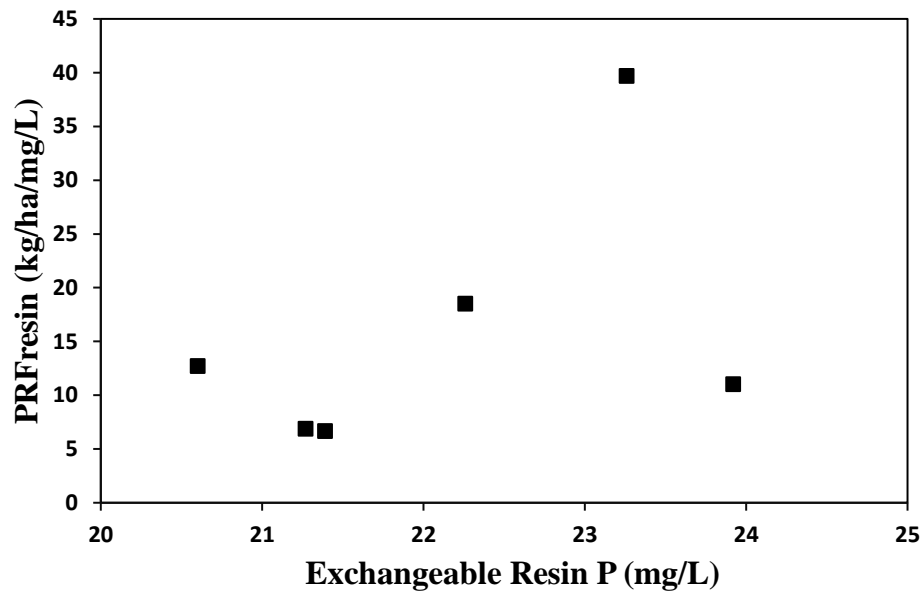
Figure 5: Phosphorus requirement factors (PRF$_{Resin}$) for a range of soils with similar extractable Resin P levels

Appendix 3: Phosphorus desorption indexes of the studied soils and their P requirement factors (*n = 39*).

Sample Id	PDI	PRF$_{Truog}$	PRF$_{Mehlich-3}$	PRF$_{Resin}$
PDI < 0.20				
Q41	0.05	22.52	27.17	39.68
Q42	0.09	20.08	16.67	23.58
Q48	0.17	7.75	25.77	12.66
Q84	0.16	8.67	18.42	20.70
Q61	0.19	7.47	7.72	18.52
Mean	**0.13**	**13.30**	**19.15**	**23.03**
PDI 0.20 - 0.40				
Q54	0.33	6.68	8.88	12.72
Q73	0.40	7.40	9.44	12.71
Q116	0.27	6.43	10.10	12.21
Q36	0.33	5.75	6.20	15.63
Q79	0.28	10.24	15.17	13.51
Q130	0.36	6.60	7.99	14.86
Q114	0.28	6.34	7.73	13.61
Mean	**0.32**	**7.06**	**9.36**	**13.61**
PDI >0.40				
Q1	0.84	4.86	4.34	11.90
Q8	0.68	3.86	2.78	7.76
Q10	1.54	3.07	6.38	9.26
Q92	0.94	3.18	2.15	7.08
Q109	0.85	2.99	2.15	6.78
Q58	0.49	5.55	7.32	7.82
Q102	0.58	4.33	5.91	9.78
Q104	0.61	5.06	5.48	10.30
Q29	0.45	4.35	6.64	6.89
Q124	0.88	2.74	2.15	4.39
Q127	0.98	2.78	1.90	5.16
Q26	0.68	3.62	3.38	11.31
Q35	0.81	3.86	1.89	6.87
Q128	0.44	5.69	10.36	9.78
Q129	0.51	5.94	10.89	9.12
Q38	0.57	4.08	5.17	9.11
Q134	0.80	2.26	2.45	4.52
Q83	0.73	4.13	2.53	8.13
Q131	0.42	4.17	3.33	11.44
Q111	0.82	2.65	2.09	6.65
Q66	0.65	5.55	3.38	13.12
Q70	0.53	3.78	4.21	9.29
Q17	0.78	2.59	2.05	6.37

Q107	0.76	4.46	2.80	7.85
Q113	0.58	4.42	3.84	14.08
Q132	0.59	3.41	2.55	7.79
Mean	**0.71**	**3.98**	**4.16**	**8.56**