

**POTASSIUM RESERVES AND FIXATION CAPACITY IN SOILS OF  
THE SOUTH AFRICAN SUGAR INDUSTRY AND POTENTIAL FOR  
THEIR INCLUSION IN SOIL TESTING AND FERTILIZER  
RECOMMENDATIONS**

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Submitted in fulfilment of the requirements for the degree of

**Doctor of Philosophy**

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January, 2018

## DECLARATION – PLAGIARISM

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**Dr Neil Miles (Co-Supervisor)**

## **ACKNOWLEDGEMENTS**

I would like to thank the following people and organisations for their assistance:

God for granting me the ability to complete this. Proverbs 4: 7 “Wisdom is the principal thing; therefore get wisdom: and with all your getting get understanding” (New King James Version).

South African Sugarcane Research Institute (SASRI) for financial assistance and opportunity to pursue this study;

Prof P Muchaonyerwa for his invaluable supervision throughout the course of this work: your insights and lessons are appreciated;

Dr N Miles for his supervision, advices, encouragement, and for believing in me and my capabilities: your mentorship and guidance is treasured;

SASRI staff for assistance on various aspects of this study particularly Drs Sandile Mthimkhulu, Peter Tweedle, Ashiel Juman, Ms Nikki Sewpersad, Ms Tashmeen Cooper, Ms Gayshree Naidoo, Mrs Orlona Jele, Mr Phumelela Dlungele, Mr Lwazi Poswa, and Mr Wiseman Goba;

Last but not least, my friends particularly Mpaki Elephant, Dr N Mathaba, Dr Alex Xulu, Mr Linda Dlamini, Mr Sandile Mthembu, Mr Sakhile Hlalukane, Ms Zama Khoza, Ms Amanda Swana; my family and Ms Bongiwe Shelembe, the support you all have given me is duly acknowledged and fully appreciated; I am grateful.

## **DEDICATIONS**

**I would like to dedicate this work to my late mother Masekantshi Elephant;  
your passing away left a hole that cannot be filled; you will always be  
remembered for love, patience, good heart, and insights**

**You groomed and raised me despite difficulties and hardships**

**You were the wind beneath my wings**

## ABSTRACT

In the South African sugar industry, some improvements in predicting potassium (K) requirements have been achieved using clay content and base status modifiers to soil K thresholds. However, indications are that inclusion of measurements of non-exchangeable K reserves ('reserve K') and K fixation could further improve the predictions. Knowledge gaps exist in the literature regarding inclusion of reserve-K and K fixation when formulating K requirements. The measurement of reserve-K and K fixation capacity is laborious and time consuming, and these considerations have limited their inclusion in soil K testing and in the formulation of K requirements. The objective of this study was to investigate the feasibility of including reserve-K and K fixation capacity in soil K testing and in the formulation of fertilizer requirements.

The investigations were carried out using field trials, laboratory incubations, and the use of the mid-infrared spectroscopy (MIR). The field trials assessed the response of sugarcane to K fertilization on soils with contrasting reserve-K and K fixation capacity. The laboratory incubations assessed the variation of reserve-K and K fixation capacity in representative soils of the industry. Lastly, the potential of multiple linear regression (MLR) models and MIR to predict reserve-K and K fixation capacity was investigated. Reserve-K was measured using 1.0 M boiling nitric acid and values of 0.8, 0.8-1.5, 1.5-2.5, above 2.5  $\text{cmol}_\text{c} \text{ kg}^{-1}$  were categorised as low, medium, high and very high, respectively. The capacity of the soil to fix added K was estimated using the K requirement factor (KRF) which involved incubating soils for six weeks with varying rates of K and then measuring exchangeable K at the end of the incubation period. The KRF values were categorised as low (1.5 - 2.5), medium (2.5 - 3.5), high (3.5 - 4.5), and very high (above 4.5).

Field trials were conducted on a cutanic Acrisol (Oakleaf), which had very high reserve-K and high K fixation, and an umbric Acrisol (Sweetwater), with low reserve-K and medium K fixation. Potassium was applied at 0, 120, and 240  $\text{kg K ha}^{-1}$  at the commencement of the trials and after each subsequent sugarcane harvest. Soil

exchangeable K was measured after each harvest and leaf K concentrations, stalk and sucrose yields were also measured in each cropping cycle. The variation of reserve-K and K fixation capacity in soils was investigated using 113 topsoil samples which included Acrisols (Oakleaf, Sweetwater, Nomanci, and Tukulu), Arenosols (Fernwood and Namib), Ferralsols (Kranskop, Magwa, Inanda, Hutton, and Clovelly), Fluvisols (Dundee), Leptosols (Mayo, Milkwood, Mispah, Glenrosa, and Cartref), Luvisols (Swartland and Valsirivier), Nitisols (Shortlands), Plinthosols (Longlands, Wasbank, Westleigh, Dresden, and Avalon), and Vertisols (Rensburg and Arcadia). The MLR models and MIR calibrations were developed and validated using wet chemistry data. Models and calibrations were developed and validated using 112 and 20 soils, respectively. The development of MLR models involved the use of routinely measured parameters, including soil pH, clay content, total carbon, total nitrogen, exchangeable acidity, AMBIC extractable cations (Ca, Cu, Fe, K, Mg, Mn, Na, and Zn), extractable Si and sample volume weight. Soil properties not routinely measured such as total K, oxalate extractable Al, Fe, and Si and, where appropriate reserve-K or KRF, were also included and were referred to as routine-plus. The MIR calibration included soil samples sieved through 1 mm and 0.5 mm screens.

The effects of K application on exchangeable K, leaf K, stalk and sucrose yields of all three ratoon crops on the cutanic Acrisol were not statistically significant, but increased exchangeable and leaf K, as well sucrose yields for the second ratoon crop on the umbric Acrisol. These field trial results indicated that K reserves and fixation influenced crop response to K application, and suggested that there is a need to investigate variations in K reserves and fixation, and that modifiers based on K reserves and fixation need to be included when calculating K requirements.

Laboratory investigation indicated that both reserve-K and KRF varied widely across and within soil types. Furthermore there were also wide variations in the relationship between reserve-K and K fixation capacity. Soils with a combination of high to very high reserve-K and low K fixation capacity are of particular concern because of the risk of luxury uptake of K resulting in reduced sucrose recovery, while soils with low to medium reserve-K and high K fixation may retain K more strongly resulting in

inadequate supplies of K for crop growth. The introduction of reserve-K and KRF in fertilizer K recommendations resulted in significant reductions in average K requirements across all soils.

The findings of the laboratory study pointed to a need to re-evaluate the basis upon which K soil testing is conducted, as well as current approaches to the development of fertilizer K recommendations, together with a need for techniques that will quickly estimate reserve-K and KRF. Prediction of the latter parameters using MLR and MIR met with variable success. The MLR models based on 'routine-plus' soil properties performed better with coefficient of determination ( $r^2$ ) and standard error of prediction (SEP) of 0.30 - 0.70 and 0.42 - 0.59, respectively, compared to a model based on routine properties only which had  $r^2$  and SEP of 0.20 - 0.63 and 0.24 - 0.56. The MIR spectra outperformed MLR models with  $r^2$  and SEP between 0.66 – 0.79 and 0.50 – 0.78, respectively. The MIR calibrations of 0.5 mm sieved samples had a ratio of performance to prediction (RPD) of 4.32 and 2.26 for reserve-K and KRF, respectively, and were better than the 1 mm calibrations which had a RPD of 3.36 and 1.85. However, the predictions based on the 0.5 mm calibration were poor, possibly due to 'overfitting'. Recommendations are that the MIR calibrations for both reserve-K and KRF using 1 mm samples can be used routinely to predict K reserves and fixation capacity, but caution must be exercised.

In conclusion, this investigation has underlined the importance of including K reserves and fixation capacity in soil K testing and in the development of fertilizer K recommendations. The evidence that these parameters can be measured using MIR is of major significance in terms of their inclusion in routine soil testing programmes. Further studies investigating calibrations based on combined NIR-MIR wavelength regions and possibly the splitting of the KRF calibration are necessary for the improvement of both reserve-K and KRF calibrations.



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# CHAPTER ONE

## GENERAL INTRODUCTION

### 1.1 INTRODUCTION

The importance of potassium (K) in the growth and development of sugarcane (*Saccharum officinarum*) is well known. Critical functions that are dependent on adequate amount of K include photosynthesis, translocation of sugars, and starch synthesis (Ng Kee Kwong 2002; Wood and Schroeder 2004; Watanabe *et al.* 2016). However, the impact of K fertilization on sugarcane yields and juice quality remains unresolved (Meyer and Wood 2001). The inconclusive results from field K response trials is presumed to arise from the inability of the current soil K tests to discriminate K responsive from non-responsive soils.

Appropriate testing for soil potassium (K) is essential for effective and sustainable fertilizer management. Recent debates on soil K testing highlight the need to review the approach to soil K testing. For example, Khan *et al.* (2014) questioned soil K testing based on exchangeable K and indicated that more than 2100 surveyed trials showed that crop yield response to KCl fertilization is unlikely. They also argued that exchangeable K does not account for the dynamic interchange between exchangeable K and reserve-K and exhibits temporal variability with or without air-drying. Reserve-K is K that is held between adjacent tetrahedral and octahedral sheets of mica and vermiculite (Chapman 1980; Wang *et al.* 2016). Furthermore, exchangeable K increased in zero K plots of a Mollisols dominated by smectite and illite minerals despite 51 years of crop K removal. Their conclusion was that soil K testing and K fertilization are unnecessary. Bar-Yosef *et al.* (2015) suggested modifications to soil K testing based on exchangeable K as opposed to rejecting soil K testing completely. They argued that the lack of response to K application could also be caused by rapid fixation (strong retention of K<sup>+</sup> ions within 2:1 layer silicates which renders K temporarily unavailable) of fertilizer K. They also proposed that K fertilizer applications should be reduced in high yielding regions. This debate illustrated two important aspects of soil K chemistry which are neglected in soil K testing. The first aspect is

that supply of K from the non-exchangeable reserves as well as K fixation are crucial in K management and in the formulation of crop nutritional guidelines. The second is that levels of reserve-K and K fixation vary with different soils.

While soil K testing should ideally provide information about levels of exchangeable K, as well as supply of K from the non-exchangeable reserves and the capacity of soils to fix added K (Wolde 2016), most laboratories currently base their fertilizer K recommendations solely on levels of exchangeable K. In order to determine the quantity of fertilizer K required for target yields, both gains (i.e. contributions from different forms of soil K) and losses (i.e. leaching and fixation) must be taken into account. Consideration of these factors involved in the K dynamics in soil should lead to improved efficiencies and reduced fertilizer costs. Few laboratories take into account the supply from reserve K (Schroeder *et al.* 2007), while the different capacities of soils to fix added K are often not considered, despite the evidence showing the inadequacy of using only exchangeable K for fertilizer recommendations (Haysom 1971; Wood and Meyer 1986; Johnston *et al.* 1999; Romheld and Kirkby 2010; Khan *et al.* 2014). These considerations, coupled with the evidence of a marked impact of K on crop physiology and health, imply that there is need for a thorough understanding of K in the soil-plant system. Incorporation of this knowledge in routine soil testing could potentially improve the reliability of recommendations for fertilizer K.

## **1.2 JUSTIFICATION FOR THE STUDY**

The reliability of fertilizer K recommendations can be compromised by wide variations in soil properties. Current fertilizer K recommendations for sugarcane production in central and southern Africa are based on the existing soil test (exchangeable) K levels, clay content, and the base status of the soil. However, the differences in supply of K from the K reserves and K fixing capacity of soils, arising from wide variations in soil properties and mineralogy, are in general not accounted for.

There have been suggestions to introduce modifiers based on K reserves and K fixing capacity of soils when formulating fertilizer K recommendations (Haysom 1971; Johnston *et al.* 1999). In their K recommendations for sugarcane in Australia, Schroeder *et al.* (2007) did introduce modifiers based on K reserves by making reductions in crop K requirements for soils with higher reserve K levels. However, the criteria for reserve-K developed by Haysom (1971) indicating the likelihood of sugarcane to respond to K fertilization on soils with variable reserve K levels have not been implemented in routine soil testing, nor have they been thoroughly validated in field trials. Similarly, Johnston *et al.* (1999) showed that there was a wide variation in K fixation of KwaZulu-Natal (South African) soils but no attempts have been made to account for the K fixation capacity of soils in the development of fertilizer K recommendations.

Previous studies on K fertilizer management focused on either reserve-K (e.g. Haysom 1971) or on K fixation capacity (e.g. Johnston *et al.* 1999). Studies investigating the implications of including both K reserves and fixation capacity in making fertilizer K recommendations are lacking. Delays in the implementation and validation of reserve-K and K fixation are no doubt due largely to the laboriousness and lengthiness of these determinations. However, the urgent need to implement these parameters in soil K testing and to validate them with crop responses has led to development of this study. Rapid measurements of both K reserves and fixation capacity will undoubtedly prove useful in such endeavours and thus techniques that will provide such rapid measurements should be sought.

### **1.3 AIMS AND OBJECTIVES**

The main objective of this study was to investigate the need and feasibility of including reserve-K and K fixation capacity in soil K testing and in the formulation of fertilizer requirements. The specific hypothesis were:

- 1) Potassium application will not affect sugarcane yields on soil with high K reserves and fixation capacity but will increase the yields on a contrasting soil with low K reserves and fixation capacity.

- 2) Potassium reserves and fixation capacity vary widely across soils and within soil groups and their inclusion in formulating fertilizer K requirement will significantly change fertilizer recommendations.
- 3) The mid-infrared spectroscopy (MIR) can successfully predict K reserves and fixation capacity of soils.

## **1.4 THESIS OUTLINE**

The chapters succeeding the current chapter attempt to address the aims mentioned above. The thesis involves four main sections, namely, literature review, laboratory experiments, field trials, and secondary quantification methods. The outline of these sections is presented below.

**Chapter 2:** Examines the dynamics of soil K and the tests used to study K in soils. The emphasis is on the nature of information contained in a particular test, as well as the challenge of implementing particular tests in soil K routine testing.

**Chapter 3:** Investigates the effects of reserve-K and K fixation on the response of sugarcane to varying rates of K application. This part of the study will serve to provide some validation of both reserve K and K fixation; importantly there are no known studies that investigate how both of these factors affect crop response to K application. Usually, either reserve-K or K fixation are investigated separately. This chapter was submitted as a full research paper for publication in Soil Research.

**Chapter 4:** Investigates the levels of reserve-K and K fixation in the soils of the South African sugar industry; the impacts these factors have on K requirements of soils; and lastly, soils are grouped according to their varying levels of reserve-K and K fixation which should assist in fine tuning fertilizer K recommendations. This chapter was also submitted as a full research paper for publication in Soil Research.

**Chapter 5:** Investigates the use of fast and reliable techniques in determining reserve-K and K fixation which should assist in their implementation in soil K testing and their validation with plant tests on soils with wide variations in properties. This chapter will be submitted as a full research paper for publication in South African Journal of Plant and Soil.

**Chapter 6:** Synthesises and discusses the findings of the thesis and the overall implications in relation to the aims of the study.



## **CHAPTER TWO**

### **THE DYNAMICS OF SOIL POTASSIUM AND POTASSIUM SOIL TESTS: A LITERATURE REVIEW**

#### **2.1 INTRODUCTION**

Potassium supply to crops is an intricate process involving a number of mechanisms and relationships among various K fractions in soil (Sharpley 1989; Prokoshev and Sokolova 1990; Srinivasa Rao *et al.* 2007; Trolove 2010). However, in general, soil K tests used to make fertilizer K recommendations do not account for these mechanisms and are still lagging behind despite many years of research on the dynamics of soil potassium. Lack of crop response to K fertilization due to factors affecting K availability has long been established (Wood and Meyer 1986; Johnston and Goulding 1990; Sharpley 1990; Simonis *et al.* 1998; Khan *et al.* 2014). Factors affecting K availability include levels of reserve-K, K fixation, cation antagonism, soil moisture, and soil temperature (Wood and Meyer 1986; Donaldson *et al.* 1990; Sharpley 1990; Johnston *et al.* 1999).

Levels of reserve-K and K fixation are characteristic of the soil and do not change significantly over long periods (Askegaard *et al.* 2004). Numerous studies have focused on reserve-K and K fixation, which are mainly affected by clay content and mineralogy and the latter varies widely between soils (Sharpley 1989; Samadi 2010b). Furthermore, levels of reserve-K and K fixation vary within a soil group mainly because they increase with increasing clay content for a given clay mineral (Srinivasa Rao *et al.* 2007). Hence, it is important that reserve-K and K fixation are accurately estimated if they are to be taken into account in fertilizer K recommendations. This points to a need to find tests that accurately estimate K fixation and levels of reserve-K, while being suitable for routine analysis.

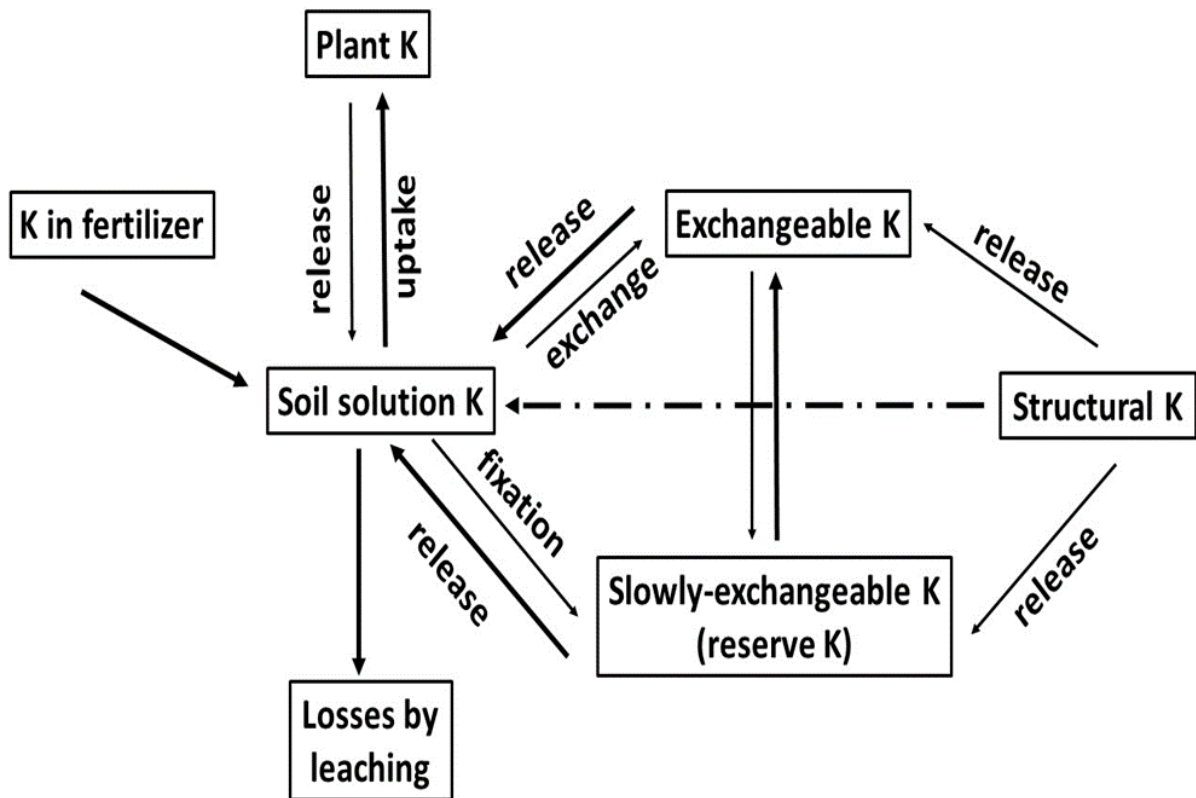
The currently used soil K tests based on exchangeable K have a number of shortfalls (Ghosh and Debnath 2010; Khan *et al.* 2014). A soil K test used routinely as a basis for fertilizer recommendations should be fast, should indicate the amount of K required

for targeted yields, and account for K dynamics in the plant-soil system (Khan *et al.* 2014). However, the exchangeable K test only meets the requirement of being fast. The inclusion of reserve-K and K fixation would meet the other two requirements but their determination is laborious and time consuming. The challenge facing most soil testing laboratories is deciding how to include the determination of reserve-K and K fixation in soil analysis without causing delays.

This review examines the dynamics of soil potassium and the tests used to evaluate potassium dynamics in soils. The emphasis is on the nature of information revealed by a particular test. The review also points to the challenge of implementing a particular test in relation to routine soil K testing.

## **2.2 FORMS OF POTASSIUM IN SOILS**

Potassium availability to crops can be understood by taking into account the different forms of potassium existing in soils (Figure 2.1). The soil solution K, exchangeable K, slowly-exchangeable K (reserve-K) and structural K have been recognized as the four distinct forms of K that are at equilibrium with each other (Askegaard *et al.* 2004; Weil and Brady 2017; Romheld and Kirkby 2010; Trolove, 2010; Moir *et al.* 2013). The relative distribution of K between these forms is 0.1-0.2% solution K, 1-2% exchangeable K, 1-10% reserve-K, and 90-98% structural K (Weil and Brady 2017). Solution K and exchangeable K are considered to be readily available while reserve-K is said to be slowly-available (Sparks 2001). Structural K, because of the low solubility of minerals, is generally considered unavailable (Weil and Brady 2017).



**Figure 2.1** Different forms of soil potassium (K), the equilibrium between different forms, and the cycling of K in the plant-soil system (Modified from Romheld and Kirkby 2010).

Potassium availability and K supply capacity of soils are ultimately controlled by the equilibrium between exchangeable K and reserve-K (Figure 2.1). The release of reserve-K increases levels of exchangeable K and thus supply to the crop (Mengel and Uhlenbecker 1993; Surapaneni *et al.* 2002a; Srinivasa Rao *et al.* 2007; Sarkar *et al.* 2014). On the other hand, fixation of added K fertilizer will result in previously plant-available K becoming unavailable (Simonis *et al.* 1998; Srinivasa Rao *et al.* 2014). Many researchers use fixed K and reserve-K interchangeably (Beckett 1970; Pettygrove *et al.* 2011; Bar-Yosef *et al.* 2015; Wang *et al.* 2016). It follows that a key question then is “to what extent does K fixation reduce K supplying capacity of soils?”, in particular since fixed K becomes part of reserve-K. The usefulness of any soil K testing protocol is dependent upon how closely it answers this question.

The limitations of soil K tests, however, will be their inability to account for time in which K becomes available or unavailable. This limitation has often been addressed with the use kinetics studies (Martin and Sparks, 1983; Wood and Schroeder, 1991; Sanyal and Majumdar 2001; Mola Ali Abasiyan and Towfighi, 2018). The kinetics of K release and fixation are affected by clay content and mineralogy. However, they are also affected by a number of temporal variable factors such soil solution K concentration, temperatures, and wetting and drying (Sparks and Huang 1985; Wood and Meyer 1986). These temporal variable factors cannot be predicted by a soil K test and also make the measurement of kinetics somewhat unreliable.

## **2.3 TESTS USED TO ELUCIDATE POTASSIUM DYNAMICS IN SOILS**

Numerous soil tests that assess K availability and soil K supply capacity exist. This section reviews a number of commonly used soil K tests and also examines how closely they answer the questions raised above.

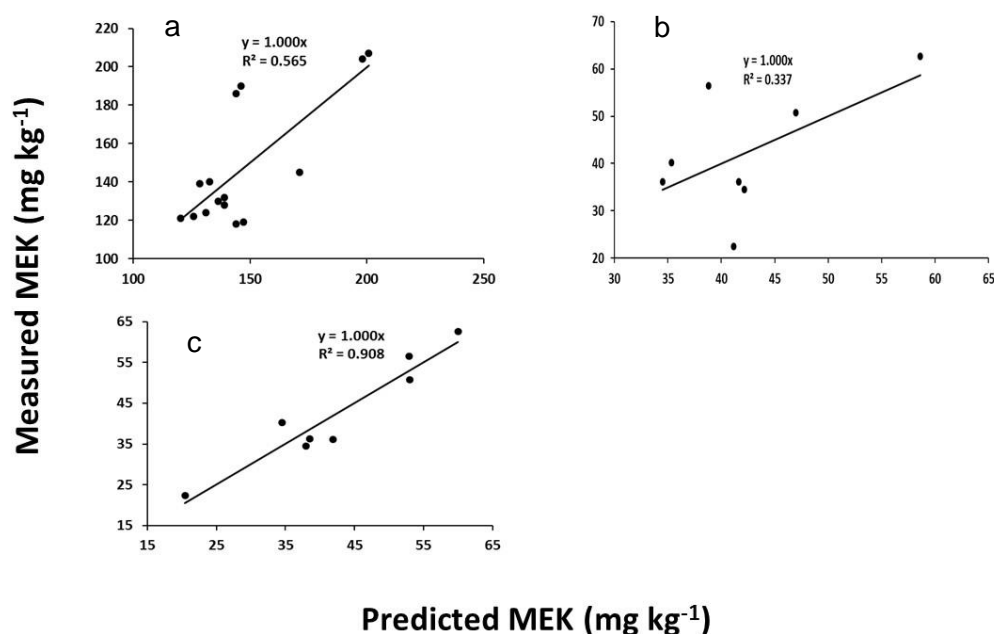
### **2.3.1 Exchangeable potassium**

The exchangeable K soil test measures soluble K and K electrostatically bound as an outer-sphere complex to the surfaces of clay minerals and which can easily be exchanged with other cations (Wang *et al.* 2010a; Zorb *et al.* 2014). Consequently, this form of K is extracted with neutral salts such as ammonium acetate, ammonium acetate lactate, ammonium nitrate, ammonium fluoride (Mehlich 3), and calcium chloride (Øgaard *et al.* 2002; Askegaard *et al.* 2004; Zorb *et al.* 2014). Exchangeable K increases rapidly with fertilization and is also decreased by plant uptake and/or leaching. Since exchangeable K is a highly dynamic and transitory variable in equilibrium with soil solution K, non-exchangeable and mineral K, it is not characteristic of the soil (Khan *et al.* 2014). Hence, measurement of exchangeable K without knowledge of prior field management provides little indication of K fixation or release from reserve-K.

All soils have a specific minimum value of exchangeable K beyond which exchangeable K cannot be depleted further. This value is referred to as minimal exchangeable K (MEK); it is characteristic of the soil and is in dynamic equilibrium with reserve-K (Srinivasa Rao and Khera 1994; Askegaard *et al.* 2004; Madaras and Koubova 2015). The measurement of MEK requires that soil be thoroughly depleted of K before exchangeable K is measured. Typically, soils with high K fixation would maintain low MEK levels while those with high levels of reserve-K will result in higher MEK levels (Srinivasa Rao and Khera 1994; Øgaard *et al.* 2001). However, relationships between K fixation and MEK have not been established while that between MEK and reserve-K is debatable. Øgaard *et al.* (2002) found no relationship between MEK and reserve-K. However, other studies have indicated that MEK reflects K release rates from reserve-K and variations in plant uptake (Srinivasa Rao and Khera 1994; Srinivasa Rao and Subba Rao 2000). Hence, MEK is also viewed as the value where reserve-K begins to replenish solution K and reserve-K becomes the sole contributor to K availability (Srinivasa Rao and Khera 1994; Sarkar *et al.* 2014; Srinivasa Rao *et al.* 2014).

Inconsistencies in the MEK studies reported above could be due to factors affecting MEK; namely clay mineralogy and clay content (Srinivasa Rao and Khera 1994; Øgaard *et al.* 2002). The study by Srinivasa Rao and Khera (1994) focused on illitic soils and the study by Srinivasa Rao and Subba Rao (2000) on smectitic soils, whereas Øgaard *et al.* (2002) used soils of varying clay mineralogy and clay content. A positive relationship between clay content and MEK has been reported (Srinivasa Rao and Subba Rao 2000; Øgaard *et al.* 2002). Srinivasa Rao and Khera (1994) on the other hand, found a non-significant positive relationship between clay content and MEK; a significant positive relationship with MEK was, however, found when using percent illite present in the clay fraction. This may be pointing to the complexity of the relationship between MEK, clay mineralogy and clay content. The complexity of these relationships was evident when smectitic soils were found to have higher MEK compared to illitic soils and this was attributed to the higher clay content of the smectitic soils (Srinivasa Rao and Khera 1994; Srinivasa Rao and Subba Rao 2000; Øgaard *et al.* 2002).

Linear regression models have been used to understand the relationship between MEK and clay content, plant K uptake, and the release of reserve-K (Srinivasa Rao and Khera 1994; Srinivasa Rao and Subba Rao 2000). It is clear from these studies that the amount of K taken by the crop and that released from K reserves increased with increasing MEK. However, more research is needed to understand the influence of soil properties on MEK. Theoretically, clay mineralogy should exert the dominant effect, followed by clay content and cation exchange capacity (CEC). Minimal exchangeable K predicted from clay models (Figure 2.2 a, b) had lower correlation coefficients compared to that predicted from models that included clay content, clay mineral proportions, and CEC (Figure 2.2 c; Srinivasa Rao and Khera 1994; Srinivasa Rao and Subba Rao 2000). This shows that the same factors affecting K fixation and levels of reserve-K affect MEK and thus there is a possibility that K fixation and levels of reserve-K can be used to infer information about MEK in a soil and plant K uptake.



**Figure 2.2** Minimal exchangeable potassium (MEK) predicted from clay models of (a) Srinivasa Rao and Subba Rao (2000) and (b) Srinivasa Rao and Khera (1994); and (c) from a model which included clay content, percent illite, and cation exchange capacity (CEC; Srinivasa Rao and Khera 1994).

### 2.3.2 Potassium fixation

Potassium fixation, in strict terms, is a process where available  $K^+$  ions are held in an inner sphere complex within 2:1 layer silicates, which renders K temporarily unavailable (Simonis *et al.* 1998; Johnston *et al.* 1999; Murashkina *et al.* 2007; Pettygrove *et al.* 2011). Common clay minerals that result in K fixation are smectites, illites, and vermiculites (McLean and Watson 1985; Johnston *et al.* 1999; Pettygrove *et al.* 2011). Vermiculites are known to have a high K fixation capacity and K fixation in this mineral results in the collapse of the mineral layers into mica-like clays (Pettygrove *et al.* 2011). Highly K depleted micaceous minerals also have a high K fixation capacity (Beckett 1970; Murashkina *et al.* 2007; Pettygrove *et al.* 2011). Potassium fixation is biphasic: it is initially rapid but then slows down, and this latter slow phase can last for more than three years (Murashkina *et al.* 2007; Zorb *et al.* 2014). It has also been found that drying and wetting of soils can promote K fixation and this is one of the reasons why exchangeable soil K tests can be unreliable (Sharpley 1990; Khan *et al.* 2014). Some of the fixed K does become available during cropping, but there are debates about the availability of fixed K and this will be discussed in the section on reserve-K. This section will discuss different views of K fixation and methods used to measure K fixation in soils.

There are two dominant views relating to K fixation. Some researchers have reported that K fixation begins above an exchangeable K threshold value (Beckett 1970; Ghosh and Debnath 2010; Datta 2011). Others have reported that K is fixed on K specific sites which can be saturated (Simonis *et al.* 1998; Johnston *et al.* 1999; Dhaliwal *et al.* 2006; Samadi 2010b). Two different studies support the concept of fixation threshold levels. Wells and Dollarhide (2000) reported a threshold for K fixation and K release while studying the effect of drying on soil K test values of soils containing vermiculites. They found that drying soils with exchangeable K levels above 100 ppm will result in K fixation while in soils with exchangeable K below 100 ppm there was release of reserve-K. Ghosh and Debnath (2010) also investigated fixation and release threshold levels as means of optimising potassium use efficiency. Their investigation involved adsorption-desorption equilibration studies. Total labile K ( $K_T$ , solution K plus

exchangeable K) was plotted against exchangeable K and the level of exchangeable K at which  $K_T$  showed a sharp rise was considered as the release threshold whereas the level above which  $K_T$  decreased sharply was considered as the fixation threshold. Their findings indicated that illite-dominated soils had greater release thresholds and fixation thresholds compared to kaolinite-dominated soils; and fixation threshold values were greater than release threshold, suggesting that K fixation does not start immediately after the exchangeable K exceeds the release threshold values. Both studies by Wells and Dollarhide (2000) and Ghosh and Debnath (2010) suggest that K fixation and K release from the reserves are concentration driven and that at a given exchangeable K level the release of reserve-K and K fixation cannot coexist. Considering that exchangeable K is in a highly dynamic state, this approach may not be useable when doing soil K testing for fertilizer recommendations.

The approach that views K fixation as occurring on K specific sites recognises the three K retention sites; namely planar, edge, and wedge sites. Potassium in planar and edge sites is weakly held and is easily exchanged by other cations whereas K in wedge sites is strongly held in hexagonal ditrigonal cavities in the interlayer positions (Bertsch and Thomas 1985; Johnston *et al.* 1999). This approach implies that K fixation will occur as long as there are vacant K specific sites irrespective of the levels of exchangeable K and reserve-K. This is supported by the work on the K requirement factor (KRF) showing equal proportions of K fixed by soil at different K application rates; even when soils have high levels of exchangeable K and reserve-K they still fixed K but to a lower extent (Johnston *et al.* 1999; Dhaliwal *et al.* 2006). The K specific site approach to K fixation is also supported by concepts such as Q/I relationships (Section 2.3.4) and the results of fixation kinetic studies (Beckett 1964b; Sanyal and Majumdar 2001). Inasmuch as this approach is theoretically sensible, it would not be easy to measure vacant K specific sites but K fixation capacity (Section 2.3.2.1; Section 2.3.2.2; Section 2.3.2.3) may be measured instead.



#### 2.3.2.1 Isotherms

Sorption isotherms are traditionally used to measure how strongly a particular nutrient is retained by the soil. Measurement of K adsorption isotherms involves equilibrating soils with various K concentrations in 0.01 M CaCl<sub>2</sub> for 24 hours and measuring K in the supernatant (Samadi 2010a; Hannan *et al.* 2011). The amount of K adsorbed (which is the difference between amount of K added and K recovered in solution) is then plotted against the K equilibration concentration. Sorption isotherms are reported to improve the prediction of fertilizer requirements when incorporated into soil K testing (Samadi 2010a; Hannan *et al.* 2011). However, sorption isotherms may be reflecting the partitioning of K between the soil solution and the exchange sites. Studies investigating the K sorption isotherms for soils with a wide range of K fixation capacities are lacking. Furthermore, adsorption isotherms are often measured at high solution: soil ratio which does not mimic natural conditions (Datta 2011). Finally, a major problem with sorption isotherms is that they are lengthy and labour-intensive, and thus not suited to routine use.

#### 2.3.2.2 Potassium recovery tests and bioassays

Another approach for measuring the K fixation capacity of soils is to measure the amount of added K in solution that is not recoverable by the exchangeable soil K test as shown in Equation 2.1 (Simonis *et al.* 1998; Murashkina *et al.* 2007; Samadi 2010b). Commonly used soil: solution ratios are 1:5 and 1:10 and these are unrealistic as they do not mimic natural conditions and present a difficulty when calculating fertilizer recommendations. Other studies have used bioassays where a plant can show K deficiency due to K fixation but they, too, present a challenge when making fertilizer recommendations (Simonis *et al.* 1998). The advantage of using bioassays to study K fixation is that they reflect how much of the added K will be recovered by the plant.

$$K \text{ fixed} = (\text{added K} + \text{initial } K_{\text{ex}}) - \text{final } K_{\text{ex}}$$

**2.1**

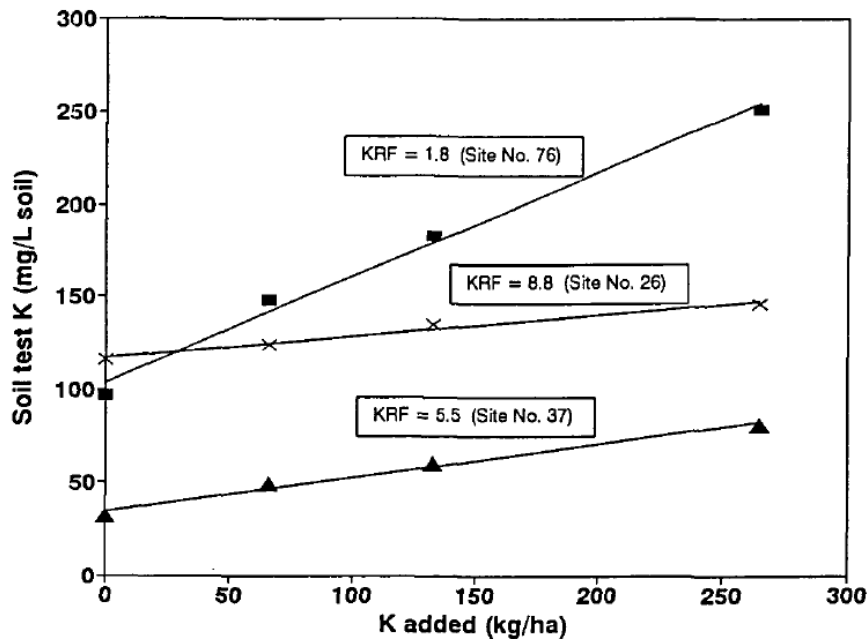
### 2.3.2.3 Potassium requirement factor

The K requirement factor (KRF) developed by Johnston *et al.* (1999) can readily be included in making fertilizer recommendations as shown in equation 2.2. In simple terms, KRF is an expression of the quantities of fertilizer K required to raise the soil exchangeable K test by a unit, and an indicator of the soil's K fixation capacity. The KRF values are obtained by treating soils with different levels of K, which are then taken through wetting and drying cycles over (typically) a 6 week period and exchangeable K is measured at the end of the incubation. Measured exchangeable K is plotted against K application rate, which results in a linear regression (Figure 2.3), and the inverse of the slope is the KRF.

Field K requirement (kg/ha) = (optimum soil K threshold – measured soil K) x KRF

## 2.2

The study by Johnston *et al.* (1999) showed that KRF in KwaZulu-Natal soils can vary from 1.5 to 8.8, indicating that soils may have distinctly different K fixation capacities. Despite the evidence that KRF varies widely between soils, soil testing laboratories generally still use a single value of KRF in the equation 2.2 instead of soil specific KRF values. By way of example, the KRF value is 3.0 for a sugarcane based soil testing service in South Africa; 2.5 for a KwaZulu-Natal (South Africa) Department of Agriculture testing service (Johnston *et al.* 1999); 5.7 for Ohio soils; and 3.0 Michigan soils (Liebhardt and Cotnoir 1979). This practice of using one single constant value for KRF could result in the underestimation of K requirement by as much as 70% (Johnston *et al.* 1999). However, KRF determinations are strenuous, which is why most laboratories use a single KRF value in calculating fertilizer K requirements. Johnston *et al.* (1999) showed that KRF prediction from routinely measured soil properties was unsatisfactory and alternative techniques are needed in order to use soil specific KRF values in calculating fertilizer K requirements. Techniques such as mid-infrared spectroscopy (MIR, Section 2.4), discussed in the section on the future of soil K testing, may play a crucial role in providing fast and reliable KRF results.



**Figure 2.3** Response in soil exchangeable potassium (K) test to different K application rates for different soils (Johnston *et al.* 1999). The inverse of the slope of each line is the potassium requirement factor (KRF).

The main drawback of using KRF values in making fertilizer recommendations is that KRF provides no indication of how much fixed K will become available to a plant in a given season. Furthermore, soils with high levels of reserve-K can still have high K fixation capacity due to the presence of vacant K specific sites. Studies assessing the balance between KRF and the release of reserve-K are lacking and this avenue of research could result in significant improvements in fertilizer recommendations.

### 2.3.3 Reserve-potassium

The importance of including reserve-K when making fertilizer recommendations has long been recognised. However, few soil testing laboratories account for reserve-K in fertilizer recommendations (Wood and Schroeder 2004). Challenges in the adoption of reserve-K measurements in fertilizer recommendations may include the laborious and somewhat hazardous analytical procedures involved as well as the lack of criteria to base subsequent recommendations on. Commonly used techniques for estimating

reserve-K are extractions with boiling nitric acid (commonly known as 'nitric K'), sodium tetraphenylboron (NaTPB), electro-ultrafiltration (EUF) and bioassays (Wood and Schroeder 1991; Mengel and Uhlenbecker 1993; Øgaard *et al.* 2001; Wang *et al.* 2016). These tests will be discussed in detail in the following sections.

#### 2.3.3.1 Boiling nitric acid

Boiling nitric acid is a widely used technique for assessing the levels of reserve-K (Sharpley 1989; Surapaneni *et al.* 2002a; Srinivasa Rao *et al.* 2007; Sarkar *et al.* 2014). Basically, 1 M nitric acid is added to a soil and allowed to boil for a specified period and K is read using spectroscopic techniques such as atomic absorption spectroscopy (AAS) or inductively coupled plasma (ICP). Reserve-K is computed as nitric acid extractable K minus exchangeable K. This test provides no indication of how much of the reserve-K has been depleted i.e. the number of vacant K specific sites. Furthermore, one of the challenges with the nitric acid extraction is that there is poor understanding of how it mimics the release of reserve-K for plant uptake. This method has also been criticised for its lack of selectivity and low extraction efficiency of reserve-K (Martin and Sparks 1985; Cox *et al.* 1996; Wang *et al.* 2016). This implies that not all of the nitric acid extractable K may be available for plant uptake.

Haylock (1956) developed a system that categorises reserve-K into two types; namely Step K and Constant rate (CR) K. These values are acquired by extracting soil five times with boiling 1 M nitric acid with each extraction being 15 minutes. Constant rate K is the value obtained when similar amounts of K are extracted in consecutive extractions (Haylock 1956). Step K is then obtained by subtracting CR K from the K extracted in each extraction and then summing up all the values (Haylock 1956; Srinivasa Rao *et al.* 2014). Step K is considered a readily available form of reserve-K, while CR K is a more slowly released form of reserve-K (Sparks and Huang, 1985; Sarkar *et al.* 2014; Srinivasa Rao *et al.* 2014). This categorisation provides no indication of K fixation capacity, but the ratio of Step K to CR K provides a measure of the sustainability of K supply from the reserves (Conyers and McLean 1969; Srinivasa Rao *et al.* 2014). Exhaustive cropping results showed little variation in CR K with

cropping (Sarkar *et al.* 2014). Exhaustive cropping also showed that the uptake of reserve-K by Italian ryegrass grown for 15 months was close to one third of the Step K (Haylock 1956; Sarkar *et al.* 2014). Based on these results, Haylock (1956) set criteria for levels of reserve-K (Step K) in soils centred on the likelihood of response to K fertilization (Table 2.1). Soils with low reserve-K are most likely to respond to K fertilization whereas those with high reserve-K are less likely to respond. Correlation has also been found between Step K and K uptake by Alfalfa (Richards and Bates 1988), ryegrass (Surapaneni *et al.* 2002b), and finger millet (Srinivasa Rao *et al.* 2014) and Step K is considered the best suited for the prediction of crop yield and K uptake (Lee and Gibson 1974; Kumar *et al.* 2002).

Despite the categorisation of K extracted with boiling nitric acid, this method still suffers from criticisms. Madaras and Koubova (2015) reported that Step K overestimated K contents, particularly in soils where uptake of K by ryegrass grown for 10 months was low. However, this could mean that the 10 months used in their experiment was not enough to allow for exhaustive uptake of K by the ryegrass. Measurement of Step K is also time consuming and not practical for routine analysis (Pal 1998). Analysis time for Step K has been reduced by boiling soil for 30 minutes with nitric acid, measuring K in the extract, and then subtracting exchangeable K from the nitric acid extractable K (Haysom 1971; Srinivasa Rao *et al.* 2014). Criteria for the likelihood of response to K fertilization was set by Haysom (1971) and these are similar to the criteria reported by Dwivedi (2001) and Srinivasa Rao *et al.* (2007) for the conventional technique (Table 2.1). This would imply that Step K measured on the reduced analysis time is similar to that measured with the conventional Step K technique. Despite the attempts to reduce analysis time for Step K, measurement of Step K and other forms of reserve-K remain unsuitable for routine analysis. Developments with non-destructive spectroscopic techniques (Section 2.4) may eliminate the problem of laborious and long analysis times.

**Table 2.1** Criteria used to categorise levels of reserve-K in soils that reflects the responsiveness of soils to K fertilization

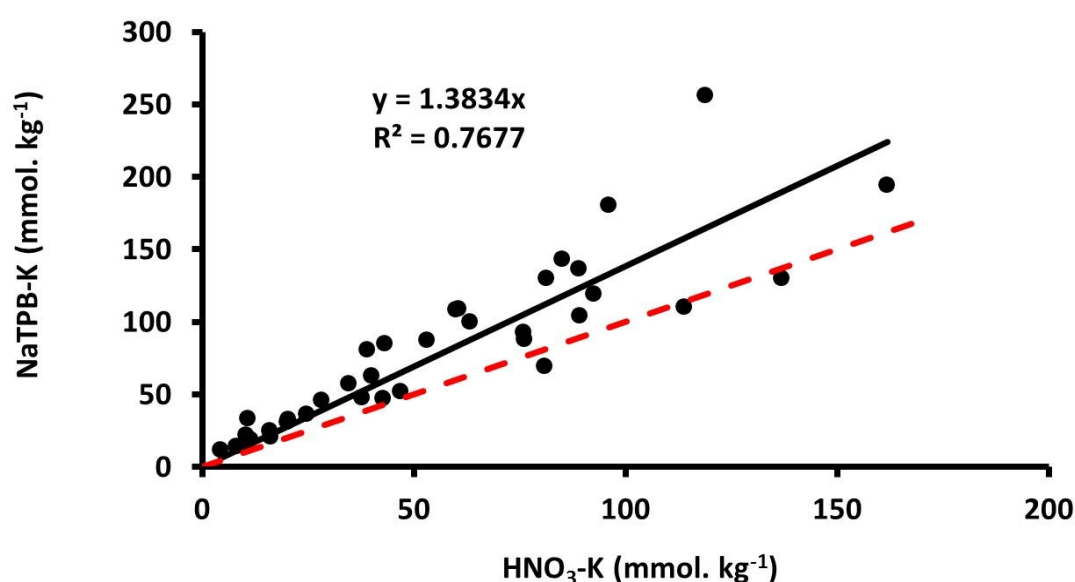
Criteria		Low	Medium	High	Very High
Reserve-K (cmol <sub>c</sub> /kg)	Haylock (1956)	<0.3	0.4	>0.5	-
	Haysom (1971)	<0.8	0.8-1.50	1.50-2.5	>2.5
	Dwivedi (2001)	<0.77	0.77-1.53	>1.53	-
	Srinivasa Rao <i>et al.</i> (2007)	<0.77	0.77-1.53	>1.53	-

### 2.3.3.2 Sodium tetraphenylboron

The use of sodium tetraphenylboron (NaTPB) to measure levels of reserve-K has gained wide acceptance over the past two decades. The NaTPB extractable K is obtained by incubating soil with 1.7 M NaCl-0.01 M EDTA-0.2 M NaTPB for 7 days. The tetraphenylboron anion is reported to combine with K<sup>+</sup> and precipitates as KTPB while Na<sup>+</sup> acts as an exchanger for interlayer K (Martin and Sparks 1985; Cox *et al.* 1996). However, Na<sup>+</sup> can only satisfy the charge requirements of the interlayer as the ionic radius of K<sup>+</sup> and Na<sup>+</sup> are different. The precipitated KTPB is dissolved by boiling and K<sup>+</sup> is recovered with HgCl<sub>2</sub> or CuCl<sub>2</sub> (Conyers and McLean 1969; Cox *et al.* 1996). The use of CuCl<sub>2</sub> introduced by Cox *et al.* (1996) instead of HgCl<sub>2</sub> could be the reason for the wider acceptance of this method, as Hg is toxic. The K<sup>+</sup> in the extract is usually determined using spectroscopic techniques and exchangeable K is subtracted in order to obtain values for reserve-K.

The NaTPB method has been commended for its selectivity compared to the boiling 1.0 M nitric acid method (Conyers and McLean, 1969; Wang *et al.*, 2016). This selectivity could be attributed to the tetraphenylboron anion reducing the concentration of K<sup>+</sup> in solution in a similar way to K<sup>+</sup> uptake by plants (Martin and Sparks, 1985). Correlations between NaTPB extractable K with plant K uptake and also boiling nitric acid extractable K has been found (Al-Kanani *et al.*, 1984; Wang *et al.*, 2010b; Madaras and Koubova, 2015). However, the relationship between NaTPB extractable K and K uptake by plants or boiling nitric acid extractable K is not straightforward. Binet

*et al.* (1984) found no relationship between NaTPB extractable K and K uptake by Italian ryegrass while Wang *et al.* (2010b) and Madaras and Koubova (2015) found a correlation ( $r^2 > 0.8$  at level of  $p < 0.01$ ) with uptake by perennial ryegrass. Similarly, a correlation between NaTPB extractable K and boiling nitric acid extractable K have been found (Al-Kanani *et al.*, 1984; Madaras and Koubova, 2015). Al-Kanani *et al.* (1984) found that NaTPB extracted more K compared to boiling nitric acid (Figure 2.4) while there are instances where boiling nitric acid extracted more K compared to NaTPB (Conyers and McLean, 1969; Moody and Bell, 2006; Madaras and Koubova, 2015). These discrepancies may be due to the different soils used and/or differences in the extraction conditions used (such as extraction time, temperature, soil-to-solution ratio, and concentration of the extractant). The latter could be addressed by harmonising the soil tests, which should allow for comparisons across different studies.



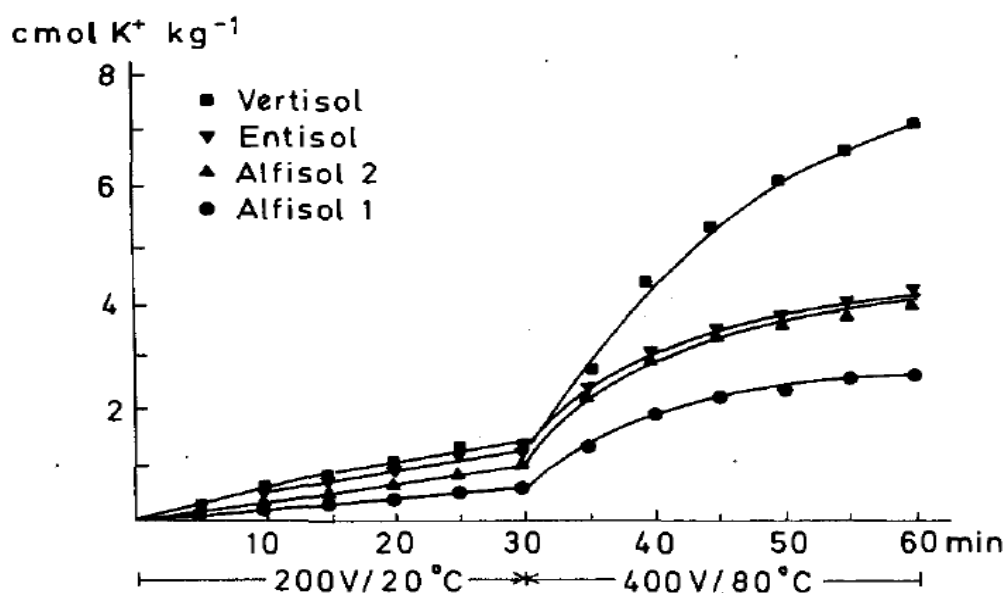
**Figure 2.4** A comparison between sodium tetraphenylboron extractable K (NaTPB-K) and boiling nitric acid extractable K (HNO<sub>3</sub>-K) of five Quebec soils (data from Al-Kanani *et al.* 1984). The dotted line represents the 1:1 line.

The NaTPB method has a number of limitations, namely; it is costly, provides no indication of how much of the reserve-K has been depleted i.e. the number of vacant K specific sites, provides no indication of K fixation capacity and lacks criteria for the likelihood of response to K fertilization, and other previously mentioned limitations. In

some studies workers have tried to reduce analysis time from 7 days to 72 hours (Conyers and McLean 1969), 4 hours (Carey *et al.* 2011), 2 hours (Wang *et al.* 2010b), and 15 minutes (Moody and Bell 2006). However, due to the other factors mentioned previously, this method still remains unsuitable for routine analysis.

### 2.3.3.3 Electro-ultrafiltration

Electro-ultrafiltration (EUF) techniques have been used in the past to measure quantities of reserve-K (Wood and Schroeder 1991; Mengel and Uhlenbecker 1993; Mehdi *et al.* 2002). In the EUF method the soil suspension is subjected to an electric field for various lengths of time and the cations migrate to the cathode and anions to the anode where they are collected (Martin and Sparks 1985; Mengel and Uhlenbecker 1993). Two successive extractions are often conducted where K accumulated is plotted against time (Wood and Schroeder 1991; Mengel and Uhlenbecker 1993). The first extraction is conducted at 20°C and 200 V for 30 minutes and the second extraction is conducted at 80°C and 400 V for an additional 30 minutes. The extractions are carried out in 5 minutes intervals to enable K-release to be plotted against time (Figure 2.5), (Mengel and Uhlenbecker 1993).



**Figure 2.5** Cumulative potassium (K) extracted by electro-ultrafiltration (UEF) against time for two successive EUF extractions for 30 minutes at 20°C and 200 V and for a further 30 minutes at 80°C and 400 V (Mengel and Uhlenbecker 1993).



The successive EUF extractions extract different forms of K. The first 30 minutes extracts easily extractable non-hydrated adsorbed K while the second 30 minutes extracts non-exchangeable K (Wood and Schroeder 1991; Mengel and Uhlenbecker 1993; Mehdi *et al.* 2002; Mengel 2007). Mehdi *et al.* (2002) construed the ratio between K released in 5-10 minutes and 30-35 minutes to represent soil K fixation capacity and potential buffering capacity (PBC). Mengel and Uhlenbecker (1993) found a strong correlation ( $r^2 > 0.99$  at level of  $p < 0.01$ ) between K uptake by perennial ryegrass and K extracted in 30-35 minutes and the sum of K extracted in 0-30 and 30-60 minutes. Wood and Schroeder (1991) found a strong correlation ( $r^2 > 0.8$  at level of  $p < 0.001$ ) between K uptake by sorghum and K extracted in 0-30 minutes and 0-60 minutes when soils with 1:1 and 2:1 clay minerals were separated. When all soils were considered, the correlation coefficient was significantly reduced. The discrepancies between these two studies may be due to different crops used for K exhaustion studies.

The use of the EUF technique to estimate reserve-K has limitations and, in particular, is unsuitable for routine analysis. It is strenuous and requires specialised personnel. Furthermore, the EUF technique does not have the criterion that indicates the likelihood of soils to respond to K fertilization.

#### 2.3.3.4 Bioassays and cation exchange resin

Bioassays and cation exchange resins (referred to as resin) are probably the two techniques that best reflect the release of reserve-K and K fixation capacity. These two techniques mimic the release of reserve-K by reducing the soil solution K. The resins are usually saturated with either Ca or H and have a very high cation exchange capacity (Martin and Sparks 1985; Johnston and Goulding 1990). However, most of the studies that use resins are focused on the kinetics of the release of reserve-K. Furthermore, the resin technique has been criticised for releasing levels of K similar to exchangeable K, destroying soil minerals, having limited capacity to adsorb released K, and the methods involved are time consuming (Martin and Sparks 1985; McLean and Watson 1985; Johnston and Goulding, 1990).

Bioassays involve growing crops either in the field or a glasshouse or growing seedlings in petri dishes. Field trials are costly, laborious, time consuming, and are subject to confounding factors which limits the usefulness of the results obtained. Growing seedlings in petri dishes, on the other hand has rarely been used to study the release of reserve-K. Consequently, this review focuses on growing crops in a glasshouse.

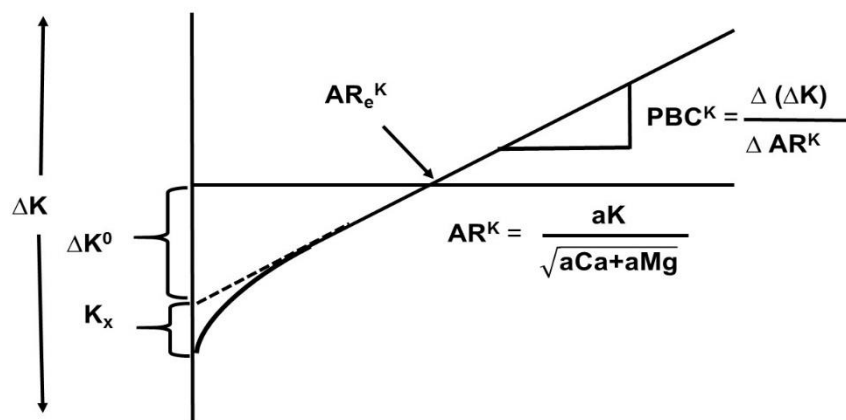
Glasshouse bioassays are conducted by growing plants in pots and harvesting them repeatedly with the intention of exhausting K. Hence, they are often referred to as exhaustive cropping. After each harvest, the plants are analysed for K to measure K uptake and sometimes even levels of K in soils are analysed (Øgaard *et al.* 2001; Sarkar *et al.* 2014). Data on K uptake are then compared to initial levels of exchangeable K and/or reserve-K and sometimes changes in these fractions of K are also computed (Øgaard *et al.* 2001; Surapaneni *et al.* 2002c; Sarkar *et al.* 2014; Srinivasa Rao *et al.* 2014). In this approach exhaustive cropping can be used as a monitoring tool where changes in K levels in soils are related to continuous cropping. Exhaustive cropping can also be used to establish at what levels of exchangeable K and reserve-K yields start to decline. Most of the criteria for the likelihood of response to K fertilization for reserve-K were established using exhaustive cropping (Haylock 1956; Haysom 1971). Lastly, exhaustive cropping is frequently used to assess the performance of the chemical extraction methods (Binet *et al.* 1984; Mengel and Uhlenbecker 1993; Øgaard *et al.* 2001; Wang *et al.* 2010b; Madaras and Koubova 2015).

The lack of uniformity is the main challenge with the exhaustive cropping method. Firstly, different crops with different K uptake capacities have been used. Crops used include German millet (one cutting) and Alfalfa (four cuttings) (Conyers and McLean, 1969), perennial ryegrass (Mengel and Uhlenbecker 1993; Surapaneni *et al.* 2002c; Samadi 2010a; Wang *et al.* 2010b; Madaras and Koubova 2015), Italian ryegrass (Binet *et al.* 1984; Ogaard *et al.* 2001; Zhan *et al.* 2014), rice (Sarkar *et al.* 2014) and sorghum (Wood and Schroeder 1991; Srinivasa Rao and Subba Rao 2000). Uptake

of K by ryegrass is higher compared to other grasses and, thus, ryegrass is more suitable for exhaustive cropping studies (Binet *et al.* 1984). Secondly, time to each successive harvest, which affects the amount of K taken up by the crop, varies between studies. Variations in time to each successive harvest include 3 weeks (Binet *et al.* 1984); 6 weeks (Øgaard *et al.* 2001; Madaras and Koubova 2015); and 8 weeks (Wang *et al.* 2010b). Some studies do not mention the duration of the exhaustive cropping (Mengel and Uhlenbecker 1993; Surapaneni *et al.* 2002c). Lastly, there is also a variation in the volume of soil used. In some studies the soil is mixed with washed sand to speed up the exhaustion of K (Surapaneni *et al.* 2002c; Madaras and Koubova 2015). These variations in the conditions used may result in inconclusive results regarding K supplying capacity of soils and thus there is a need for more uniformity in the exhaustive cropping studies.

#### 2.3.4 Quantity/Intensity relationships

Quantity-intensity (Q/I) relationships provide an alternative to soil K testing for fertilizer recommendations. One of the advantages of this method is that it takes into account the antagonistic relationships between K and Mg or Ca in their uptake by plants. The Q/I relationships were established by Beckett (1964a,b) and are based on Schofield's Ratio Law. There are four parameters (Figure 2.6) in Q/I relationships that can be used for K fertilizer management. Before discussing the parameters of the Q/I relationships it is necessary to describe the construction of the Q/I diagrams.



**Figure 2.6** A typical quantity/intensity diagram showing the four important parameters which relate to K availability.

Construction of the Q/I diagrams involves equilibrating subsamples of the same soil with variable amounts of KCl in 0.002 M CaCl<sub>2</sub> solution. The concentration of K, Ca, and Mg in solution is measured and then converted into activities using activity coefficients obtained from the Guggenheim equation (Le Roux and Sumner 1968a), Davies equation (Ajiboye *et al.* 2015) or Debye-Huckel equation (Tinker 1964; Sparks and Liebhardt 1981; Lalitha and Dhakshinamoorthy, 2015). The difference in concentration of K before and after equilibration is  $\Delta K$  and is plotted on y-axis. The ratio of K activity over the square root of Ca plus Mg activities is termed the activity ratio and is plotted on x-axis. The Q/I diagrams are characterised by a linear upper part and a curvilinear lower part (Figure 2.6). The four parameters in Q/I relationships are as follows: the potential buffering capacity ( $PBC^K$ ) is the slope of the curve; the equilibrium activity ratio ( $AR_e^K$ ), also known as the intensity factor, is the intercept of the curve on the x-axis; labile or exchangeable K ( $\Delta K^0$ ) is obtained by extrapolating the linear part to intersect the y-axis; and specific K sites ( $K_x$ ) are obtained by subtracting the value where the curvilinear line intersects the y-axis from  $\Delta K^0$  (Figure 2.6).

The Q/I relationships relate K availability to the amount of labile K present. Some believe that Q/I relationships relate immediate K availability to the levels of reserve-K (Hamdan *et al.* 1999). All four parameters in Q/I relationships are useful in describing K availability. The  $AR_e^K$  is a measure of immediate availability and it increases with K fertilization but decreases with liming (Le Roux and Sumner 1968a; Sparks and Liebhardt 1981). An  $AR_e^K$  value  $<0.01$  is indicative of K adsorbed at the K specific sites while a value  $>0.01$  will indicate that K was adsorbed at non-K specific sites (Sparks and Liebhardt 1981; Tan 1998; Lalitha and Dhakshinamoorthy, 2015). The  $\Delta K^0$  is the measure of labile K and is believed to be a better estimate of K availability than exchangeable K (Tan 1998). This parameter increases with K fertilization and liming (Le Roux and Sumner 1968a; Sparks and Liebhardt 1981; Tan 1998). The  $K_x$  is an indicator of K retained in K specific sites and is less available (Lalitha and Dhakshinamoorthy, 2015). The  $PBC^K$  is a measure of the ability of soil to maintain soil solution K against depletion and is correlated to CEC (Sparks and Liebhardt 1981; Tan 1998). High  $PBC^K$  is indicative of good K availability while low  $PBC^K$  would suggest a

need for frequent fertilization (Le Roux and Sumner 1969). This parameter has also been found to increase with liming (Prokoshev and Sokolova 1990).

Despite the commendations of Q/I relationships, this approach suffers a number of limitations and uncertainties. The latter are mainly centred around their description of K availability. For instance, high PBC<sup>K</sup> is known to indicate good K availability, yet it increases with K depletion (Le Roux and Sumner 1968a, b). Beckett and Nafady (1967), however, reported that Q/I relationships, including PBC<sup>K</sup>, were not affected by K additions, K fixation, and K depletion. Sakar *et al.* (2014) also reported that PBC<sup>K</sup> was unaffected by exhaustive cropping with rice. This suggests that Q/I relationships are, at best, poorly understood. In addition to these contradictions, determinations of Q/I relationships are arduous. Furthermore, their application is limited to a small pH range between 5 and 6 (Moss and Beckett 1971); in fact they were unsuccessful in predicting K availability in acid (pH range of 4.5-5.6) Nigerian soils (Tinker 1964). There is thus a need to clarify the meaning of the parameters in terms of their practical application.

## **2.4 FUTURE OF POTASSIUM SOIL TESTS**

Developments in instrumental analysis have had a marked impact on the evolution of soil testing. For instance, in the Q/I relationships K was determined using flame photometry, while Ca and Mg were determined using versenate titration (Beckett 1964a). Presently, all three elements may be determined by AAS or ICP, which significantly reduces analysis times. These developments are particularly noteworthy, seeing that laboriousness is a major drawback for most of the techniques used in understanding K dynamics. Furthermore, non-destructive spectroscopic techniques such as infra-red spectroscopy are being increasingly used in soil testing (Janik *et al.* 1998; Nocita *et al.* 2015; Towett *et al.* 2015). These techniques are expected to revolutionise soil testing, including tests for soil K. Mid-infrared spectroscopy (MIR) has been reported to accurately estimate soil nutrient buffering capacity (Towett *et al.* 2015). Nutrient buffering capacity may include levels of reserve-K and K fixation capacity. Furthermore, there is also potential for MIR to fingerprint clay mineralogy of soils (Janik *et al.* 1998; Towett *et al.* 2015). Bearing in mind that clay mineralogy plays

an important role in K dynamics, these developments are expected to revolutionise soil K testing. It should be noted, however, that the success of the use of techniques such as MIR is crucially dependent on the availability of reliable 'wet chemistry' data.

Attempts have been made to estimate soil exchangeable K using infrared (IR, which includes near-infrared, NIR). The quality of the calibration is evaluated using coefficient of determination ( $r^2$ ) and the ratio of prediction to deviation (RPD, Table 2.2). The quality of IR calibrations range from poor (low  $r^2$  and RPD values) to excellent. The quality of the calibrations are most likely affected by the spectral region, multivariate method, calibration range, number of samples used, and the extractant used to measure exchangeable K. The spectral region refers to either MIR or NIR; and these regions give varying details of soil properties (Soriano-Disla *et al.* 2014). While the multivariate method, calibration range, number of samples used have influence on the statistical rigour of the model obtained. Lastly, extractants that reliably estimate exchangeable K might result in better calibration models compared to unreliable extractants. More research is being conducted globally to understand the influence of these factors. However, data presented in Table 2.2 shows that mid-infrared has potential application in soil K testing. However, no attempts could be accessible in the literature on the estimation of reserve-K and/or K fixation capacity using MIR and this is an opportunity for further K research.

**Table 2.2** A comparison of quality of infrared calibrations for the prediction of exchangeable potassium. The quality of the calibration is evaluated using coefficient of determination ( $r^2$ ), ratio of prediction to deviation (RPD), and root mean square error of estimation (RMSEE).

Spectral region	Multivariate method	Calibration range (mg/kg)	$R^2$	RPD	RMSSE	n	Extractant	Reference
MIR	PLSR	-	0.33	-	-	183	-	Janik <i>et al</i> (1998)
UV-VIS-NIR	MLR	51 – 1443	0.29	0.8	254	121	Silver thiourea	Islam <i>et al</i> (2003)
MIR	PLSR	8 – 1290	0.92	1.0	94	366	Ammonium chloride	Minasny <i>et al</i> (2009)
NIR	PLSR	20 – 1878	0.71	2.65	67	481	Ammonium acetate	Van Vuuren <i>et al</i> (2006)
NIR	PLSR	130 – 1400	0.80	-	100	317	Ammonium acetate	Cozzolino and Moron (2003)
MIR	PLSR	45 – 248	0.65	-	42	42	Ammonium acetate	Du <i>et al</i> (2009)
NIR	PLSR	29 – 192	0.78	-	31	135	-	He <i>et al</i> (2007)
NIR	PLSR	0 - 547	0.34	1.2	39	79	Mehlich	Vendrame <i>et al</i> (2012)

MIR = mid infrared; NIR = near infrared; UV = ultraviolet; VIS = visible

PLSR = partial least square regression; MLR = multiple linear regression

## 2.5 CONCLUSIONS

This review focused on soil K tests used for fertilizer recommendations and how they account for the dynamics of soil K. Release of reserve-K and K fixation are the most important processes that can be used to describe potassium dynamics in soils. However, most of the tests used to estimate the levels of reserve-K and K fixation capacity are tedious and time consuming. Furthermore, no single test is able to

accurately estimate release of reserve-K and K fixation in soils. Non-destructive spectroscopic techniques are fast and provide the potential for multiple-analyses from a single scan and may eliminate the tediousness currently experienced when estimating levels of reserve-K and K fixation capacity. It is suggested that in future routine testing for K availability will rely increasingly on spectroscopic methodologies.

The main limitation of currently used soil K testing is that they do not account for K dynamics in plant-soil system. This is linked to the tediousness and lengthy analysis time associate with measurement of reserve-K and K fixation capacity. Consequently, various combination between reserve-K and K fixation capacity have not been researched. Furthermore, the impact of these various combination on crop response to K application has not been research either. Lastly, the impact of modifiers based on reserve-K and K fixation capacity on fertilizer K requirements has not been research as well. These highlights the need for research investigating various combination between reserve-K and K fixation capacity, their impact on crop response to K application and fertilizer K requirements, and the potential of secondary techniques to estimate reserve-K and K fixation capacity.



## **CHAPTER THREE**

### **SUGARCANE RESPONSE TO POTASSIUM FERTILIZATION ON SOILS WITH CONTRASTING POTASSIUM RESERVES AND FIXATION**

#### **3.1 INTRODUCTION**

Potassium (K) is one of the most important nutrients in sugarcane production. It plays a critical role in growth and development of the crop, and large quantities of K, ranging from 1.9 to 2.4 kg K/ tonne of cane (Wood and Schroeder 2004), are removed in harvested stalks. Functions such as photosynthesis, translocation of sugars, and starch synthesis require adequate amounts of K (Ng Kee Kwong 2002; Wood and Schroeder 2004; Watanabe *et al.* 2016). In deficient soils, K application may improve both sugarcane yields and sugarcane juice quality (Meyer and Wood 2001). However, excessive amounts of K can suppress sucrose yields and increase the ash content, resulting in economic losses in the recovery of sugar in the mill (Schroeder and Wood 2002; Whitbread *et al.* 2004; Munsamy 2013). Hence, reliable recommendations based on accurate soil K testing are essential to ensure optimum sugarcane yields and quality.

In developing recommendations for sugarcane in central and southern Africa, the South African Sugarcane Research Institute's (SASRI) Fertilizer Advisory Service (FAS) uses modifiers to soil exchangeable K thresholds based on clay content and base status (Wood and Meyer 1986; Donaldson *et al.* 1990). This has improved K recommendations, but the observation is that there are still discrepancies between soil test results and sugarcane yield responses to K applications. Lack of yield response to K applications in field trials has been attributed to contributions of reserve-K, while K fixation may result in reduced uptake even at high K applications (Wood and Meyer 1986; Schroeder and Wood 2002; Zhan *et al.* 2014). This suggests that accounting for levels of reserve-K and K fixation could be important when making fertilizer K recommendations. However, difficulties in the measurement of these parameters has limited their inclusion in recommendation packages.

Haysom (1971) developed criteria for levels of reserve-K in soils, which indicated the likelihood of sugarcane responding to K fertilization. Haysom proposed four categories of reserve-K as follows: low ( $<0.8 \text{ cmol}_c \text{ kg}^{-1}$ ); medium ( $0.8 - 1.5 \text{ cmol}_c \text{ kg}^{-1}$ ); high ( $1.5 - 2.5 \text{ cmol}_c \text{ kg}^{-1}$ ); and very high ( $>2.5 \text{ cmol}_c \text{ kg}^{-1}$ ). Crops growing on soils with low reserve-K were most likely to respond to K fertilization whereas on soils with high reserve-K a response was less likely. However, these criteria have not been thoroughly validated in field trials. An experiment conducted by Chapman (1980) is the only known study in which the criteria set by Haysom (1971) were investigated. However, Chapman's findings were inconclusive possibly because the four soils used in the experiment had medium and high reserve-K of 0.85, 1.17, 1.19, and  $1.59 \text{ cmol}_c \text{ kg}^{-1}$  and did not include soils with low and very high reserve-K.

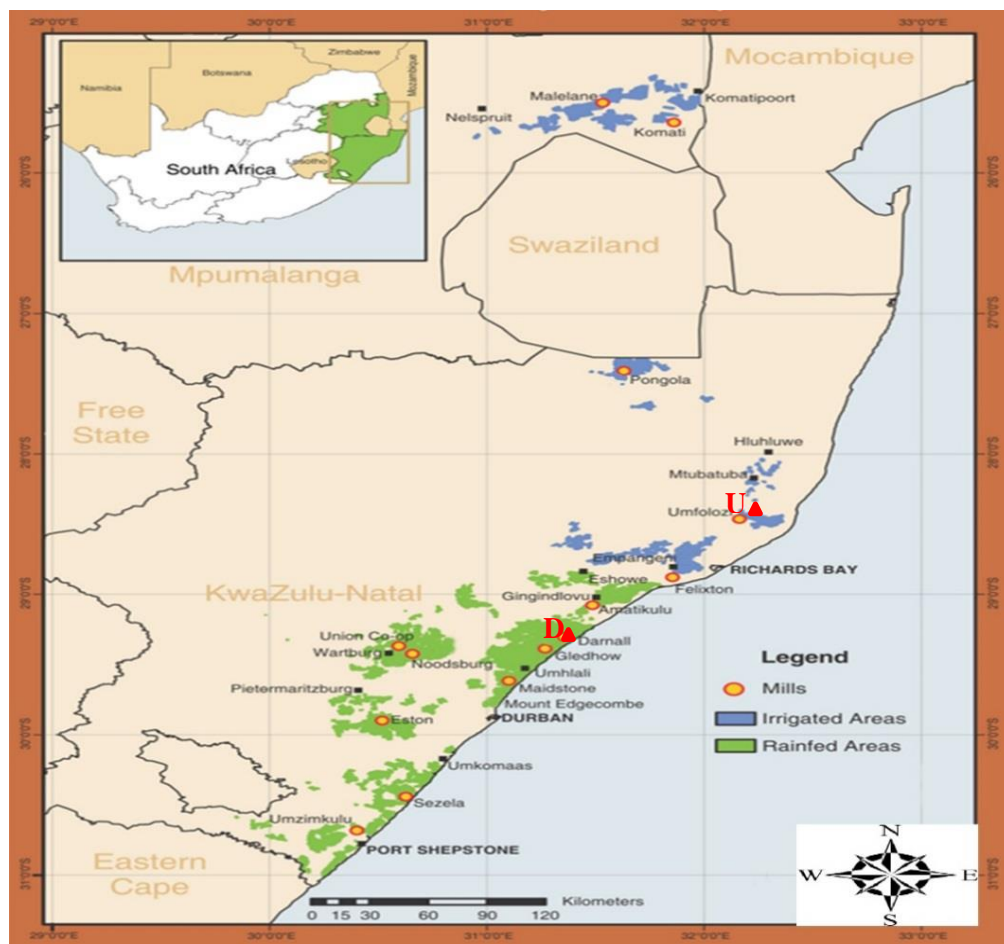
In terms of K fixation, Wood and Meyer (1986) recognised that soils such as Vertisols with high K fixation require more fertilizer K than soils with low K fixation. However, criteria for including K fixation in fertilizer K recommendations were not set. Johnston *et al.* (1999) proposed a potential solution by introducing the potassium requirement factor (KRF) as an index of K fixation. The KRF indicates the amount fertilizer K required to raise the soil test by one unit (i.e.  $1 \text{ mg kg}^{-1}$ ). In their study, Johnston *et al.* (1999) found that KRF in soils of KwaZulu-Natal (South Africa) varied widely between 1.5 and  $8.8 \text{ kg K ha}^{-1}$  per unit soil test and they recommended using soil-specific KRF values instead of a constant value when making fertilizer K recommendations. Again, their recommendations have not been implemented in soil testing facilities nor have they been validated in yield-response trials.

This study investigated the response of sugarcane stalk yield, sucrose yields, exchangeable K, and sugarcane leaf K concentration to K application on two soils with contrasting levels of reserve-K and K fixation. In the past, either reserve-K or K fixation have been investigated separately. It was hypothesised that sucrose yields would increase in response to K fertilization for sugarcane grown on soils with low reserve-K but not on soils with high reserve-K and that high K fixation would suppress K uptake, lowering leaf K and sucrose content.

## 3.2 MATERIALS AND METHODS

### 3.2.1 Trial sites

Response to K fertilisation was investigated in field trials at Umfolozi and Doringkop in KwaZulu-Natal, South Africa (Figure 3.1). The Umfolozi site ( $28^{\circ}27'0''$  S,  $32^{\circ}13'0''$  E; 15 m. a.s.l.) has mean annual rainfall of  $1033 \text{ mm annum}^{-1}$ , with the most occurring between October and April. The minimum and maximum daily temperatures are  $17.1$  and  $28.3^{\circ}\text{C}$ , respectively. The parent material was alluvium and the soil classified as cutanic Acrisol (IUSS Working Group WRB, 2014), locally known as Oakleaf (Soil Classification Working Group, 1991). The soil was characterised by very high levels of reserve-K and high K fixation capacity (Section 3.2.2; Table 3.1).



**Figure 3.1** Location of trial sites within the province of KwaZulu-Natal, South Africa. Red triangles with 'U' (Umfolozi, cutanic Acrisol) and 'D' (Doringkop, umbric Acrisol) indicate the location of each trial site. (Image: W. Mthembu, South African Sugarcane Research Institute).

**Table 3.1** Selected topsoil properties for the cutanic Acrisol at Umfolozi and umbric Acrisol at Doringkop.

Determinant		Cutanic Acrisol (Umfolozi)	Umbric Acrisol (Doringkop)
pH (CaCl <sub>2</sub> )		5.31	4.60
AMBIC <sup>(a)</sup> extractable cations (cmol <sub>c</sub> kg <sup>-1</sup> )	K	0.25	0.25
	Ca	10.82	5.14
	Mg	6.50	1.07
	Na	0.30	0.04
Truog P (mg kg <sup>-1</sup> )		37	64
CaCl <sub>2</sub> Si (mg kg <sup>-1</sup> )		28	18
Exchangeable acidity (cmol <sub>c</sub> kg <sup>-1</sup> )		0.01	0.21
Total cations <sup>(b)</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )		17.88	6.71
Reserve-K (mg kg <sup>-1</sup> )		3.84	0.58
KRF <sup>(c)</sup> (kg K ha <sup>-1</sup> per unit soil test)		4.44	3.24
Total carbon (%)		0.73	2.45
Clay (%)		35	33
Silt (%)		21	12
Sand (%)		44	55

<sup>(a)</sup> AMBIC = ammonium bicarbonate

<sup>(b)</sup> Total cations obtained by summing the quantities of AMBIC extractable Ca, Mg, K, and Na and KCl exchangeable acidity (Al + H)

<sup>(c)</sup> KRF = potassium requirement factor, indicative of K fixation capacity

The Doringkop site, which is inland of KwaDukuza (29°13'6" S, 31°14'19" E; 434 m. a.s.l.), has a mean annual rainfall is 998 mm annum<sup>-1</sup>, mostly occurring between September and March. The mean minimum and maximum daily temperatures are 14.3 and 26.7°C, respectively. The parent material was a table mountain sandstone and soil was classified as umbric Acrisol (IUSS Working Group WRB, 2014), locally known as Sweetwater (Soil Classification Working Group, 1991). The soil was characterised by low levels of reserve-K and medium K fixation capacity (Section 3.2.2; Table 3.1).

### 3.2.2 Soil characteristics

Before trial establishment, composite soil samples (25 cores) were collected from 0-200 mm at the Umfolozi trial site in December 2012 and the Doringkop site in October 2011. The characteristics of the two soils are presented in Table 3.1. Samples from each site were air-dried, milled to pass through a 1 mm sieve, and analysed unreplicated. The pH (CaCl<sub>2</sub>) was measured in a 1:2.5 (soil: solution) ratio and exchangeable acidity (Al + H) was extracted with KCl (Farina and Channon 1991). Exchangeable K, calcium (Ca), magnesium (Mg) and sodium (Na) were obtained by ammonium bicarbonate (AMBIC) extraction (van der Merwe *et al.* 1984). Total cations were obtained by summing the quantities of KCl-exchangeable acidity (Al + H) and AMBIC extractable Ca, Mg, K, and Na. Plant available phosphorus (P) was measured using the modified Truog method (Truog 1930), plant available silicon (Si) measured in a CaCl<sub>2</sub> extract (Miles *et al.* 2011). Total carbon was determined by automated (Dumas) dry combustion using a Leco Analyzer (Leco Corporation, St Joseph, Michigan). Clay content was measured using the hydrometer method (Bouyoucous 1962) and sand and silt content determined using MIR. Reserve-K was determined by boiling 2.5 g of soil in 100 mL of 1.0 M HNO<sub>3</sub> for 30 minutes and categorised as low, medium high, and very high as proposed by Haysom (1971). Potassium requirement factor (KRF), adapted from Johnston *et al.* (1999), was used to estimate K fixation and involved adding increasing levels of K to soils and incubating them for six weeks after which the relationship between exchangeable K and K added was used to give a measure of K fixation. The following classification of K fixation was used: low, medium, high, and very high with KRF values of 1.5 - 2.5, 2.5 - 3.5, 3.5 - 4.5, above 4.5, respectively.

### 3.2.3 Trial establishment and treatments

The trial at Umfolozi was established during the summer of 2012/2013 on the first ratoon of N23, a South African bred sugarcane variety. The trial was a 3Nx3Px3K unreplicated factorial design with 27 plots each with a surface area of 68.5 m<sup>2</sup> (10 m x 6.85 m) and each plot had five rows with row spacing 1.37 m, with the three inside rows being sampled and harvested. The K application rates were 0, 120 and 240 kg ha<sup>-1</sup>. The sources of K, N, and P were KCl, limestone ammonium nitrate (LAN), and double superphosphate, respectively. The treatments were applied at the commencement of the trial and after each harvest as shown in Table 3.2. The treatments were also accompanied by basal applications of gypsum (200 kg ha<sup>-1</sup>), zinc sulphate (23 kg ha<sup>-1</sup>), copper sulphate (10 kg ha<sup>-1</sup>), solubor (B, 2.5 kg ha<sup>-1</sup>), and sodium molybdate (0.26 kg ha<sup>-1</sup>). There were no interactions between K and N and P treatments for any of the parameters measured, and responses to N and P are not given further consideration in this paper. Because there was no response to P application at Umfolozi, P treatments were used as replicates.

The trial at Doringkop on the umbric Acrisol was established during the summer of 2011 on a plant crop of N39, a South African bred sugarcane variety. The trial had a 3Nx3K factorial design with three replicates and 27 plots of 45 m<sup>2</sup> each (9 m x 5 m) and each plot had five rows with row spacing 1.0 m, with the three inside rows being sampled and harvested. Potassium was applied as KCl at the rates of 0, 120 and 240 kg K ha<sup>-1</sup>. The treatments were applied at the commencement of the trial and after each harvest as shown in Table 3.2. The treatments were also accompanied by basal applications of double superphosphate (246 kg ha<sup>-1</sup>), gypsum (1000 kg ha<sup>-1</sup>), zinc sulphate (45 kg ha<sup>-1</sup>), copper sulphate (16 kg ha<sup>-1</sup>), solubor (B, 5 kg ha<sup>-1</sup>), and sodium molybdate (0.64 kg ha<sup>-1</sup>).

**Table 3.2** Chronological sequence of activities in the Umfolozi and Doringkop field trials.

Umfolozi (cutanic Acrisol)		Doringkop (umbric Acrisol)	
Date	Activity	Date	Activity
<b>Dec 2012</b>	Plant crop harvested	<b>Nov 2011</b>	1) Planting
<b>Jan 2013</b>	1) Trial commenced 2) N, P and K application 3) Basal applications	<b>Dec 2011</b>	1) N and K application 2) Basal applications
<b>Apr 2013</b>	Leaf sampling	<b>Mar 2012</b>	Leaf sampling
<b>Nov 2013</b>	Flooding interfered first ratoon harvesting	<b>May 2013</b>	1) Plant crop harvested 2) Soil sampling for first ratoon
<b>Dec 2013</b>	N application	<b>Oct 2013</b>	N and K application
<b>Mar 2014</b>	Leaf sampling	<b>Jan 2014</b>	Leaf sampling
<b>Nov 2014</b>	Second ratoon harvested	<b>Sep 2014</b>	First ratoon harvested
<b>Dec 2014</b>	Soil sampling for third ratoon	<b>Oct 2014</b>	1) Soil sampling for second ratoon 2) N and K application
<b>Jan 2015</b>	1) N, P and K application 2) Basal application	<b>Mar 2015</b>	Leaf sampling
<b>Feb 2015</b>	Leaf sampling	<b>May 2016</b>	1) Second ratoon harvested 2) Soil sampling for third ratoon
<b>Oct 2015</b>	Third ratoon harvested		
<b>Dec 2015</b>	1) Soil sampling for fourth ratoon 2) N, P and K application		
<b>Apr 2016</b>	Leaf sampling		
<b>Nov 2016</b>	1) Fourth ratoon harvested 2) Soil sampling for fifth ratoon		

#### 3.2.4 Soil and leaf sampling

Soil samples were collected from the 0-20 cm depth at each site after each harvest. Soil sampling events were for three ratoon crops (crops which regrow following harvest). Composite samples from each plot were dried (35 to 40°C) and milled to pass through a 1 mm sieve before analysis. Exchangeable K was extracted with the AMBIC extractant (van der Merwe *et al.* 1984) and K in the extract analysed using inductively coupled plasma (ICP-OES, VARIAN ICP 720-ES).

Sugarcane leaf samples were collected at each trial site for each cropping cycle when the crop was between 3 and 8 months old. Leaf sampling was undertaken for three ratoon crops at Umfolozi and at Doringkop for plant and two ratoon crops. The third leaf (top visible dewlap) was sampled in each case and 30 leaves were collected from each plot. The tops and bottoms of the leaves were chopped off, leaving roughly 20-30 cm of the central portion of the leaf blade. The midrib was stripped out and discarded. The leaf samples were dried, ground, and analysed for K using X-ray fluorescence spectrometry (XRF: Rigaku, ZSX Primus II).

#### 3.2.5 Harvesting

Four harvests were taken at Umfolozi and three at Doringkop. Sugarcane was burnt a maximum of 12 hours before it was harvested manually. All leaf materials were removed and the stalks were weighed using a balance mounted on a vehicle to determine sugarcane yield. Harvested stalks were sent to the laboratory (SASRI Millroom) where sucrose contents were measured using near infrared (NIR) spectroscopy. Yield data could not be obtained for the first harvest at Umfolozi because of flooding of the field following heavy rainfall.

The amount of K removed ( $\text{kg ha}^{-1}$ ) by the crop was estimated by multiplying sugarcane stalk yields ( $\text{t ha}^{-1}$ ) by 1.5 according to the value reported by the International Plant Nutrition Institute (IPNI 2014). This assumes that 1.5 kg K is removed per ton of cane harvested.

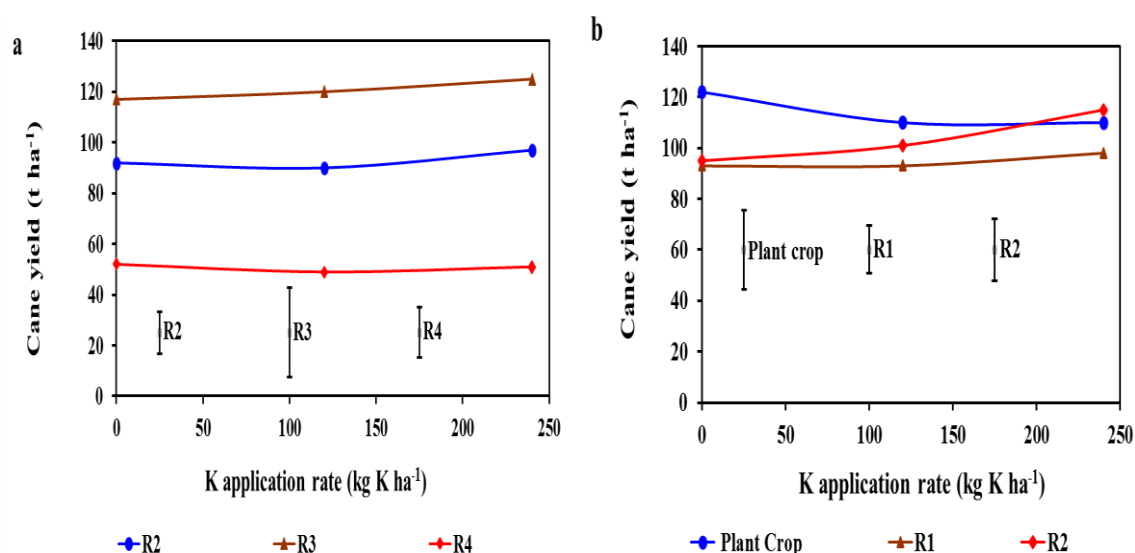


### 3.2.6 Statistical analysis

Exchangeable K, leaf K, sugarcane stalk and sucrose yields were analysed using analysis of variance (ANOVA; Genstat, 18th Edition) for each cropping cycle. Where treatments showed significant effects, means were separated using Fisher's protected least significant difference (LSD) test at  $p < 0.05$ .

## 3.3 RESULTS

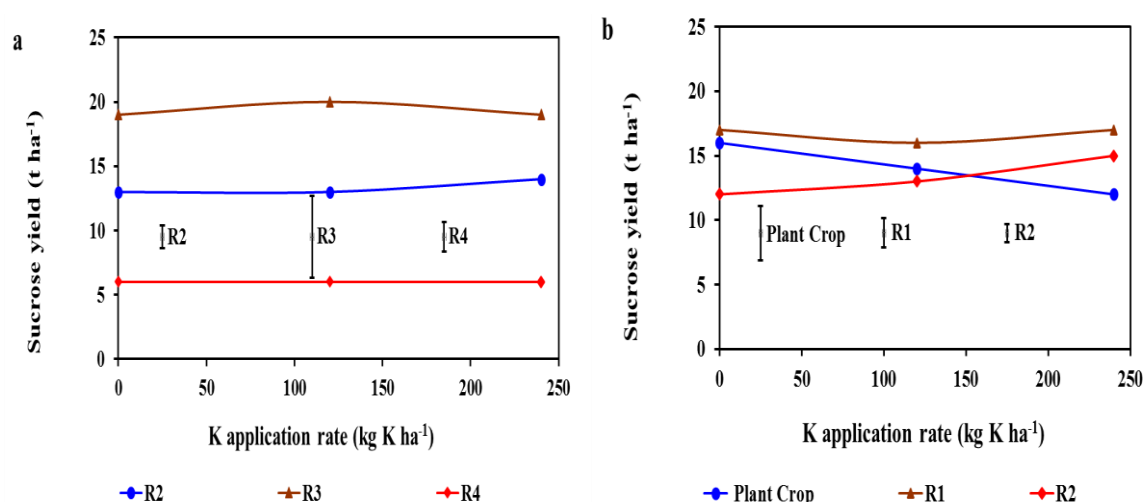
There were no stalk yield response to K application at the trial sites in either plant crop or ratoons (Figure 3.2 a, b).



**Figure 3.2** Relationships between applied potassium (K) and sugarcane yields for (a) second ratoon (R2), third ratoon (R3), and fourth ratoon (R4) on the cutanic Acrisol at Umfolozi and (b) plant crop, first ratoon (R1), and second ratoon (R2) on the umbric Acrisol at Doringkop. Potassium application was repeated after each harvest. The LSD (0.05) bars for each crop are indicated as vertical lines.

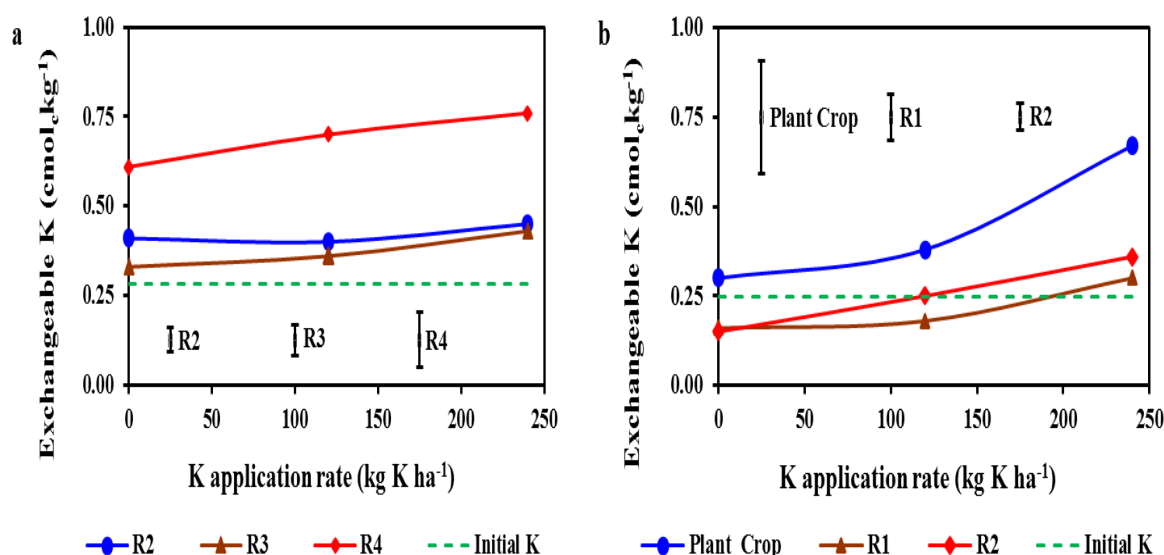
In terms of sucrose yields, there was response to K application for any of the ratoon crops ( $p > 0.05$ ) on the cutanic Acrisol (Figure 3.3a). Similarly on the umbric Acrisol, sucrose yields were not affected by K treatments for the plant and first ratoon crops;

however, a significant response to K was evident in the second ratoon crop (Figure 3.3b)



**Figure 3.3** Relationships between applied potassium (K) and sucrose yields of (a) second ratoon (R2), third ratoon (R3), and fourth ratoon (R4) grown on cutanic Acrisol at Umfolozi and (b) plant crop, first ratoon (R1), and second ratoon (R2) on umbric Acrisol at Doringkop. Potassium application was repeated after each harvest. The LSD (0.05) bars for each crop are indicated as vertical lines.

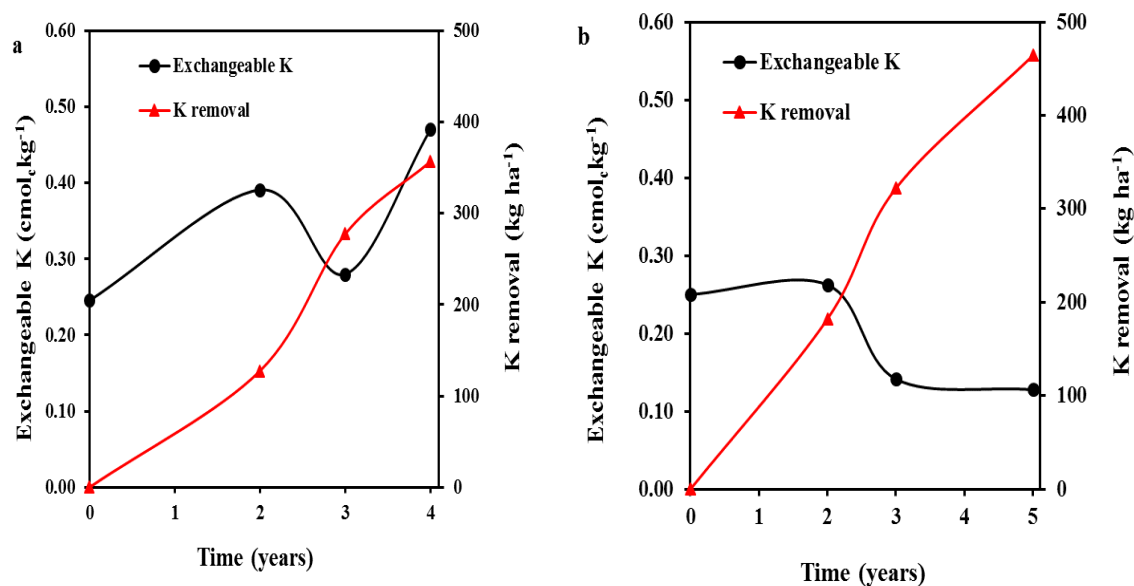
Generally, the K treatments did not significantly affect exchangeable K measured in the cutanic Acrisol after the harvest of second ratoon ( $p=0.24$ ), third ratoon ( $p=0.07$ ), and fourth ratoon ( $p=0.12$ ; Figure 3.4a). However, exchangeable K at the rate of 240 kg K ha<sup>-1</sup> was significantly higher than the control after harvest of the third ratoon. For all three K application rates, exchangeable K, after harvest of second, third, and fourth ratoons, did not drop below the initial levels. Exchangeable K in the treated umbric Acrisol increased significantly with treatments after harvest of the second ratoon ( $p<0.05$ ; Figure 3.4b). Although the difference in exchangeable K was not statistically significant after harvest of the plant crop ( $p=0.063$ ) and first ratoon ( $p=0.071$ ) in the treated umbric Acrisol, the rate of 240 kg K ha<sup>-1</sup> was significantly higher than the control for the second ratoon. Exchangeable K after harvest of the plant crop was higher than at the commencement of the trial for the 240 kg ha<sup>-1</sup> application rate. With cropping, on the umbric Acrisol levels of exchangeable K tended to diminish at the application rate of 0 and 120 kg ha<sup>-1</sup>.



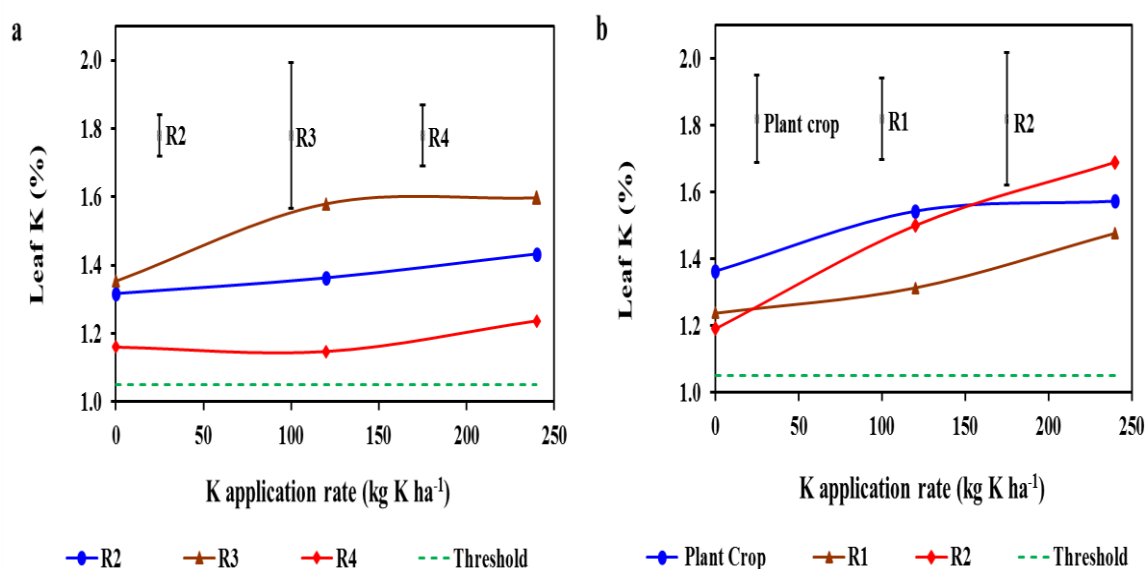
**Figure 3.4** Relationships between applied potassium (K) and exchangeable K after harvest of (a) second ratoon (R2), third ratoon (R3), and fourth ratoon (R4) on cutanic Acrisol at Umfolozi and after harvest of (b) plant crop, first ratoon (R1), and second ratoon (R2), on umbric Acrisol at Doringkop. Exchangeable K at the commencement of the trials is indicated by the green dotted line. Potassium application was repeated after each harvest. The LSD (0.05) bars for each crop are indicated as vertical lines.

During the four years in which the trial on the cutanic Acrisol at Umfolozi was conducted, there was an upward trend in exchangeable K in the control with time despite increasing cumulative K removals by the crop (Figure 3.5a). In contrast, there was a downward trend in exchangeable K with increasing cumulative K removal by the crop in the control of the umbric Acrisol (Figure 3.5b).

Although third leaf K values tended to increase with the amount of K applied on cutanic Acrisol, these differences were not significant for any of the crops (Figure 3.6a). The leaf K was not affected by treatments on the umbric Acrisol, except in the case of second ratoon, where leaf K at the rate of 240 kg K ha<sup>-1</sup> was significantly higher than the control (Figure 3.6b). In both soils, leaf K concentrations at all K treatment levels and harvests were above the SASRI recommended threshold value of 1.05 %.



**Figure 3.5** Changes in topsoil exchangeable potassium (K) with time and cumulative K removals by the sugarcane crop from zero (untreated) K treatments of the (a) cutanic Acrisol at Umfolozi and (b) umbric Acrisol at Doringkop.



**Figure 3.6** Relationships between applied potassium (K) and leaf K of (a) second ratoon (R2), third ratoon (R3), and fourth ratoon (R4) grown on cutanic Acrisol at Umfolozi and (b) plant crop, first ratoon (R1), and second ratoon (R2) on umbric Acrisol at Doringkop. The green dotted lines indicate the threshold value for leaf K in a sugarcane crop. Potassium application was repeated after each harvest. The LSD (0.05) bars for each crop are indicated as vertical lines.

### 3.4 DISCUSSION

Soil factors influencing sugarcane response to K application are exchangeable K, clay content, clay mineralogy, base status (exchangeable Ca and Mg), subsoil K, reserve-K, release rate of reserve-K, and K fixation (Wood and Meyer 1986; Donaldson *et al.* 1990; Schroeder and Wood 2002). It is necessary to establish which of these factors will explain the differences in yield responses from the two soils used in this study. It was proposed that the observed difference in response to K application would be explained by subsoil K, reserve-K, release rate of reserve-K, and K fixation. Initial exchangeable K and clay content of the two soils were similar (Table 3.1) and will not explain the different response to K application. Clay mineralogy, although not measured, was expected to differ in the two soils. Wood and Schroeder (1991) indicated that alluvial soils were dominated by vermiculite, smectite, and mica while those derived from table mountain sandstone were dominated by kaolinite and gibbsite. The different clay mineralogy from the two trial sites would explain the difference responses to K application but ultimately their effect was linked to reserve-K and K fixation. The cutanic Acrisol, which would be dominated by vermiculite, smectite, and mica would have high reserve-K and K fixation capacity, as measured in this study. Similarly, umbric Acrisol, on the hand would have low reserve-K and K fixation capacity as measured in this study because it would be dominated by kaolinite and gibbsite. In terms of base status, while cutanic Acrisol had higher base status, it would not explain the different responses to K application. The high base status influence on crop response to K application is operational when clay content is above 40% and base status above 30 cmol<sub>c</sub> kg<sup>-1</sup>) and results in reduced uptake of K (Donaldson *et al.*, 1990; Henry *et al.*, 1992; Duvenhage and King, 1996).

The lack of stalk and sucrose yield responses to K applications on the cutanic Acrisol are consistent with its very high reserve-K levels (Table 3.1). Anecdotal evidence of optimum yields with no applied K have frequently reported by the growers in the southern African sugar industry; and these optimum yields are thought to be associated with high levels of reserve-K, and this was strongly implied from the results of this study. Somewhat surprisingly, there was also a lack of stalk yield response to K on the umbric Acrisol, which had a low reserve-K level and was depleted of subsoil

exchangeable and reserve K (Appendix 3.1). Nonetheless, sucrose yield at the second ratoon did increase with increasing K application indicating that application of K can improve yields in later ratoons on a soil with low reserve K. This finding is consistent with earlier reports of higher responses to applied K in ratoons compared to plant crops (Chapman 1980; Wood and Meyer 1986). In this study, the delayed response on the umbric Acrisol is most likely associated with a decline in exchangeable K with time. Chapman (1980) also reported that the observed delayed response to K application is influenced by depletion of K reserves in control treatments. In fact, K requirements in the umbric Acrisol also increased with time (Appendix 3.2). Hence, positive sucrose yield responses to K application on the umbric Acrisol are expected to persist for succeeding ratoons, while the lack of crop response on the cutanic Acrisol is also expected to persist for more ratoons.

The effects of K applications on exchangeable K levels in the two soils is most likely influenced by K reserves and fixation (the latter reflected in the KRF values in Table 3.1). Exchangeable K in the control of the cutanic Acrisol, which had very high reserve-K, did not decrease below the initial levels, but in the umbric Acrisol it did decrease below the initial levels. Likewise, in the cutanic Acrisol, which had a high K fixation capacity there was no response to K application, but exchangeable K on umbric Acrisol increased with all K applications after harvest of second ratoon and at 240 kg K ha<sup>-1</sup> after harvest of plant crop and first ratoon. The lack of exchangeable K response to K applications could be caused by either the release of K from the non-exchangeable reserves, K removal being equal to the amount of K applied, or K fixation, or the combination thereof. However, since there was no stalk yield response to K, it is unlikely that the lack of response was caused by K removal equalling the amount of K applied. Inasmuch as there was an apparent release of reserve-K to exchangeable K in the control, the amount of K released was always below the amount of K applied. Hence, it is suggested that the lack of effect on exchangeable K levels in this study was caused predominantly by high K fixation capacity of the cutanic Acrisol.

The increase in exchangeable K in the zero K treatment of the cutanic Acrisol over the years, despite K removal, is most likely explained by the release of reserve-K. Similar

results were found by Bar-Tal *et al.* (1991), where applied K was fixed by smectitic soils but K was released from the reserves at zero K treatment. It is proposed then that high K fixation and high reserve-K serve as buffers for soil K and regulate exchangeable K concentrations. Another aspect for consideration is that the increase in exchangeable K in zero K treatments, despite K removal by the crop, occurred only in the cutanic Acrisol whereas there was a decrease in exchangeable K in the umbric Acrisol. This observation is at variance with the reports of Khan *et al.* (2014). These authors observed an increase in exchangeable K in zero K treatments in Morrow plots (University of Illinois) despite 51 years of crop K removal and concluded that testing soils for exchangeable K was unnecessary. The results of the current study highlight how in zero K treatments exchangeable K may increase or decrease with cropping, depending on levels of reserve-K. It would appear, therefore, that instead of discarding soil testing using exchangeable K, there is a need to supplement this parameter with measurements of soil K fixation and levels of reserve-K. Clearly, in our study the changes in exchangeable K in both the umbric Acrisol and cutanic Acrisol following K application or removal could be explained by considering soil K fixation and levels of reserve-K.

Increasing leaf K concentration with increasing K application is to be expected and is widely reported for crops (Simonis *et al.* 1998; Ogaard *et al.* 2001; Oborn *et al.* 2010) and this was expected for the umbric Acrisol because it had low levels of reserve-K. However, leaf K concentration results should be interpreted with caution because of the phenomenon of luxury consumption of K, where the plants have sufficient K but continue to absorb K without any effect on yields (Ogaard *et al.* 2001; Staines *et al.* 2014). Three critical sugarcane leaf K concentrations are reported in the literature: the first is 1.05 %, the threshold below which the crop will be deficient in K; the second is 1.25%, beyond which yield response to K is unlikely; and lastly 1.5%, above which luxury consumption is considered to occur (Wood and Meyer 1986; Meyer *et al.* 1989). Leaf K in the umbric Acrisol control was below 1.25% and significantly lower than that at 240 kg K ha<sup>-1</sup> for the second ratoon. Interestingly though, sucrose yield responses were also observed only in the second ratoon on that soil, indicating that leaf K concentrations could also be used as indicators of the likelihood of response to K fertilization.

The findings of this study indicated that K reserves and fixation does influence the response of exchangeable K, sugarcane stalk and sucrose yields to K application. It is thus argued that these should be incorporated in routine soil testing and formulation of K recommendations. It is also recognised that subsoil K and release rate on K reserves can influence the response of sugarcane to K application. However, for several reasons, their incorporation in routine soil testing and formulation of K recommendations remains a challenge. Routine soil testing is based solely on the topsoil and does not include subsoils and furthermore, subsoil exchangeable K of the soils used was lower than that of topsoil which is in agreement with Miles (2012) who reported depletion of subsoil K in the soils of the South African sugar industry. While cutanic Acrisol had subsoil reserve-K, the main cause on the lack of response to K application is believed to be topsoil reserve-K. Further studies are required to investigate the contribution of reserve-K and subsoil K reserves on K uptake. Release rate of K reserves, on the other hand, is influenced by a number of temporal variable factors such soil solution K concentration, temperatures, and wetting and drying (Sparks and Huang 1985; Wood and Meyer 1986). It is presumed that levels of reserve-K and K fixation control release rate but this requires further investigations. Combinations of reserve-K and K fixation will be investigated in Chapter 4.

### **3.5 CONCLUSIONS**

This study demonstrated that reserve-K and K fixation influence the response to K fertilization of stalk yields and sucrose yields, soil exchangeable K, and leaf K. Sugarcane depleted K on a soil low in reserve-K, which resulted in sucrose yield and leaf K responses to applied K, whereas on a soil high in reserve-K there was no K depletion nor a response to K application. These findings provide some validation of published criteria for very high reserve-K, and also suggest that the criteria for low reserve-K is possibly conservative. The soil with high K fixation capacity maintained steady levels of exchangeable K whereas K application increased exchangeable K on the soil with low K fixation capacity. Results from this study also indicated that reserve-K and K fixation provides a measure of K buffering capacity, which regulates



exchangeable K concentrations and K uptake by the crop. This study indicated the importance of including modifications based on levels of reserve-K and K fixation when calculating K requirements. Such modifications will bring medium to long-term benefits, including improvements in fertilizer use efficiency.

## CHAPTER FOUR

### ACCOUNTING FOR VARIATION OF POTASSIUM RESERVES AND IMMOBILIZATION IN DEVELOPING SUGARCANE FERTILIZER REQUIREMENTS

#### 4.1 INTRODUCTION

Appropriate testing for soil potassium (K) is essential for effective and sustainable fertilizer management. Traditionally, K requirements have been calculated largely from soil K test results based on levels of exchangeable K. However, basing K requirements on only exchangeable K is questionable (Khan *et al.* 2014). Over the years attempts have been made by FAS to improve the reliability of K recommendations. This has involved modifying soil exchangeable K thresholds by including clay content and base status in calculating K requirements (Wood and Meyer 1986; Donaldson *et al.* 1990). These initiatives are widely considered to have improved the reliability of K recommendations, but there remains a clear need to include reserve-K and K fixation when calculating K requirements, as indicated by sugarcane responses to K application in field trials (Chapter 3). Reserve-K and K fixation are expected to vary widely between soils, soil depths and horizons. This is because factors such as clay content, clay mineralogy, soil pH, and cation exchange capacity which influence reserve-K and K fixation (Beckett 1970; Sharpley 1989; Johnston *et al.* 1999; Oborn *et al.* 2005; Srinivasa Rao *et al.* 2007; Zorb *et al.* 2014) also vary widely between soils, soil depths and horizons. However, majority of soil K testing programmes have not accounted for these variations when formulating K recommendations. Furthermore, the impact of including reserve-K when formulating K recommendations has not been evaluated in combination with K fixation capacity of soils.

Knowledge gaps exist in the literature regarding the inclusion of reserve-K and K fixation when formulating K requirements. This study investigated the levels of reserve-K and K fixation in the soils of the South African sugar industry, their impacts on K requirements of soils, and grouped soils according to their varying levels of

reserve-K and K fixation, with the objective of improving the reliability of fertilizer K recommendations.

## 4.2 MATERIALS AND METHODS

The investigations were carried out on 113 topsoil (0-200 mm) samples from fields located throughout the South African sugar industry. Soil groups included Acrisols (Oakleaf, Sweetwater, Nomanci, and Tukulu); Arenosols (Fernwood and Namib), Ferralsols (Kranskop, Magwa, Inanda, Hutton, and Clovelly); Fluvisols (Dundee), Leptosols (Mayo, Milkwood, Mispah, Glenrosa, and Cartref); Luvisols (Swartland and Valsirivier); Nitisols (Shortlands); Plinthosols (Longlands, Wasbank, Westleigh, Dresden, and Avalon); and Vertisols (Rensburg and Arcadia), according to the World Reference Base for Soil Resources (IUSS Working Group WRB 2014) and the South African soil classification names are given brackets (Soil Classification Working Group, 1991). The soils were dried and milled to pass through a 1 mm sieve and analysed in the FAS laboratory as described in Chapter 3. Salient soil characteristics are presented in Table 4.1.

Reserve-K was determined by boiling 2.5 g of soil in 100 mL of 1.0 M HNO<sub>3</sub> for 30 minutes. The concentration of K in the extract was measured using ICP-OES. Exchangeable K values were then subtracted from the nitric acid extractable K values, and the resultant data are referred to, hereafter, as 'reserve-K'. For interpretive purposes, reserve K values were split into four categories, namely low, medium, high, and very high (Table 4.2), after the adaptation from Haysom (1971) and Schroeder *et al.* (2007). These categories are suggested to impact fertilizer recommendations as follows: very high reserve K implies zero fertilizer K requirement, while for the low category no change to the routine fertilizer K recommendations is required (Table 4.2). This implies that the low reserve-K criterion is currently being applied uniformly across all soils in the formulation of K recommendations for the sugar industry. For the medium and high categories, 30% and 60% reductions in fertilizer K applications, respectively, are applied, in accordance with the proposal by Haysom (1971).

**Table 4.1** Mean values of pH<sub>CaCl2</sub>, total organic carbon, clay content, and total cations for the different soil types. Values in parentheses represent ranges.

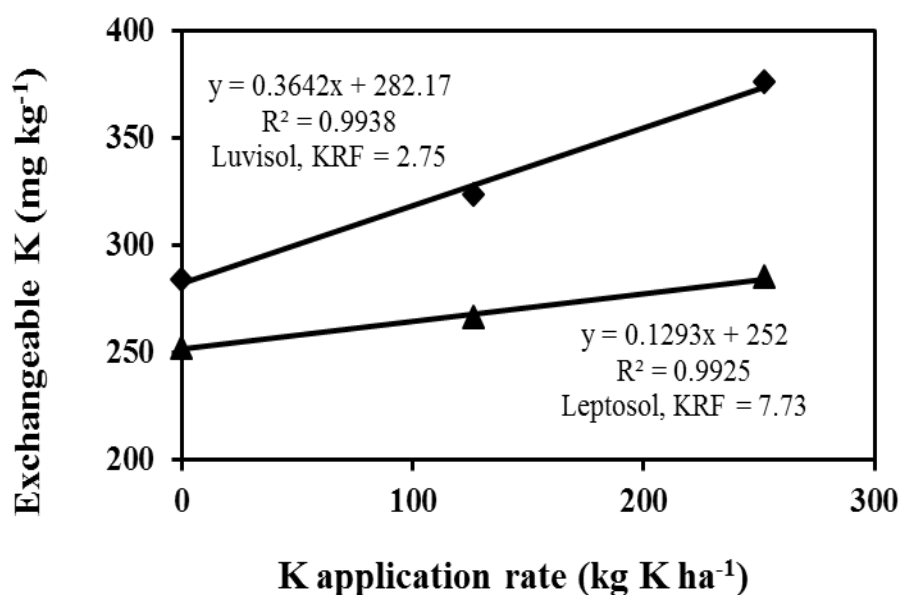
Soil type	Number of samples	pH <sub>CaCl2</sub>	Total carbon (%)	Clay content (%)	Total cations <sup>(a)</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )
<b>Acrisols</b>	20	4.83 (3.77–6.62)	2.17 (0.61–9.72)	24 (8–43)	9.05 (1.97–23.63)
<b>Arenosols</b>	4	5.06 (4.34–5.45)	0.78 (0.44–1.29)	8 (7–9)	4.38 (2.25–6.22)
<b>Ferralsols</b>	23	4.86 (3.7–6.76)	2.57 (0.49–6.47)	30 (10–54)	7.45 (2.46–22.82)
<b>Fluvisols</b>	3	5.81 (4.7–6.33)	1.62 (1.02–1.97)	34 (18–60)	23.72 (9.53–38.69)
<b>Leptosols</b>	29	4.88 (3.8–6.92)	2.07 (0.52–6.86)	25 (5–56)	8.12 (1.40–25.67)
<b>Luvisols</b>	4	5.08 (4.0–6.19)	1.90 (1.17–3.35)	29 (19–39)	10.83 (2.91–16.59)
<b>Nitisols</b>	10	5.28 (4.4–6.62)	2.18 (1.22–3.57)	42 (13–61)	13.59 (2.72–25.57)
<b>Plinthosols</b>	12	4.72 (4.1–6.52)	1.56 (0.69–2.55)	22 (5–33)	7.19 (2.29–15.10)
<b>Vertisols</b>	8	5.65 (4.85–6.85)	2.86 (1.60–4.43)	52 (39–70)	28.14 (17.70–36.44)

(a) Total cations obtained by summing the quantities of AMBIC extractable Ca, Mg, K, and Na and KCl exchangeable acidity (Al + H)

**Table 4.2** Critical levels and categories of soil reserve potassium (K) using the nitric acid method and recommendations for sugarcane (modified from Haysom 1971)

Soil reserve K (cmol <sub>c</sub> kg <sup>-1</sup> )	Category	Recommendation
<0.80	Low	Fertilise based on exchangeable K
0.80 – 1.50	Medium	Reduce K fertilisation by 30%
1.50 – 2.50	High	Reduce K fertilisation by 60%
>2.50	Very high	Do not apply fertilizer K

The capacity of the soil to fix added K is estimated through medium-term incubations and is termed the K requirement factor (KRF), which essentially reflects the amount of fertilizer K required to raise the exchangeable K by a single unit (Johnston *et al.* 1999). The method for the determination of KRF (kg K/ha/unit soil test, where the soil test is in mg kg<sup>-1</sup>), was adapted from Johnston *et al.* (1999), and involved treating 1.5 L of soil with three different levels of KH<sub>2</sub>PO<sub>4</sub> (supplying equivalents of 0, 126.2 and 252.4 kg K ha<sup>-1</sup> based on a soil depth of 200 mm). Soils were brought to field capacity by adding distilled water, and incubated in open containers at ambient temperatures in a glasshouse for six weeks. The period of six weeks is deemed sufficient for equilibration: Liebbhardt and Cotnoir (1979) indicated that KRF values measured over periods ranging from four, eight, and twenty four weeks were not statistically different. Re-wetting of the soil to field capacity was done every fortnight. Following incubation, soils were air-dried, milled (<1 mm) and tested for K using ICP-OES following AMBIC extraction (van der Merwe *et al.* 1984). Slopes of all relationships between soil test K and applied K were linear (Figure 4.1). The values of KRF were determined from the inverse of the slope for each soil. Measured KRF values were compared to the constant value of 3.0, which is currently used in FAS. This KRF value of 3.0 assumes some degree of K fixation. Assuming zero K fixation, and a ploughing depth of 20 cm, the KRF would be 2.0 kg K ha<sup>-1</sup> per unit soil test. Therefore, values below 2.0 are indicative of soils that release K with wetting and drying (Weil and Brady 2017). It was reasoned that KRF values between 2.0 and 2.5 represent soils with negligible K fixation while soil samples with a high level of K fixation will have KRF values above 3.5. The following categories of K fixation are proposed: low, medium, high, and very high with KRF values of 1.5 - 2.5, 2.5 - 3.5, 3.5 - 4.5, above 4.5, respectively.



**Figure 4.1** Relationships between applied potassium (K) and exchangeable K for two soils (leptosol and luvisol) in the incubation study.

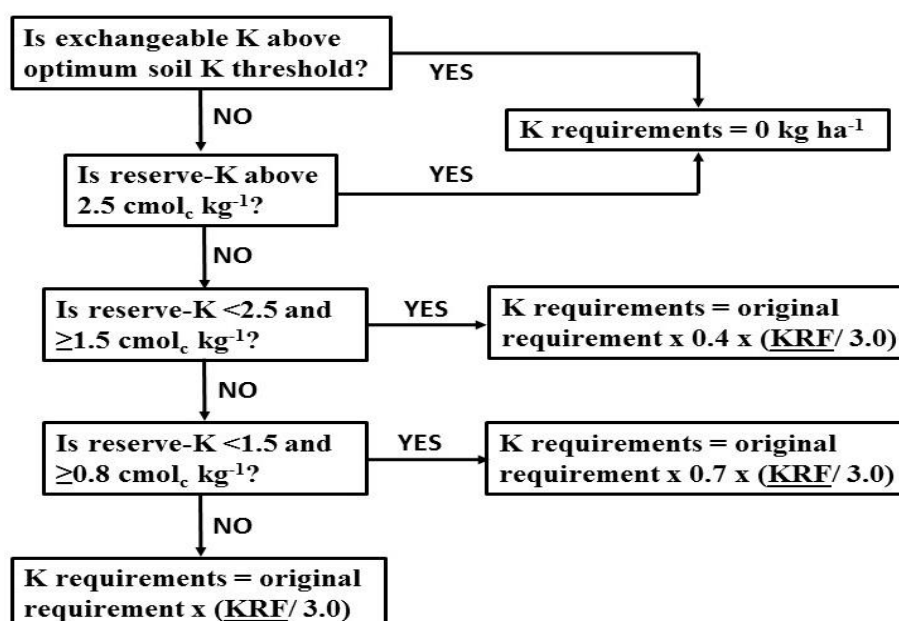
Soils were grouped according to the varying levels of reserve-K and KRF, which enabled an assessment of how many combinations of reserve-K and K fixation were possible. It was postulated that each combination provides some reflection of the extent of soil K buffering capacity.

The impact of introducing reserve-K and KRF factors into fertilizer recommendations was evaluated by comparing fertilizer K requirements based on exchangeable K only and those obtained by accounting for levels of reserve-K and KRF. Fertilizer K requirements were calculated using exchangeable K values for sugarcane yields of 100 t ha<sup>-1</sup> as shown in Equation 4.1. The yield of 100 t ha<sup>-1</sup> was chosen because it approximates the industry average and is comparable to the yields observed in field trials (Chapter 3). In the recommendations provided by FAS, the optimum soil K threshold in Equation 4.1 is modified on the basis of clay content and base status. When reserve-K was taken into account, fertilizer K requirements determined by Equation 1 were modified as indicated by the modifiers presented in Table 4.2. In order to obtain K requirements based on KRF values, exchangeable K-based fertilizer K requirements were multiplied by the ratio of KRF to 3 (Equation 4.2).

$$\text{K requirement (kg ha}^{-1}\text{)} = (\text{optimum soil K threshold} - \text{measured soil K}) \times 3.0 \quad (4.1)$$

$$\text{K requirement (kg ha}^{-1}\text{)} = (\text{optimum soil K threshold} - \text{measured soil K}) \times (\text{KRF} / 3.0) \quad (4.2)$$

Fertilizer K requirements were also calculated by simultaneously accounting for both reserve-K and KRF; following the criteria shown in Figure 4.2. The first criterion used was exchangeable K: if sufficient, then no K would be required. The second criterion was level of reserve-K, which would apply to samples with low exchangeable K as shown in Figure 4.2. The KRF was used on samples that still require application of K after taking into account both exchangeable K and reserve-K. This means that KRF was used even for samples with high reserve-K, as long as reserve-K is less than 2.5  $\text{cmol}_c \text{ kg}^{-1}$ . This was based on the assumption that high KRF indicates a high tendency for K fixation, which may reflect slow release from the non-exchangeable reserves.



**Figure 4.2** A flow chart showing the criteria used to calculate potassium (K) requirements when both reserve-K and K requirement factor (KRF) are taken into account.

Changes to fertilizer K requirements due to the introduction of both reserve-K and KRF were also calculated (Equation 4.3). Fertilizer K requirements based only on exchangeable K are regarded as original recommendations and those that account for both reserve-K and KRF are modified recommendations.

$$\text{Changes in K requirements (\%)} = (\text{modified recommendations} - \text{original recommendations}) / \text{original recommendations} \times 100 \quad (4.3)$$

#### 4.2.1 Statistical analysis

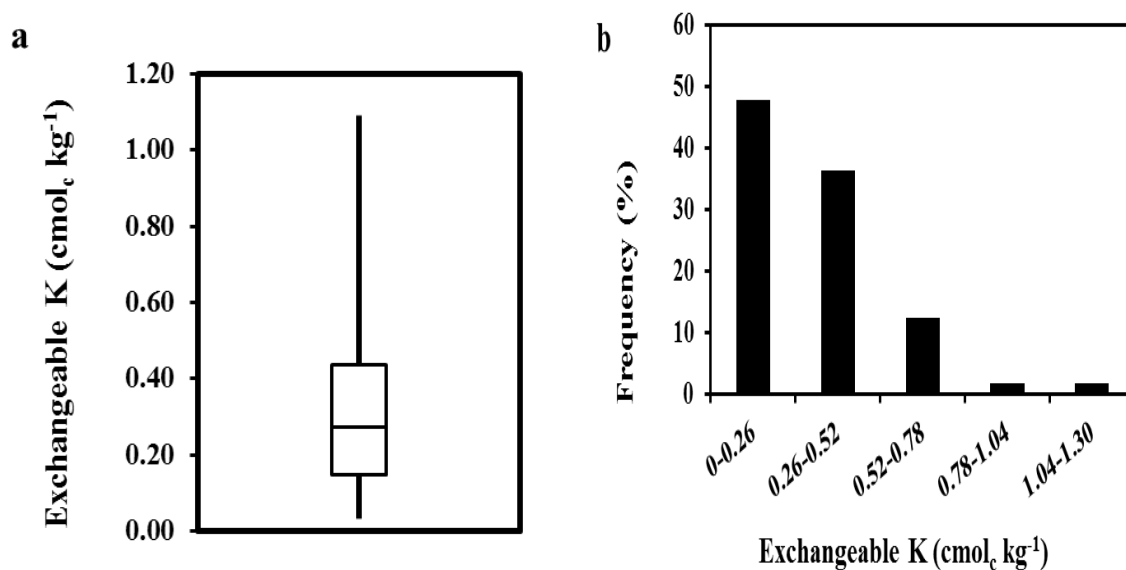
The comparison between fertilizer K requirements based on exchangeable K and those obtained after accounting for levels of reserve-K and KRF were made using Microsoft Excel's t-Test: paired two samples for means. If the output p value was less than 0.05 then the modified fertilizer K requirements were statistically different from those based on exchangeable K.

### 4.3 RESULTS

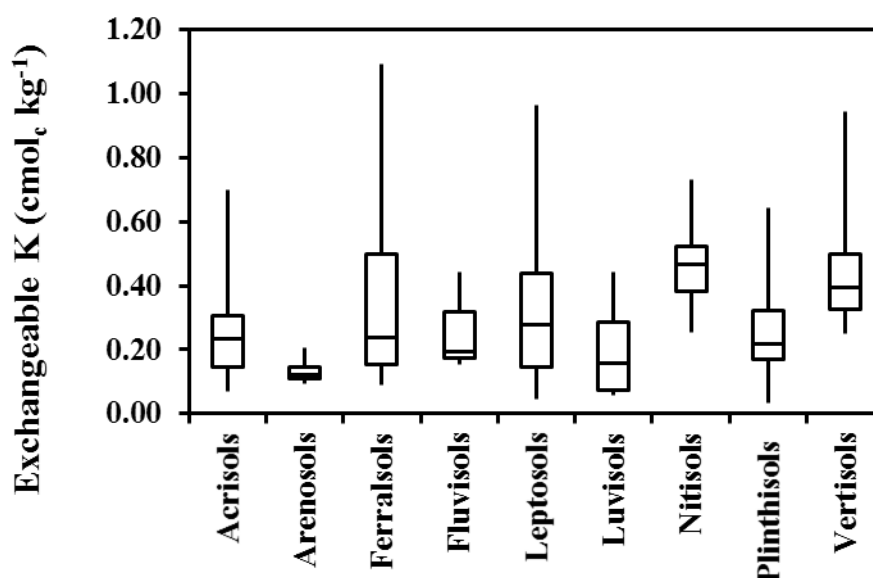
#### 4.3.1 Exchangeable K

Exchangeable K values ranged from 0.03 to 1.09  $\text{cmol}_c \text{ kg}^{-1}$ , with the median being 0.27  $\text{cmol}_c \text{ kg}^{-1}$  (Figure 4.3a). The frequency distribution (Figure 4.3b) shows that 48% of the samples had exchangeable K values below 0.26  $\text{cmol}_c \text{ kg}^{-1}$  and 36% of the samples had exchangeable K values between 0.26 and 0.52  $\text{cmol}_c \text{ kg}^{-1}$ . Samples with exchangeable K above 0.52  $\text{cmol}_c \text{ kg}^{-1}$  comprised less than 20% of the set. The few samples with exchangeable K above 0.52  $\text{cmol}_c \text{ kg}^{-1}$  belonged to the Acrisols, Ferralsols, Leptosols, Nitisols, Plinthosols and Vertisols (Figure 4.4). It is also worth noting that there was a wide variation in exchangeable K values even within the same groups of soils.





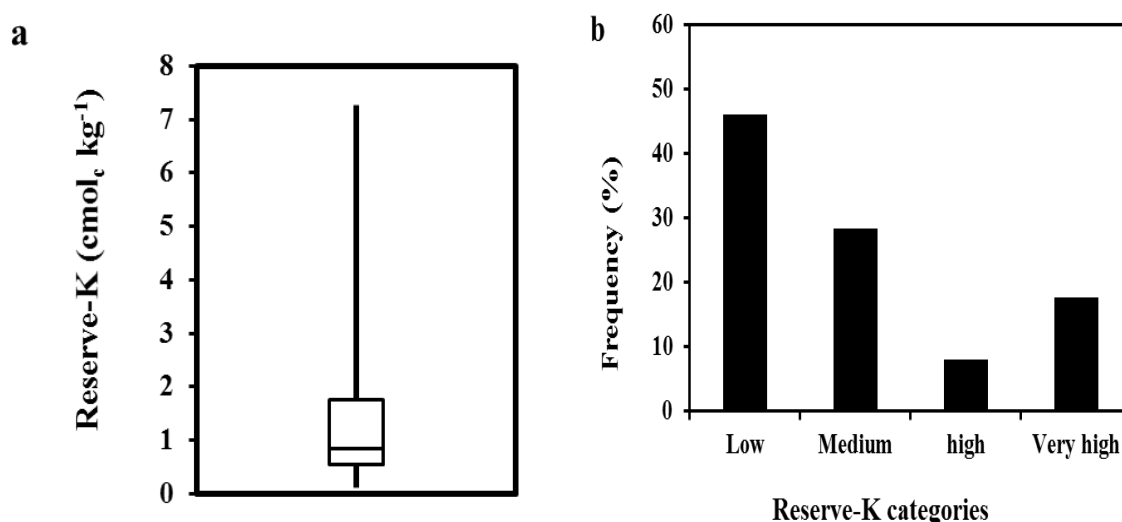
**Figure 4.3** Variations in the exchangeable potassium (K) for all soils included in the study as indicated by (a) boxplot and (b) frequency distributions of exchangeable K. The two vertical lines in (a) which form the top and bottom ends of each box represent 25th and 75th percentiles, respectively, of the distribution in each class. The middle horizontal line in the box represents the median (50th percentile).



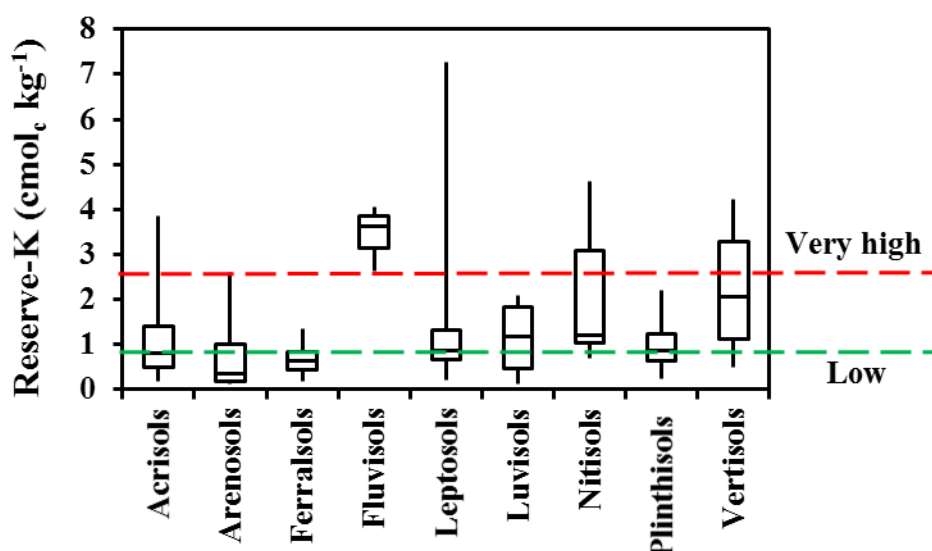
**Figure 4.4** Variations in exchangeable potassium (K) for different soil types as indicated by boxplots. The two vertical lines which form the top and bottom ends of each box represent 25th and 75th percentiles, respectively, of the distribution in each class. The middle horizontal line in the box represents the median (50th percentile).

### 4.3.2 Reserve-K

There was also a wide variation in reserve-K content for all the soils, with a range from 0.11 to 7.27  $\text{cmolc kg}^{-1}$ , and median of 0.85  $\text{cmolc kg}^{-1}$  (Figure 4.5a). The distribution of reserve K (Figure 4.5b) between low, medium, high, and very high categories (Hansom, 1971) was 46, 28, 8 and 18%, respectively. Reserve-K in Fluvisols was in the very high category (Figure 4.6). There was a wide variation in reserve-K for Nitisols and Vertisols, but the values were predominantly in the high and very high categories. Ferralsols and Arenosols were characterised by low reserve-K levels. Acrisols, Leptosols, Luvisols, and Plinthosols also had wide variations in reserve-K, but their medians were above 0.80  $\text{cmolc kg}^{-1}$  (Figure 4.6).



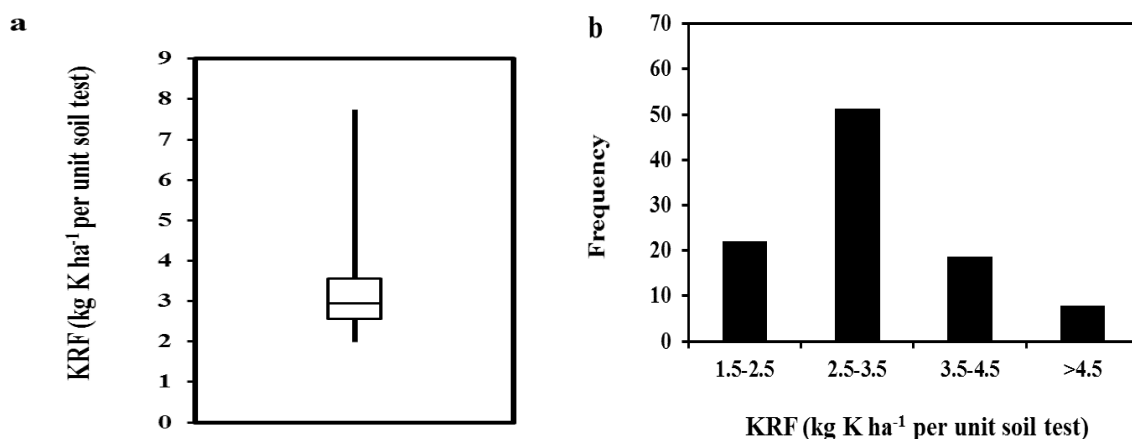
**Figure 4.5** Variations in the reserve potassium (K) as indicated by (a) boxplot and (b) frequency distributions of reserve-K for different categories. The two vertical lines in (a) which form the top and bottom ends of each box represent 25th and 75th percentiles, respectively, of the distribution in each class. The middle horizontal line in the box represents the median (50th percentile).



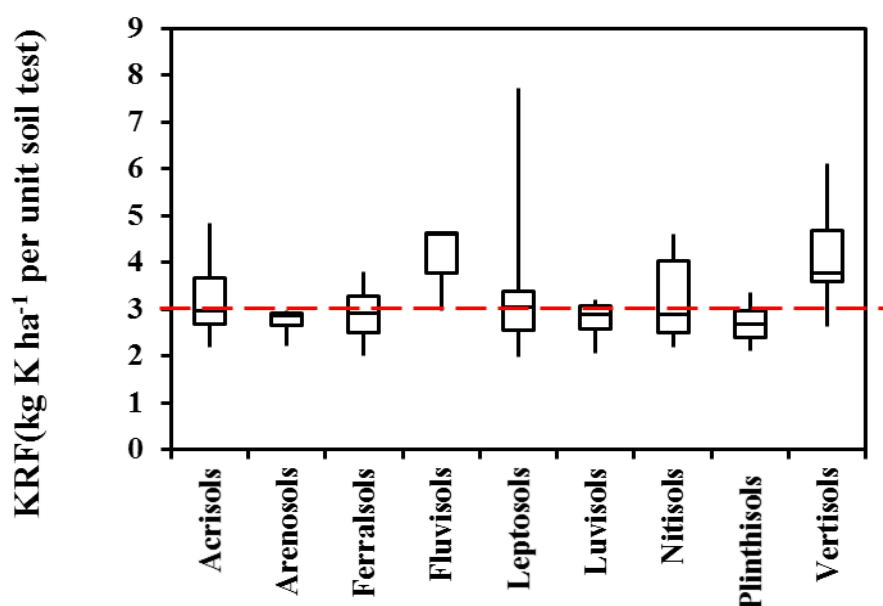
**Figure 4.6** Variations in reserve potassium (K) for different soil types as indicated by boxplots. The dotted horizontal lines indicate the ‘low’ and ‘very high’ levels specified in the Australian studies of Haysom (1971). The two vertical lines which form the top and bottom ends of each box represent 25th and 75th percentiles, respectively, of the distribution in each class. The middle horizontal line in the box represents the median (50th percentile).

#### 4.3.3 KRF values

As was the case with exchangeable K and reserve-K, there was a wide variation in the measured KRF values ranging from 1.99 to 7.73 kg K ha<sup>-1</sup> per unit soil test, with the median for all soils being 3.0 (Figure 4.7a). Notably, this median coincides with the value currently used by FAS in developing K fertilizer recommendations. Given that more than 50% of the samples had KRF values between 2.5 and 3.5 (Figure 4.7b), the indication is that the constant value of 3.0 could approximate K fixation for half of the samples analysed. The remaining half of the samples were equally distributed between low KRF (1.5-2.5) and high KRF (>3.5) values. The median of 3.0 was also observed for Acrisols, Ferralsols, Leptosols, and Nitisols (Figure 4.8). Wide variations in KRF were observed within soil types. Arenosols, Luvisols, and Plinthosols were characterised by low KRF values while Fluvisols and Vertisols were characterised by high KRF values.



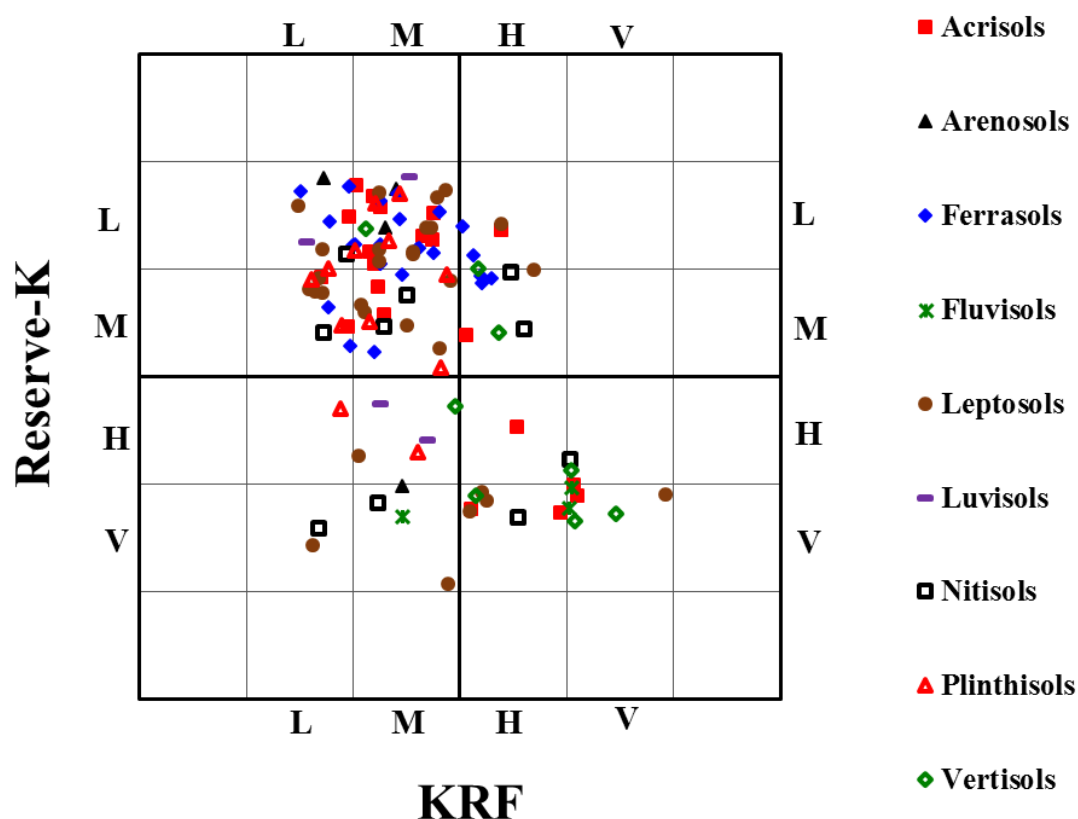
**Figure 4.7** Variations in the potassium requirement factor (KRF, an indicator of soil's K fixation capacity) as indicated by (a) boxplot and (b) frequency distributions of KRF for different categories. The two vertical lines in (a) which form the top and bottom ends of each box represent 25th and 75th percentiles, respectively, of the distribution in each class. The middle horizontal line in the box represents the median (50th percentile).



**Figure 4.8** Variations in potassium requirement factor (KRF) for different soil types as indicated by boxplots. The dotted horizontal line indicate the constant value of 3.0 currently used in the Fertilizer Advisory Service. The two vertical lines which form the top and bottom ends of each box represent 25th and 75th percentiles, respectively, of the distribution in each class. The middle horizontal line in the box represents the median (50th percentile).

#### 4.3.4 Combination of reserve-K and KRF

The combinations of reserve-K and KRF varied between soils and within soil types (Figure 4.9). There were 14, out of potentially 16, combinations of reserve-K and KRF found in this study. There were no samples with a combination of low to medium reserve-K and very high KRF. The combination of low reserve-K with low, medium, and high KRF had 10, 31, and 5% samples, respectively. Samples with a combination of medium reserve-K and low, medium, and high KRF were 10, 12, and 6%. There was 3% of samples having combination of low KRF but high to very high reserve-K and 8% of samples having medium KRF and high to very high reserve-K. The remaining 15% of the samples had a combination of high to very high reserve-K and KRF.



**Figure 4.9** A grid representation of the combinations of low (L), medium (M), high (H), and very high (V) categories of reserve potassium (K) and K requirement factor (KRF).

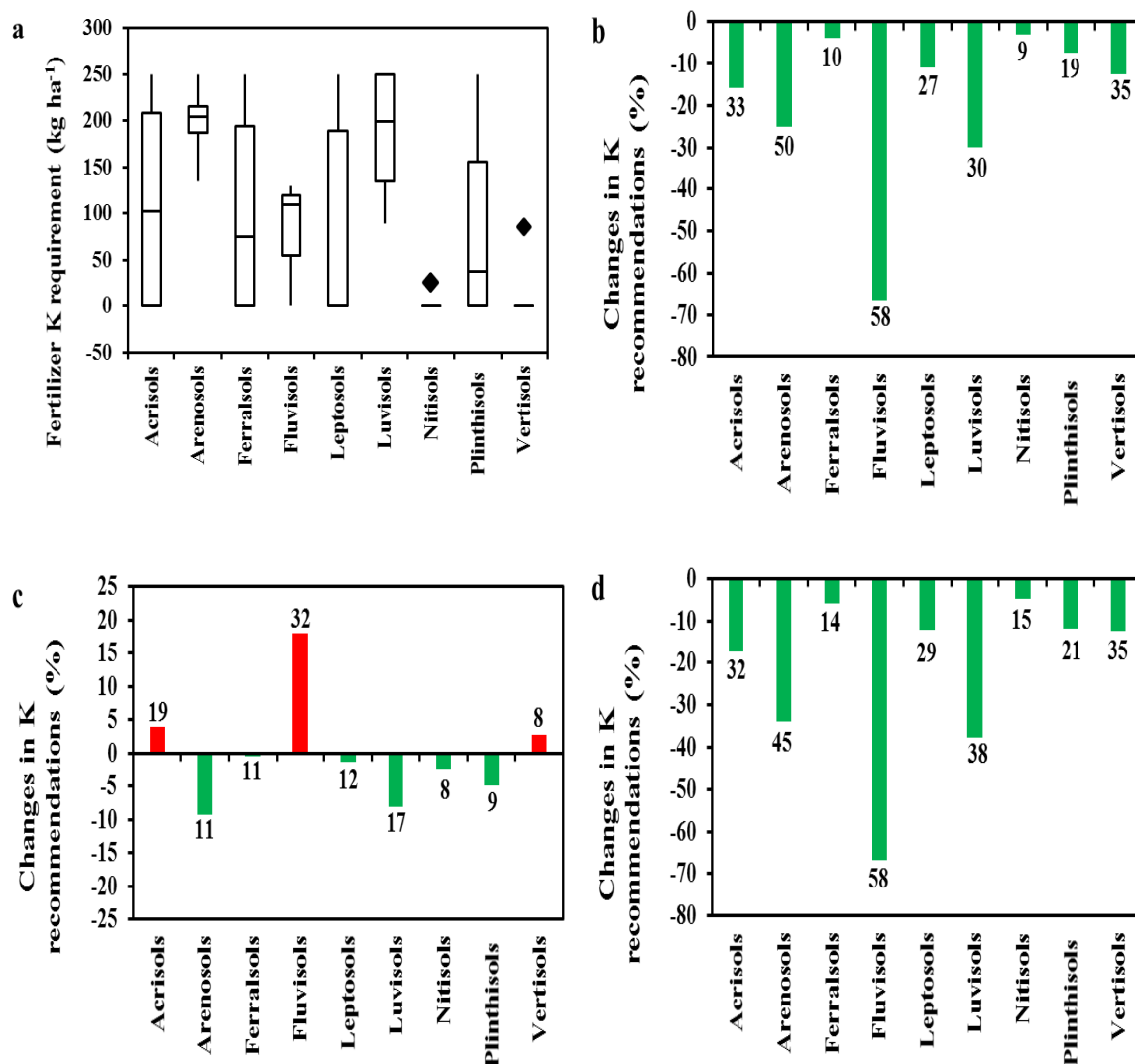
#### 4.3.5 Fertilizer K requirement

Fertilizer K requirement, based on equation 4.1, varied widely within soil types (Figure 4.10a). More than 50% of Leptosols, Nitisols, and Vertisols had zero K requirement. Maximum K requirement was 200 kg ha<sup>-1</sup> and was observed for Acrisols, Arenosols, Ferralsols, Leptosols, Luvisols, and Plinthosols. Most samples from arenosol and luvisol soil types had K requirements above 100 kg ha<sup>-1</sup>.

Introduction of reserve-K resulted in a significant reduction in K requirements for all soil types (Figure 4.10b) and the overall average change was 20%. The average changes for different soil types was below 30% with the exception of Fluvisols that had 67% average change in K requirement. The t-test confirmed that the modified K requirement based on reserve-K was statistically different from K requirement based on exchangeable K. It is also worth noting that there were wide variations in the changes in K requirement within the same soil type.

There were reductions in K requirements as a result of introducing KRF in the calculations for most soil groups except Acrisols, Fluvisols, and Vertisols in which the average K requirements increased (Figure 4.10c). Similarly to reserve-K, there were wide variations in the changes in K requirement within the same soil type. Overall, K requirements that accounted for KRF were not statistically different to K requirements based only on exchangeable K.

The average changes in K requirement as a result of introducing both reserve-K and KRF for soils were similar to those observed when only reserve-K was introduced with the exception of Arenosols and Luvisols (Figure 4.10b, 4.10d). Statistical analysis also confirmed that these two approaches were not statistically different. Nonetheless, introduction of both reserve-K and KRF did result in further reductions in K requirements for Arenosols and Luvisols, compared to the introduction of only one of these components.



**Figure 4.10** The potassium (K) status of different soil types as represented by (a) K requirements based on exchangeable K and corresponding changes in K requirements as a result of accounting for (b) levels of reserve-K, (c) KRF values, and (d) both reserve-K and KRF. The bars represent the average changes while the numbers in the bar charts represent standard deviation for a given data set. The two vertical lines, in the box plot, which form the top and bottom ends of each box represent 25th and 75th percentiles, respectively, of the distribution in each class. The middle horizontal line in the box represents the median (50th percentile).

#### 4.4 DISCUSSION

All three K measurements (i.e. exchangeable K, reserve-K, and KRF) varied widely between soils as well as within soil types. The wide variations in exchangeable K could be expected as this parameter is not influenced only by soil properties but also by K inputs and K removals (Khan *et al.* 2014). The current soil testing programmes account for this variation in exchangeable K when developing fertilizer recommendations. The variations in reserve-K in soils of the South African sugar industry are comparable to those in other parts of the world (Srinivasa Rao *et al.* 2007) and those of K fixation to the soils of KwaZulu-Natal, South Africa (Johnston *et al.* 1999). Clearly, the variations in reserve-K should be accounted for in soil K testing, in view of levels of reserve-K affecting K supplies to the crop. Similarly, accounting for K fixation is deemed necessary because about 50% of the soils were not accommodated by the currently assumed KRF value and K fixation capacity is likely to affect the plant-availability of added K.

The variations of reserve-K and KRF between soil groups and within a soil group could be explained by fertilization and cropping history, clay content, and clay mineralogy. In Vertisols, for instance, which are dominated by vermiculites, fertilization would result in K fixation and the collapse of 2:1 layer sheets to form mica and illites (Barre *et al.* 2008; Skiba 2013). This collapse due to K fixation often results in mixed layer vermiculites/illites. Vermiculites have high K fixation capacity while illites will have high reserve-K and that explains the variations, and the high KRF and reserve-K values of Vertisols. The mixed layer vermiculites/illites is also known for causing high buffering capacity (Velde and Peck 2002) which is what was observed in the combination of high reserve-K and KRF. Fluvisols on the other hand are formed from alluvial material and are often dominated by mica and illites. Long term cropping results in vermiculitization of mica and illite (Hinsinger and Jaillard 1993; Vetterlein *et al.* 2013) which in most alluvial soils are reported to be dominated by mica/ illite, vermiculites, and smectite (Wood and Schroeder 1991; Murashkina *et al.* 2007). Similar to Vertisols, the varying degrees of combinations between illites and vermiculites explain the variations, and the high KRF and reserve-K values of Fluvisols. The behaviour of Arenosols which had small variation is influenced by a narrow range of clay contents



(Table 4.1) and high sand content of these soils. The high sand content can explain the values of reserve-K obtained because feldspars which are found in coarser materials can release substantial amounts of reserve-K (Sparks 2001). Since Arenosols are sandy soils their capacity to fix K is minute and this is the reasons for the observed combination of reserve-K and KRF. The combination of low reserve-K and low KRF of Ferralsols and Plinthosols is caused by large quantities of highly weathered minerals such as kaolinite and sesquioxides (IUSS Working Group WRB 2014). Acrisols, Leptosols, Luvisols, and Nitisols are often formed from various parent materials which include, but not limited to, alluvium material (IUSS Working Group WRB 2014). This is reason why there is wide variation in terms of reserve-K and KRF in soils and this is possibly linked to their varying clay mineralogy and clay content. These various combinations of reserve-K and KRF influenced the changes in calculated fertilizer K requirements.

Accounting for reserve-K and/or K fixation when formulating fertilizer K recommendations should give more accurate K requirements, in line with the body of literature (Johnston *et al.* 1999; Bar-Yosef *et al.* 2015; Wolde 2016). Including either reserve-K or K fixation separately in fertilizer K recommendations was shown to significantly change the calculated K requirements. However, this study showed that inclusion of both parameters will have added benefit from a K recommendations perspective. In terms of the proposed categories, the current FAS approach assumes low reserve-K and medium KRF across all soils, but only 31% of the samples were in this category. Potassium requirements based on the current approach would be overestimated, due to overestimated K fixation, for samples that had low to medium reserve-K and low KRF. Similarly, K requirements would be overestimated for samples with a combination of high to very high reserve-K and low KRF due to underestimation of reserve-K and overestimation of K fixation capacity. Soils with this combination could result in excessive K applications and associated luxury uptake of K, which could cause reduced sucrose recovery. It is postulated that some of the soils of sugarcane estates in Zambia (Munsamy 2013), Malawi (Whitbread *et al.* 2004), and Tanzania (JR Lincoln, personal communication) where reduced sucrose recovery is caused by excessive K content have high to very high reserve-K and low KRF. The most common feature of these soils is that they are derived from alluvium materials (Whitbread *et al.*

2004; Heathman and Meyer 2013; Taylor 2013). Potassium requirements for samples with high to very high reserve-K and medium KRF would also be overestimated due to underestimated reserve-K. There would be an underestimation of K requirements for samples with low to medium reserve-K and high KRF because of underestimated K fixation capacity. Lastly, a combination of high to very high reserve-K and high to very high KRF possibly relates to soils with high K buffering capacity, which regulates levels of exchangeable K. The consequence of using the current approach in soil K testing on soils with this combination would be unnecessary fertilizer K costs but the risk of luxury consumption was deemed low because of high K fixation capacity. The postulate of high K buffering capacity was validated (Chapter 3) where exchangeable K in control plots was not depleted by 5 years of sugarcane cropping and did not increase in treated plots despite three applications of 120 and 240 kg K ha<sup>-1</sup> over 5 years.

In this study, the effect of introducing KRF on K requirements was masked when the impact was averaged over all samples. This could be explained by changes in recommendations for samples with high KRF being balanced by those for samples with low levels. Hence, assessment of the impact of KRF on K requirements at the industry scale may hide under-application or over-application at a field scale. Reserve-K on the other hand resulted in significant reductions in K requirements over all samples. There were also significant reductions in K requirements for all soils when both reserve-K and KRF were introduced. Reductions in K requirements will result in appreciable cost savings. With the current estimates of R500 million (ZAR) spent on fertilizer K per year by the South African sugar industry, a 20% reduction in K requirement due to the introduction of these parameters will result in more than R100 million savings per year. However, because there are wide variations in the changes in K requirements within soil types, impacts will be field-specific. This further emphasises the need to account for reserve-K and KRF on a field-by-field basis when making fertilizer K recommendations.

## **4.5 CONCLUSIONS**

Investigations carried out in this study revealed wide variations in exchangeable K, reserve-K and KRF values across all soils and within soil types in the South African sugar industry. Furthermore, there were also variations in the way levels of reserve-K was related to K fixation capacity. The K requirement is currently overestimated for some of the soils, particularly those with high to very high reserve-K and low K fixation capacity, and underestimated for soils with low to medium reserve-K and high K fixation capacity. Data presented highlight the errors inherent in the use of constant values for reserve-K and KRF in formulating fertilizer K recommendations; instead, measured reserve-K and KRF values should be used.

Emerging from this study is an urgent need to investigate the impact of revised fertiliser recommendations that include variation in reserve-K and KRF on yield and plant K uptake from soils. In addition, considering that the tests for both reserve-K and KRF are laborious and time-consuming and thus not suited for use in routine soil testing, fast and robust techniques that can predict reserve-K and KRF need to be identified.

## CHAPTER FIVE

### PREDICTING POTASSIUM RESERVES AND FIXATION IN SOILS OF THE SOUTH AFRICAN SUGAR INDUSTRY USING MULTIPLE LINEAR REGRESSION AND MID-INFRARED SPECTROSCOPY

#### 5.1 INTRODUCTION

A soil potassium (K) test for use in routine soil fertility testing, capable of accounting for K dynamics in the plant-soil system, remains a challenge. Literature reports suggest that such a test would reflect three components, namely: exchangeable K, reserve-K, and K fixation capacity of the soil. However, measurement of reserve-K and K fixation capacity is laborious and time consuming. Traditionally, multiple linear regression (MLR) models were used to estimate soil properties whose determination is lengthy and arduous (Babaeian *et al.* 2015). In an effort to include K fixation capacity in soil K testing Johnston *et al.* (1999) used MLR to predict potassium requirement factor (KRF, a measure of soil's capacity to fix added K) from routinely measured soil properties. Their MLR model had a coefficient of determination ( $r^2$ ) of 0.47, which was not satisfactory for predictive purposes. There are no known studies reporting the prediction of reserve-K using MLR models.

Recent developments in mid-infrared spectroscopy (MIR) appear to provide soil testing facilities with an opportunity to rapidly measure a wide range of soil properties with moderate to excellent reliability (Janik *et al.* 1998). Infrared techniques in soil analysis involve interaction of incident radiation with soil components to produce a spectrum that contains information about the composition of organic and inorganic phases of the soils (Chakraborty *et al.* 2015). The MIR calibrations are obtained by correlating MIR spectra to primary data using chemometric techniques such as partial least squares (PLS) analysis. To date, MIR has been used successfully to predict numerous soil properties, including organic carbon, clay content, pH, cation exchange capacity (CEC), exchangeable acidity, exchangeable Ca and exchangeable Mg (Janik

*et al.* 1998; Viscarra Rossel *et al.* 2006; Janik *et al.* 2009). It would appear that little or no attempts have apparently been made to predict reserve-K and K fixation using MIR.

The present study investigates the potential of MLR and MIR to predict reserve-K and KRF for the soils of the South African sugar industry. This involves the development of the MLR models and MIR calibrations for these properties and external validation using an independent set of soil samples.

## **5.2 MATERIALS AND METHODS**

### **5.3.1 Materials**

The investigations were carried out on 132 topsoil (0-200 mm, 113 of these soils were used in Chapter 4) which were used in the development of MLR models, calibration of the MIR and for the independent validation of both MLR and MIR models. The classification of the soils was described in Chapter 4. The soil samples were randomly split into two parts: 112 (85%) for MLR models development and MIR calibrations and 20 (15%) for validation purposes. These soils varied widely in physicochemical properties (Table 5.1).

### **5.3.2 Wet chemistry analysis**

Measurement of pH ( $\text{CaCl}_2$ ), exchangeable acidity ( $\text{Al} + \text{H}$ ), exchangeable K, Ca, Mg, and Na, plant available P and Si, total C, clay, silt, and sand were described in Chapter 3. Total nitrogen was determined by automated (Dumas) dry combustion using a Leco Analyzer (Leco Corporation, St Joseph, Michigan). Volume weight (VW, sample density) was by measuring the mass of 10 mL scoop. Oxalate extractable Al, Fe, and Si were determined using 0.2 M ammonium oxalate and total K was measured using X-ray fluorescence spectrometry (Rayment and Lyons 2011). Reserve-K and KRF were measured as described in Chapter 4.

**Table 5.1** Mean values for selected soil properties used in the development of multiple linear regression models and mid-infrared spectroscopy calibrations, and for validations. Values in parentheses reflect ranges.

<b>Determinant</b>		<b>Calibration set (n = 112)</b>	<b>Validation set (n = 20)</b>
<b>pH (CaCl<sub>2</sub>)</b>		5.01 (3.46 – 6.92)	4.73 (3.78 -5.71)
<b>AMBIC extractable cations (cmol<sub>c</sub> kg<sup>-1</sup>)</b>	<b>K</b>	0.36 (0.07 – 1.27)	0.29 (0.05 – 0.77)
	<b>Ca</b>	6.37 (0.11 – 23.81)	6.32 (1.05 – 18.29)
	<b>Mg</b>	2.46 (0.06 – 13.39)	2.62 (0.36 – 9.27)
	<b>Na</b>	0.22 (0.02 – 2.80)	0.27 (0.04 – 1.95)
<b>Exchangeable acidity (cmol<sub>c</sub> kg<sup>-1</sup>)</b>		0.53 (0.00 – 4.67)	0.59 (0.01 – 2.67)
<b>Total cations<sup>(a)</sup> (cmol<sub>c</sub> kg<sup>-1</sup>)</b>		9.91 (1.21 – 36.44)	10.06 (2.29 – 30.06)
<b>Si (mg kg<sup>-1</sup>)</b>		17.33 (1.00 - 48.00)	17.15 (3.00 – 44.15)
<b>Reserve-K (cmol<sub>c</sub> kg<sup>-1</sup>)</b>		1.31 (0.11 – 7.27)	1.32 (0.12 – 4.24)
<b>KRF<sup>(b)</sup> (kg K ha<sup>-1</sup> per unit soil test)</b>		3.14 (1.99 – 7.73)	3.25 (2.18 – 4.84)
<b>Total organic carbon (%)</b>		2.08 (0.42 – 9.72)	1.74 (0.62 – 3.75)
<b>Total nitrogen (%)</b>		0.15 (0.03 – 0.60)	0.13 (0.06 – 0.32)
<b>Clay (%)</b>		28 (5 – 70)	26 (5 – 67)
<b>Silt (%)</b>		13 (2 – 31)	12 (3 – 28)
<b>Sand (%)</b>		59 (5 – 91)	61 (5 – 90)

<sup>(a)</sup> Total cations obtained by summing the quantities of AMBIC extractable Ca, Mg, K, and Na and KCl exchangeable acidity (Al + H)

<sup>(b)</sup> KRF = potassium requirement factor, indicates K fixation capacity

### 5.3.3 Multiple linear regression models and mid-infrared calibration

The MLR models for predicting reserve-K and KRF from measured properties were developed using Genstat version 18. Soil properties that were used to develop MLR models were divided into two, namely routinely-determined and routine-plus properties. The routine properties included soil pH, clay content, total carbon, total nitrogen, exchangeable acidity, AMBIC extractable cations (Ca, Cu, Fe, K, Mg, Mn, Na, and Zn), extractable Si, total cations and VW. The routine-plus properties included routine properties plus total K, oxalate extractable Al, Fe, and Si and where appropriate reserve-K and KRF. Inclusion of the selected non-routine properties depended on the data availability. Samples with large standardized residuals were not included in the development of the MLR model. Similarly, some parameters were excluded in the development of the MLR model and these were identified by using stepwise regression.

The calibrations for exchangeable K, reserve-K, and KRF were developed using a diffuse reflectance spectrometer MIR (Bruker Optics: Tensor 2, HTS-XS) with a spectral range including the mid-infrared wavelengths (375-4000/cm). The MIR is a secondary technique where primary data is correlated to the infrared spectrum (Appendix 5.1) using data using chemometric techniques. Soil components which are infrared active, i.e. vibrate at specific wavelengths when illuminated, absorb and reflect some of the incident radiation (Appendix 5.2). The infrared spectrum, then, is a plot of wavelengths against the intensity of the reflected radiation caused by the interaction of incident radiation with soil components. Before a calibration is developed a number of pre-processing techniques (Appendix 5.3) are explored and the pre-processing giving best results is used to normalize the spectra. Partial least squares (PLS), which is a multivariate technique that compares the information in the spectra with primary data, is used to obtain a calibration. Results on unknown samples is also obtained by comparing the information in the spectra with primary data but against an existing calibration.

In this study, the calibrations for exchangeable K, reserve-K, and KRF were developed using soil samples ground to less than 1 mm and 0.5 mm. The FAS is currently using the 1 mm limit and the 0.5 mm limit represents a finer material. Scanning time for a single sample was approximately 90 seconds, each sample was scanned in triplicate. The results obtained for the independent validation set were averaged to get the mean. Calibrations and associated cross-validations were developed using Opus software (OPUS version 7.5), which employs partial least squares analysis for data processing. The quality of the calibration was evaluated in terms of the classification suggested by Niederberger *et al.* (2015), which uses coefficient of determination ( $r^2$ ) and ratio of performance to deviation (RPD) as shown in Table 5.2. By these criteria, excellent calibrations are useable for all purposes; the successful and moderately successful calibrations should be used with caution; the moderately useful calibrations should be used only for screening of samples; and the rough calibrations are unusable.

**Table 5.2** Criteria based on coefficient of determination ( $r^2$ ) and ratio of performance to deviation (RPD) used to evaluate the quality of the mid-infrared calibration (Niederberger *et al.* 2015)

Level	$r^2$	RPD	Classification
Level A	> 0.95	>4	Excellent calibration
Level B	0.90 – 0.95	3 – 4	Successful calibration
Level C	0.80 – 0.90	2.25 – 3	Moderately successful calibration
Level D	0.70 – 0.80	1.75 – 2.25	Moderately useful calibration
Level E	< 0.70	< 1.75	Rough calibrations



## 5.3 RESULTS

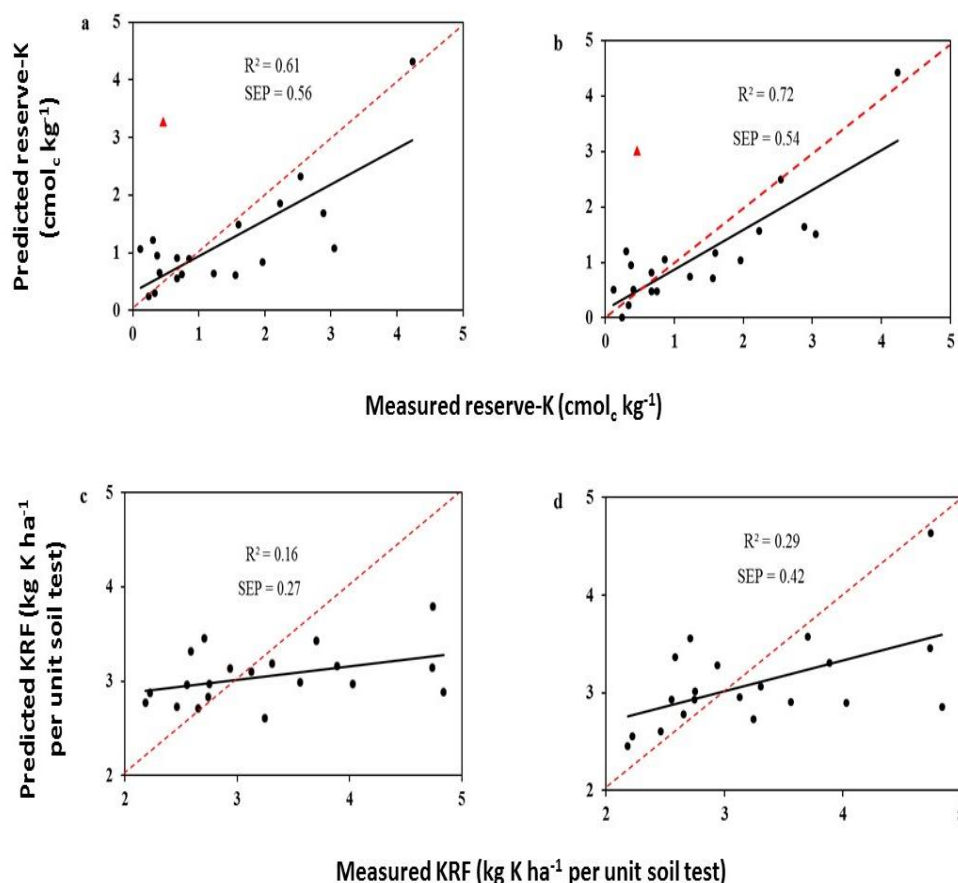
### 5.3.1 Multiple linear regression models

Multiple linear regression models for predicting reserve-K and KRF are presented in Table 5.3. The model for reserve-K based on routinely measured soil properties had an  $r^2$  of 0.79 and a standard error of estimation (SEE) of 0.47. The most important soil properties explaining reserve-K were total N, volume weight, total C, pH and exchangeable acidity. The regression model for reserve K based on routine-plus soil properties had an  $r^2$  of 0.80 and SEE of 0.46, with the major factors contributing to the regression being total N, volume weight, ratio of total cations to clay (cations/clay), total C, KRF, and exchangeable acidity. A model for KRF based on routinely measured soil properties had an  $r^2$  of 0.30 and SEE of 0.55; here, the most important soil properties were total N, volume weight, total C and pH. A regression model for KRF based on routine-plus soil properties had an  $r^2$  of 0.53 and SEE of 0.49, with the most important soil properties contributing to the regression being total N, volume weight, total C and pH.

Reserve-K and KRF of an independent validation set predicted from the linear regression models were plotted against measured values (Figure 5.1). Values of reserve-K predicted from both routinely measured and routine-plus soil properties were closer to the measured values. Reserve-K predicted from routinely measured soil properties plotted against measured reserve-K yielded an  $r^2$  of 0.61 and a standard error of prediction (SEP) of 0.60 while that predicted from routine-plus soil properties yielded an  $r^2$  of 0.72 and SEP of 0.54. The KRF values predicted from both routinely measured and routine-plus soil properties differed markedly from the measured values. The model based on routine-plus soil properties was better because an  $r^2$  of 0.29 and SEP of 0.42 were obtained when predicted KRF values were plotted against measured values whereas an  $r^2$  of 0.16 and SEP of 0.27 was obtained for the model based on routinely measured properties.

**Table 5.3** Regression models and their corresponding coefficient of determination ( $r^2$ ) and standard error of estimates (SEE) developed for reserve-K and potassium requirement factor (KRF) using routinely measured and routine-plus soil properties.

		Regression model	n	$r^2$	SEE
Reserve-K	Routine	Reserve-K = $0.16EA^a + 0.02Si^b - 0.87VW^c - 0.01Clay - 0.17pH + (4.16N - 0.44C)^d + (3.02E-4Ca + 2.00E-3K + 1.36E-3Mg + 2.90E-3Na + 0.03Zn - 0.04Cu)^e + 2.08$	102	0.79	0.47
	Routine-plus	Reserve-K = $0.15EA + 0.02Si - 1.35VW - 0.01Clay + 0.01K_{tot}^f + 0.23KRF - 0.88cations/clay^g + (4.94N - 0.50C) + (2.73E-4Ca + 1.77E-3K + 1.19E-3Mg + 2.72E-3Na + 0.03Zn - 0.05Cu) + 1.51$	103	0.80	0.46
KRF	Routine	KRF = $1.91VW + 0.15pH + 0.01K_{sat}^h + (0.44C - 5.12N) + (1.15E-3Mg - 1.41E-3K + 9.36E-4Na) - 0.57$	107	0.30	0.55
	Routine-plus	KRF = $3.17VW + 0.18pH + 0.01K_{sat}^h + 4.76E-3AcidSat^i + 1.10E-4Fe_{ox}^j + 0.07reserve-K + (0.32C - 4.41N) + (1.08E-3Mg - 1.02E-3K - 0.02Zn) - 2.58$	105	0.53	0.49
<sup>a</sup> potassium chloride exchangeable acidity <sup>b</sup> calcium chloride extractable Si <sup>c</sup> volume weight <sup>d</sup> total carbon and nitrogen <sup>e</sup> ammonium bicarbonate (AMBIC) extractable Ca, K, Mg, Na, Cu, and Zn <sup>f</sup> total K measured using X-ray fluorescence <sup>g</sup> total cations (sum of AMBIC extractable Ca, K, Mg, Na and EA) divided by clay content <sup>h</sup> AMBIC extractable K divided by total cations <sup>i</sup> acid saturation = (EA/total cations)*100 <sup>j</sup> oxalate extractable Al and Fe					



**Figure 5.1** Prediction using multiple linear regression models of reserve potassium (K) from (a) routinely measured and (b) routine-plus soils properties against measured reserve-K and of K requirement factor (KRF) from (c) routine measured and (d) routine-plus soils properties against measured KRF. Red dashed lines represents 1:1 relationships, while  $R^2$  and SEP are coefficient of determination and standard error of prediction, respectively. Red triangles represents sample values that were excluded from the comparisons.

### 5.3.2 Mid-infrared spectroscopy

The quality of MIR calibrations for exchangeable K, reserve-K, and KRF were variable (Table 5.4). The exchangeable K calibrations for 1 mm and 0.5 mm samples were of similar quality with low  $r^2$  of 0.69 and 0.68 and RPD of 1.81 and 1.77, respectively. The calibrations for reserve-K were stronger, with the 1 mm calibration having  $r^2$  of 0.91 and RPD of 3.36 while the 0.5 mm calibration had  $r^2$  of 0.95 and RPD of 4.32.

For KRF the  $r^2$  and RPD values for 1 mm samples were 0.71 and 1.85, respectively, and for the 0.5 mm samples  $r^2$  was 0.80 and RPD 2.26.

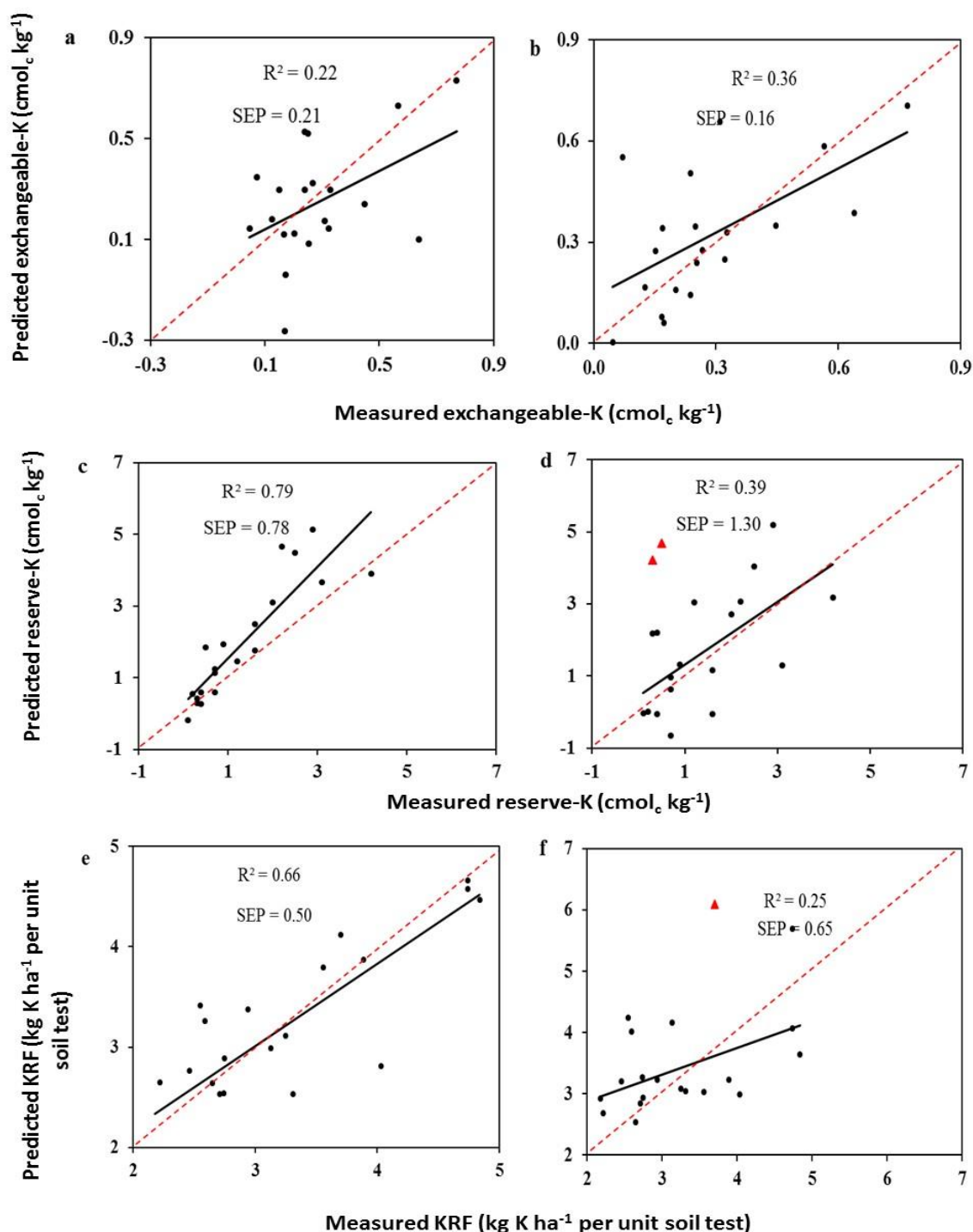
**Table 5.4** The quality of mid-infrared calibrations for exchangeable K, reserve-K, and potassium requirement factor (KRF) developed for 1 mm and 0.5 mm samples. The quality of calibrations is evaluated on the basis of coefficient of determination ( $r^2$ ), ratio of performance to deviation (RPD), and root mean square error of estimation (RMSEE).

		<b>Interactive Region (cm<sup>-1</sup>)</b>	<b>Preprocessing</b>	<b><math>r^2</math></b>	<b>RPD</b>	<b>RMSEE</b>
<b>Exchangeable K</b>	1 mm	3658.9 – 3317.5 2639.2 – 2299.3 1620.9 – 939.7	First derivative + MSC <sup>a</sup>	0.69	1.81	0.13
	0.5 mm	3997.4 – 3317.6 2639.2 – 1619.5	SNV <sup>b</sup>	0.68	1.77	0.14
<b>Reserve-K</b>	1 mm	3658.9 – 1619.5 1281.0 – 939.7	First derivative + SNV	0.91	3.36	0.39
	0.5 mm	3997.4 – 939.7	None	0.95	4.32	0.31
<b>KRF</b>	1 mm	3997.4 – 3317.5 2979.1 – 2637.7 2299.3 – 1619.5 941.1 – 601.2	First derivative + MSC	0.71	1.85	0.50
	0.5 mm	3658.9 – 3317.5 2979.1 – 601.3	First derivative + MSC	0.80	2.26	0.41

<sup>a</sup> multiple scatter correction

<sup>b</sup> vector normalization

The predictions of exchangeable K, reserve-K, and KRF on an independent validation set for 1 mm and 0.5 mm samples are shown in Figure 5.2. The quality of prediction varied widely. The prediction of exchangeable K was poor for both 1 mm and 0.5 mm with  $r^2$  of 0.22 and 0.36 and SEP of 0.21 and 0.16, respectively. The prediction of reserve-K using 1 mm samples was reasonably good with  $r^2$  of 0.79 and SEP of 0.78. The prediction of reserve-K using 0.5 mm was poor with  $r^2$  of 0.39 and SEP of 1.30. In terms of KRF, the prediction using 1 mm samples was satisfactory with  $r^2$  of 0.66 and SEP of 0.50, while that of 0.5 mm samples was poor with  $r^2$  of 0.25 and SEP of 0.65.



**Figure 5.2** Predicted exchangeable potassium (K) (a, b), reserve-K (c, d), and K requirement factor (KRF) (e, f) using mid-infrared spectroscopy and 1 mm (a, c, e) and 0.5 mm samples (b, d, f) against measured exchangeable K, reserve-K and KRF. Red dashed line represents 1:1 relationship while  $R^2$  and SEP are coefficient of determination and standard error of prediction, respectively. Red triangle represents samples that were excluded from the comparisons.

## 5.1 DISCUSSION

The differing qualities of the models and their prediction capacities have implications in terms of their usability. The superior model quality and prediction capacity for reserve-K suggests that the MLR model can be used to estimate this parameter, but KRF cannot be estimated using MLR models. The improved model quality and prediction capacity where routine-plus soil properties are included, compared to routine soil properties, underlines an important limitation with MLR models in that their performances are dependent on measured soil properties. The MLR model for KRF using routine-plus soil properties was comparable to that of Johnston *et al* (1999) where the reciprocal of KRF was correlated to effective cation exchange capacity (ECEC) and sample density (i.e. VW). It is hypothesized that KRF models could be improved by including other soil properties such as clay mineralogical composition, since KRF is strongly influenced by clay mineralogy, particularly vermiculites (Johnston *et al.* 1999). However, measurements of such properties require specialised techniques and are not possible for routine soil testing.

The performance of MIR was better than that of MLR, particularly for KRF. Furthermore, the MIR calibration for reserve-K was superior to the MLR routine-plus model, but their quality of prediction was similar. This implies that both techniques could be used for predicting reserve-K but the MLR 'routine-plus' model requires total K and KRF which are not readily determined in routine soil testing facilities. This gives MIR an advantage over MLR models because an MIR spectra is developed from all soil components (Janik *et al.* 1998). Thus, because of better performance, MIR should be the preferred technique to predict reserve-K and KRF for routine analytical purposes.

The success of MIR calibrations for exchangeable K, reserve-K, and KRF varied. Calibration for reserve-K was the most successful followed by that of KRF, while that of exchangeable-K was poor. The success with the reserve-K and KRF calibrations could be due to the fact that they are dependent on the chemistry of the soil matrix, particularly mineralogy (Sharpley 1989; Janik *et al.* 1998; Johnston *et al.* 1999;

Srinivasa Rao *et al.* 2007). In contrast, exchangeable K is a soil property involving transitory phases between soil particles and aqueous solution; hence the poor calibration (Janik *et al.* 1998; Soriano-Disla *et al.* 2014). However, a better exchangeable K calibration, with an  $r^2$  of 0.77 and SEP of 0.20, has been obtained in the NIR region by Van Vuuren *et al.* (2006). Soriano-Disla *et al.* (2014) stated that the better NIR calibrations for exchangeable K are due to absorbance by illites of NIR frequencies and furthermore the spectra of illites and smectite in the MIR region are similar. These authors suggested that a combined NIR-MIR could produce better exchangeable K calibrations and this is achievable with new instruments which have both MIR and NIR regions.

The poor prediction of reserve-K and KRF MIR calibrations for samples passed through a 0.5 mm sieve, relative to a 1 mm sieve, was unexpected. Generally, 0.5 mm sieving is used for MIR samples and size distribution was expected to give better calibrations and predictions (Rayment and Lyons 2011). The results of this study show that 0.5 mm calibrations predicted reserve-K and KRF poorly compared to calibrations of 1 mm samples. Le Guillo *et al.* (2015) found that there were no statistical differences between MIR calibrations for soil texture and organic carbon using 1 mm, 0.5 mm, and 0.25 mm sieved samples. The poor prediction of the 0.5 mm calibrations in the current study is suspected to have been caused by overfitting because the factors used in the 0.5 mm calibrations models for reserve-K and KRF were 43 and 32, respectively, compared to 27 and 27 for 1 mm calibrations. Overfitting, where a model includes unnecessary factors, is known to cause poor predictions (Hawkins 2004). Overfitting with 0.5 mm samples may most likely be due to the finer particle size used which may have more peaks than those of 1 mm samples. The use of 1 mm samples would, therefore, appear preferable for routine use considering the poor predictions of 0.5 mm calibrations and extra work required to mill samples to 0.5 mm.

The 1 mm MIR calibrations for reserve-K and KRF were the most successful compared to 0.5 mm calibrations and MLR models. However, the category for reserve-K calibration was level B and for KRF it was level D (Table 5.2). It is postulated that calibrations based on combined NIR-MIR regions, as suggested above, can improve

both reserve-K and KRF calibrations. In the interim the MIR reserve-K calibration could be used with caution and the KRF calibration for screening purposes. The implication, as far as the inclusion of reserve-K and KRF in routine soil testing and the development fertilizer recommendations is concerned, is that reserve-K criteria set by Haysom (1971) and KRF criteria set in Chapter 4 be adjusted to accommodate the SEP; these suggested changes are shown in Table 5.5. The reduction of K requirements as a result of introducing different reserve-K categories (Chapter 3) will remain unchanged whereas a KRF value of 3.0 would be used for non-fixing and 4.5 for K fixing soils. The KRF value of 3.0 was chosen because it represents non-fixing soils (Chapter 4) and 4.5 was the average of K-fixing soils when extreme fixing were omitted. Another alternative would be to split the KRF calibration for non-fixing and K fixing soils and use the current calibration to decide which of the split calibrations to use. However, this requires further investigations.

**Table 5.5** The original and modified criteria for reserve potassium (K) and K requirement factor (KRF). The modified criteria are applicable where mid-infrared is used to estimate reserve-K and KRF. Changes in K requirements as a result of introducing reserve-K and KRF modifiers to use for modified K fixing categories.

		Criteria			
		Low	Medium	High	Very high
<b>Reserve-K</b> (cmol <sub>c</sub> kg <sup>-1</sup> )	<b>Original</b>	<0.8	0.8 – 1.5	1.5 – 2.5	>2.5
	<b>Modified</b>	1.5	1.5 – 2.5	2.5 – 3.5	>3.5
	<b>Changes in K requirements</b>	no changes	Reduce by 30%	Reduce by 60%	Zero K application
<b>KRF</b> (kg K ha <sup>-1</sup> per unit soil test)	<b>Original</b>	<b>Low</b>	<b>Medium</b>	<b>High</b>	<b>Very high</b>
		1.5 - 2.5	2.5 - 3.5	3.5 - 4.5	>4.5
	<b>Modified</b>	<b>Non-fixing</b>		<b>K fixing</b>	
		<3.5		>3.5	
	<b>KRF modifiers</b>	3.0		4.5	



## **5.2 CONCLUSIONS**

The potential of MLR models and MIR to predict exchangeable K, K reserves and fixation capacity (KRF) of soils of the South African sugar industry was investigated in this study. The MLR models, particularly those based on routine-plus soil properties, were satisfactory for reserve-K but not KRF. The MIR calibrations for both reserve-K and KRF using 1 mm sieved samples had superior predictive capability compared to those of 0.5 mm samples and to MLR models. It is thus recommended that in the interim the MIR calibrations for both reserve-K and KRF using 1 mm samples can be used to predict K reserves and fixation capacity. Caution must be exercised for MIR-estimated K reserves, while MIR can only be used to screen K fixing soils from non-fixing soils. Further studies are required to improve both reserve-K and KRF calibrations and should include calibrations based on combined NIR-MIR regions and the splitting of KRF calibrations.

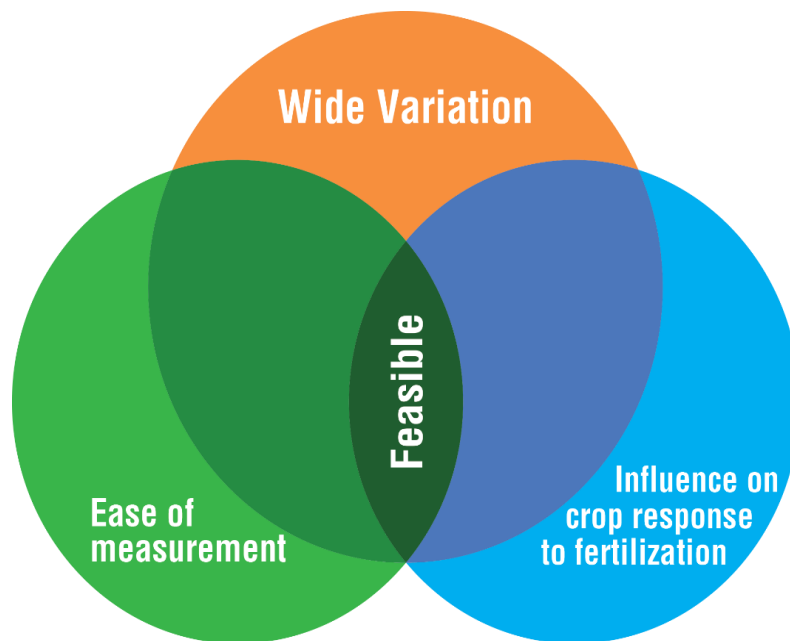
## CHAPTER SIX

### GENERAL DISCUSSION AND CONCLUSIONS

#### 6.1 INTRODUCTION

Soil potassium (K) testing plays a crucial role in yield optimisation because it measures the amount of K in the soil from which the amount of fertilizer K required to achieve optimum yields is calculated. Currently, most soil testing laboratories quantify levels of exchangeable K and base fertilizer recommendation on this test. This practice is questionable because measurement of exchangeable K alone does not form a sound basis for making fertilizer K recommendations (Haysom 1971; Wood and Meyer 1986; Khan *et al.* 2014). Much research has shown the importance of K reserves and fixation capacity in the dynamics of K in the soil-plant system, but their inclusion in soil K testing remains relatively unexplored (Haysom 1971; Wood and Meyer 1986; Johnston *et al.* 1999; Schroeder and Wood 2002; Zhan *et al.* 2014). The challenge is that the measurement of K reserves and fixation capacity is laborious and time consuming.

The objective of this study was to investigate the feasibility of including K reserves and fixation capacity in soil K testing and in the formulation of fertilizer requirements. This involved assessing the response of sugarcane to K fertilization on soils with contrasting K reserves and fixation capacity; the variation of K reserves and fixation capacity in soils; and the potential of multiple linear regression (MLR) models and mid-infrared spectroscopy (MIR) to predict K reserves and fixation capacity. The inclusion of these soil properties in soil testing and in the development of fertilizer requirement recommendations is feasible if they vary widely in soils, the variation influences crop response to fertilization, and they are easy to measure (Figure 6.1).



**Figure 6.1** Three critical factors required to make the inclusion of soil properties in the development of fertilizer requirement feasible.

## 6.2 MAIN FINDINGS

Potassium reserves and fixation capacity had an influence on the response of sugarcane to K fertilization. Sugarcane depleted K in the control plots (zero K application) of a soil with low K reserves whereas on a soil high in K reserves there was no K depletion. Furthermore, there were sugarcane sucrose yields and leaf K responses to K application on the soil with low K reserves but on the soil with high K reserves there was no response to K application. The lack of response on soil high in K reserves indicate that there was no need for K fertilization in this soil which is in agreement with the proposed changes to calculating K requirements. Based on the findings of the field K response trials, it was clear that fertilizer recommendations must be modified to account for K reserves and fixation capacity. The soil with high K fixation capacity regulated exchangeable K concentration and it was postulated that the combination of K reserves and fixation capacity provide a measure of soils K buffering capacity. The cutanic Acrisol which had high K reserves and fixation capacity buffered exchangeable K but umbric Acrisol with low K reserves and medium K fixation capacity did not. Combination of high K reserves and fixation capacity accounted for 15% of samples analysed in this study while those with low K reserves and medium K fixation

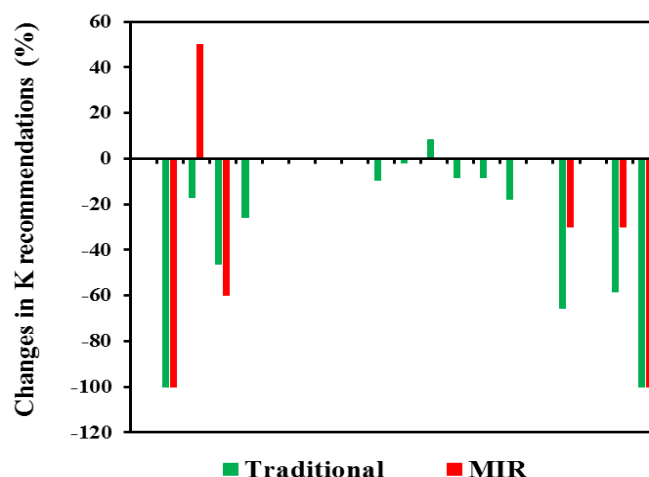
capacity accounted for 31%. There is thus a need to assess how the various combination of K reserves and fixation capacity and modified fertilizer K requirement influence crop response to K application.

In terms of variations, the current study revealed wide variations in K reserves and fixation capacity. In addition, there were also variations in the way levels of reserve-K related to K fixation capacity (which was postulated in the K response trial) to represent soil K buffering capacity. Lastly, K requirements were modified using K reserves and fixation based modifiers and the modified K requirements were often appreciably different from the 'original' K requirements. Introduction of K reserve modifiers resulted in reduced K requirements whereas K fixation modifiers resulted in both reductions and increases in K requirements depending on the K fixing capacity of the soil. Fertilizer requirements resulting from the introduction of both K reserves and fixation modifiers were, however, not different from those obtained when only K reserves modifiers were introduced, with the exception of few soils (about 10 % of soils used in this study). This finding coupled with the fact that only reserve-K could be predicted well with MIR and MLR, suggest that it might be necessary to include modifiers based on MIR predicted reserve-K alone. It is envisaged that the modified fertilizer K requirement would result in significant savings in terms of fertilizer costs and what is more, yields will be improved on soils with high K fixation capacity when the MIR calibration for KRF has been improved. Thus, it is recommended that K reserves and fixation based modifiers are introduced when formulating K requirements and this would require routine measurement of K reserves and fixation capacity.

The measurements of K reserves and fixation capacity are, however, laborious and time consuming, but they could be estimated using either MLR models or MIR. The success of estimating K reserves and fixation with these secondary techniques will be of huge value considering the wide variation of K reserves and fixation in soils and their influence on crop response to K application. This implies that if estimation of K reserves and fixation with MLR and MIR is successful then K responsive soils can be discriminated from non-responsive soils. Estimation of K reserves with MLR, particularly when 'routine-plus' soil properties were included, was satisfactory, but that

of K fixation capacity was unsuccessful. The K reserves obtained from MLR could at this stage be used only for the screening of soils that will respond to K fertilization from non-responsive soils.

Estimation of K reserves and KRF (fixation capacity) using MIR was better than that of MLR. A successful calibration was obtained for K reserves using 1 mm samples and thus can be implemented in routine soil testing, albeit with caution. The calibration for KRF, however, was not as good but could be used for screening K fixing soils from non-fixing soils. The outcome from the MIR calibrations and predictions can be approached from two possible angles. The first would be to include K reserves, estimated from MIR, when formulating fertilizer K requirements, and to continue using a KRF of 3.0 across all soils. However, modifiers based on reserve-K would need to be adjusted to accommodate the SEP obtained when predicting K reserves. This would be justified because for about 90% of the samples, K requirements formulated by introducing K reserve modifiers only were no different than when both K reserves and fixation modifiers were introduced. The second approach would be to use both K reserves and fixation modifiers, but adjust both K reserves and KRF modifiers so as to accommodate the SEP obtained when predicting K reserves and KRF. The implication is that the criteria for K reserves (predicted from MIR) would be higher than that used by Haysom (1971) and a KRF value of 3.0 would be used for non-fixing soils and a value of 4.5 for K fixing soils. Changes in K requirements as a result of introducing MIR K reserves and fixation modifiers would be an improvement from the current approach and would be closer to what would have been from modifiers based on traditional 'wet chemistry' K reserves and fixation measurements (Figure 6.2).



**Figure 6.2** Changes in K requirements (%) for twenty soils used as validation set in Chapter 5 as a result of accounting for K reserves and fixation capacity measured using traditional ‘wet chemistry’ and mid-infrared (MIR) analysis.

### 6.3 GENERAL CONCLUSIONS

The feasibility of including K reserves and fixation capacity in soil K testing and the development of fertilizer requirements was investigated and it is concluded that their inclusion is feasible because they vary widely in soils, their variation influences sugarcane response to K fertilization, and they can easily be measured using MIR. There was absence of yield response to K application from a soil with very high reserve-K and K fixation capacity but there was a response on the soil with low reserve-K and medium K fixation. Introducing variations in K reserves and fixation when formulating fertilizer recommendations resulted in significant reductions in K requirements. Finally, MIR can predict reserve-K and can also distinguish K fixing soils from non-fixing soils.

### 6.4 FUTURE RESEARCH

The following endeavours are proposed as future studies that will assist in improving our understanding of K dynamics in plant-soil systems and accounting for these dynamics in routine soil K testing.

- 1) A study validating the hypothesis that a combination of K reserves with fixation capacity represent soil K buffering capacity. The investigation of this hypothesis would require identification of soils with various combinations of K reserves and fixation capacity and the availability of land for research trials. This study may be costly and could take long to establish. In the meanwhile, soils can be sampled, where K deficiency symptoms are observed despite K fertilization or where poor sucrose recovery is caused by high K content, and analysed for K reserves and fixation capacity.
- 2) There is also a need for a study investigating the contributions from subsoil K and how these interact with various combinations of reserve-K and K fixation. This investigation will close the gaps between K dynamics in plant-soil systems and soil K tests.
- 3) Further improvements of MIR calibrations for both K reserves and fixation capacity are required. An investigation assessing the quality of calibrations using combined NIR-MIR regions may prove useful. Splitting of the calibrations could also provide additional benefits. Furthermore, calibrating MIR to predict both clay and coarser fraction mineralogy will contribute significantly in the prediction of both K reserves and fixation capacity using MIR because minerals present in soils affect their levels and variations.

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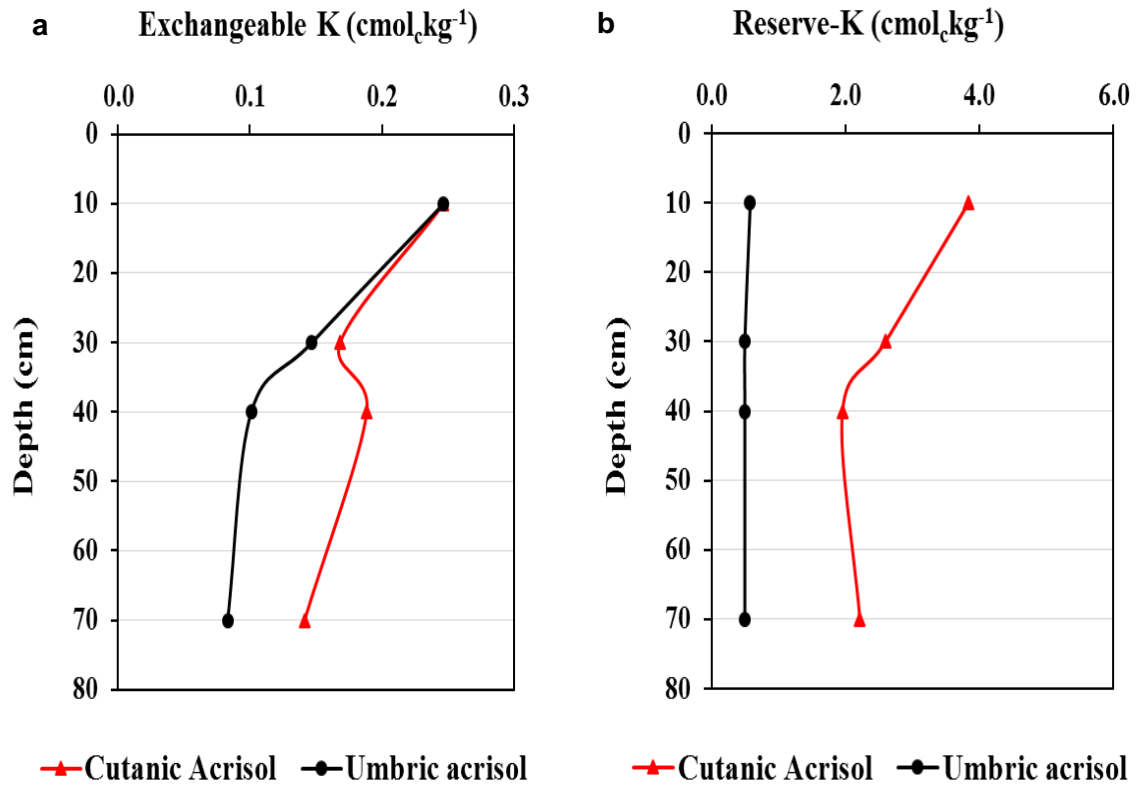
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## APPENDICES

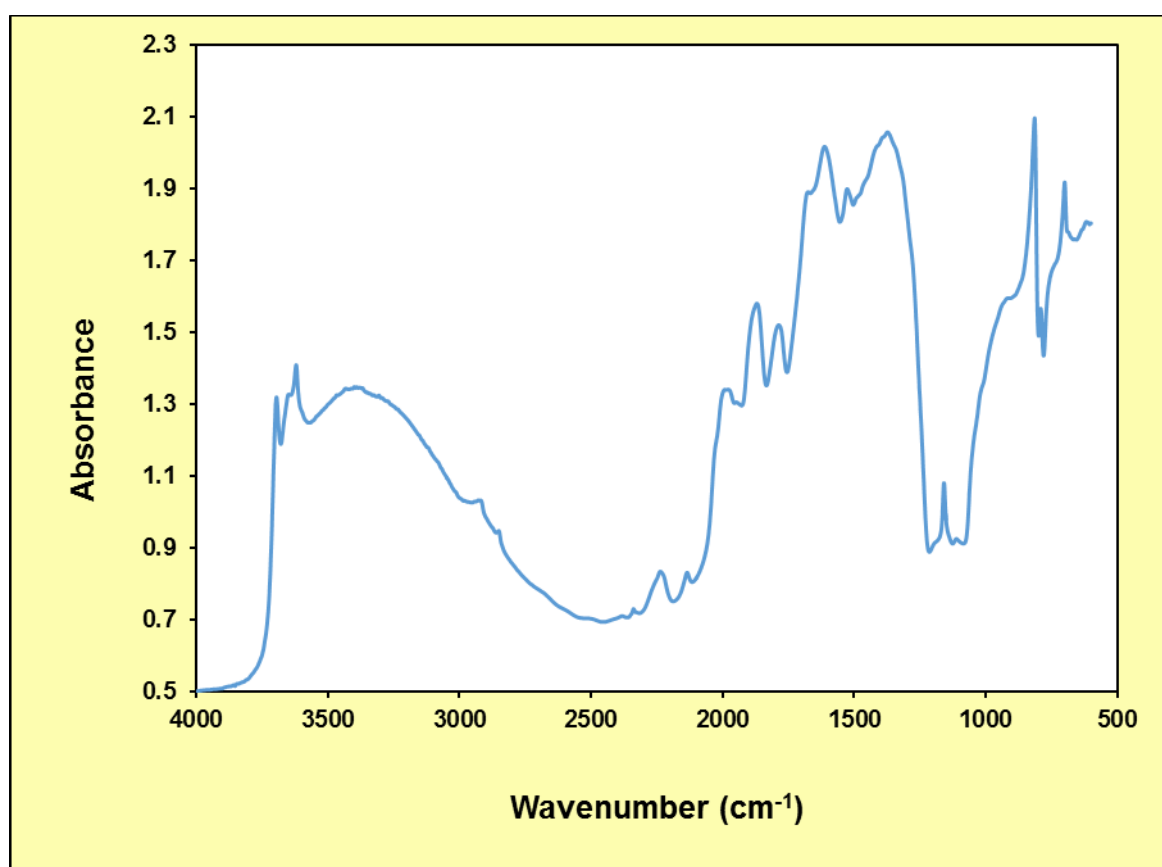
**Appendix 3:1** Distribution of (a) exchangeable potassium (K) and (b) reserve-K down the soil profile of cutanic and umbric Acrisols from Umfolozi and Doringkop trials sites, respectively, before the commencement of the trials.



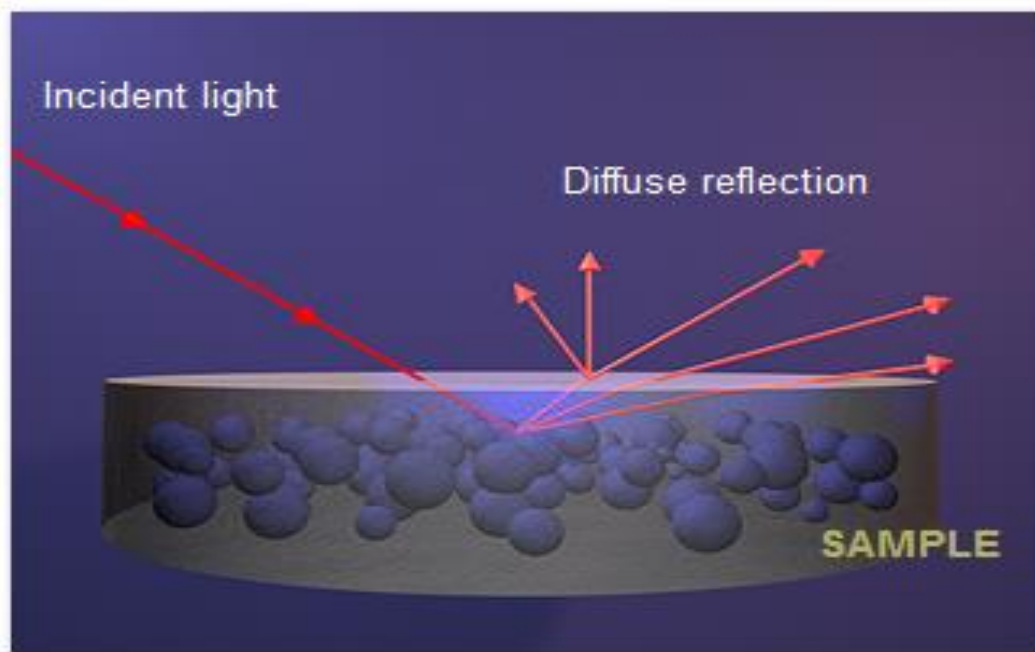
**Appendix 3:2** Changes in potassium (K) requirements for different K application rates and cropping cycles. The K requirements were calculated from exchangeable K values and using a target yield of 100 t ha<sup>-1</sup>.

Cutanic Acrisol (Umfolozzi)				
Rate (kg K ha <sup>-1</sup> )	First ratoon	Third ratoon	Fourth ratoon	Fifth ratoon
0	135	0	80	0
120	135	0	40	0
240	135	0	0	0
Umbric Acrisol (Doringkop)				
Rate (kg K ha <sup>-1</sup> )	Plant Crop	First ratoon	Second ratoon	Third ratoon
0	115	95	260	275
120	115	0	235	155
240	115	0	95	25

**Appendix 5:3** A typical spectrum for a soil obtained from a mid-infrared spectroscopy.



**Appendix 5:2** Visual description of the interaction of the incident radiation with soil samples (taken from Bruker OPUS online tutorial).





**Appendix 5:3** Various pre-processing techniques and their brief description (taken from Bruker OPUS Version 7 Quant Manual)

<b>Pre-processing Technique</b>	<b>Description</b>
<b>Linear Offset Subtraction</b>	Shifts the spectra in order to set the y-minimum to zero.
<b>Straight Line Subtraction</b>	Fits a straight line to the spectrum and subtracts it. This accounts for a tilt in the recorded spectrum.
<b>Vector Normalization</b>	Normalizes a spectrum by first calculating the average intensity value and subsequent subtraction of this value from the spectrum. Then the sum of the squared intensities is calculated and the spectrum is divided by the square root of this sum. This method is used to account for different samples thickness, for example.
<b>Min-max Normalization</b>	First subtracts a linear offset and then sets the y-maximum to a value of 2 by multiplication with a constant. Used similar to the vector normalization.
<b>Multiplicative Scatter Correction</b>	Performs a linear transformation of each spectrum for it to best match the mean spectrum of the whole set. This method is often used for spectra measured in diffuse reflection.
<b>First Derivative</b>	Calculates the first derivative of the spectrum. This method emphasizes steep edges of a peak. It is used to emphasize pronounced, but small features over a broad background. Spectral noise is also enhanced.
<b>Second Derivative</b>	Similar to the first derivative, but with a more drastic result.