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**POTASSIUM RELEASING AND SUPPLYING POWER  
OF SELECTED YELLOW GREY EARTH SOILS OF  
NEW ZEALAND**

**A thesis presented in partial fulfilment of the requirements for the degree of  
Doctor of Philosophy in Soil Science at Massey University**

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**1994**

## ABSTRACT

The supply of soil potassium (K) to New Zealand pastures is currently being assessed by the quick test K (QTK) and reserve K ( $K_c$ ) methods, which measure soil exchangeable K ( $K_{ex}$ ) and non-exchangeable K ( $K_{nex}$ ), respectively. QTK is based on a routine soil test and  $K_c$  is an assigned estimate appropriate to the soil group. No consideration is given to the variations of the  $K_{nex}$  supply within a soil group. The objective of this research was to examine the K releasing and K supplying power of selected soils from the yellow-grey earth (YGE) group.

A wide variation was observed in the measured  $K_c$  values of the YGE soils in the North and South Islands. A glasshouse experiment showed that the supply of  $K_{nex}$  to ryegrass grown on the 13 North Island YGE soils ranged from 0-41 mg 100 g<sup>-1</sup> and that of the 6 South Island YGE soils ranged from 3-35 mg 100 g<sup>-1</sup>. The experiment also showed that there were lower levels of  $K_{nex}$  supply in the pasture sites, compared to the virgin sites with respect to the South Island YGE soils. These results have implications to the use of the soil group concept which is used to estimate  $K_{nex}$  supply in the Computerised Fertilizer Advisory Service (CFAS) K model, currently used by AgResearch.

In a laboratory study, the threshold K levels in terms of K concentration and the activity ratio in the equilibrated soil solution,  $K_{ex}$ , and the amount of specifically held K were determined, in order to explain the variations in  $K_{nex}$  supply. The threshold K levels were not related to the  $K_{nex}$  release and supply.

The uptake of K by ryegrass was at best poorly to moderately correlated with the K extracted by current methods of determining K releasing power viz, QTK and  $K_c$ . The highest simple correlation was obtained from an improved acid-extractable K procedure ( $r = 0.96$ ;  $P < 0.01$ ). The differences in the  $K_{nex}$  uptake by ryegrass from various soils were better explained by a simple method of determining soil  $K_{nex}$  i.e., step K, than by the existing  $K_c$  method. A multiple regression equation with QTK

and step K as independent variables explained 96 % of the variation in total K uptake among soils.

On the basis of  $K_{\text{nex}}$  taken up by ryegrass in the glasshouse experiment, the 19 soils in this study were broadly grouped into two categories (i) soils with step K values of less than 35 mg 100 g<sup>-1</sup> and a  $K_c$  range of 8-10 mg 100 g<sup>-1</sup> and (ii) soils with step K values greater than 35 mg 100 g<sup>-1</sup> and a  $K_c$  range of 12-19 mg 100 g<sup>-1</sup>.

Selected soils were fractioned into sand, silt, and clay separates and acid-extractable K levels of the fractions were measured. There was a wide range in the acid-extractable K levels among the soils for the same size fraction e.g., clay, and for different size fractions within the same soil. When weighted according to the particle size distribution of the soil, the sand was found to contribute 4-45 %, silt 10-40 %, and clay 15-85 % of the K released by the sum of the 3 separates, using the improved acid extraction method. In all the soils, the clay separate released the most K per unit weight.

An agar pot trial technique was developed to measure the K supplying power of the soil separates. Although on a unit weight basis the clay separates showed a much greater activity than the other separates on a weighted basis, the contributions of sand and silt separates to the total K uptake of Marton (38 %), Matapiro (41 %), and Wharekaka (25 %) soils was of considerable importance. The results demonstrated that the role of sand and silt separates deserve more consideration in estimating potential K releasing and supplying power than has hitherto been the case.

The study also attempted to relate  $K_{\text{nex}}$  release and supply to the soil mineralogy. Although the gross mineralogy of the 19 soils was similar, differences in the  $K_{\text{nex}}$  release and supply could be related to subtle differences and gradual changes in the clay mineralogy. The XRD patterns of the clays with a  $K_c$  range of 8-10 mg 100 g<sup>-1</sup> of soil differed from those with a  $K_c$  range of 12-19 mg 100 g<sup>-1</sup> of soil. The latter group of clays contain more K bearing minerals than the former group.

The practical implications of the measured differences in  $K_c$  values ( $K_{dex}$  supply) within the YGE soil group were dealt with. The measured  $K_{dex}$  supply in the North Island YGE soils ranged from 20-40 kg ha<sup>-1</sup> yr<sup>-1</sup>, whereas the expected  $K_{dex}$  supply based on an assigned  $K_c$  value is 30 kg ha<sup>-1</sup> yr<sup>-1</sup>. The difference between the expected and the measured  $K_{dex}$  may be sufficiently economically significant as to invalidate applying a single  $K_c$  value to a soil group. Possible improvements to the soil K supply component of the CFAS K model were suggested, particularly that step K values should replace  $K_c$  in the K supply model.

## ACKNOWLEDGEMENTS

I would like to express my sincere thanks, gratitude and appreciation to the following people for their contribution towards the completion of this thesis.

My supervisors, Drs. J.H. Kirkman, P.E.H. Gregg, A.H.C. Roberts and R.W. Tillman for their valuable guidance. Thank you for your time, patience and encouragement.

All the past and present staff in the Department of Soil Science. I would like to take this opportunity to thank, in particular, Drs. N.S. Bolan, M.J. Hedley, and A. Basker all of whom were ready to discuss and forward sound criticism of the research presented here.

Dr. A.S. Palmer for helping in soil classification, Dr. R.C. Wallace for identifying primary minerals, and Dr. S. Saggar for resin K analysis.

The department's technical staff, headed by Lance Currie, is acknowledged. I would like to thank Mike Bretherton and Anne West for preparing some diagrams in this thesis, and Malcolm Boag for his proof reading.

Denise and Nicola for their friendship.

All my fellow postgraduates for their friendship.

The Fertilizer and Lime Research Centre and the University Grants Committee for funding my study.

Lee, Katy and Mike. Let us never forget the days of the alternative tea club.

Rosie, Henry and John at the Dynasty Restaurant. Their friendship during my time at the Dynasty was invaluable.

My mother and brothers in India, and my brothers in U.S. Thank you for your strength, blessings and support.

Finally I would like to thank my family - my wife, Chaithanya, and my son, Theja - for looking after me steadfastly during my last few years of study; especially you, Chaithanya, for you have been through so much since your arrival in New Zealand. I cannot thank you enough.

This thesis is dedicated to my late father and beloved mother.

## GLOSSARY OF K TERMS USED IN THIS THESIS

### GENERAL TERMS

- Structural K* : Strongly bonded K in the crystal structure of minerals. It is variously called *mineral K*, *native K*, *inert K*, *matrix K*, or *unweathered K*.
- Fixed K* : K present in the wedge (w-), step (s-), crack (c-), and interlayer (i-) positions of weathered micaceous minerals and amorphous clays.
- K<sub>nex</sub>/Reserve K* : Non-exchangeable K (structural K plus fixed K).  
Also known as  $K_c$  in New Zealand.
- K<sub>ex</sub>* : K present on planar (p-) and edge (e-) positions of clays and K sorbed at exchange sites on organic matter.
- K<sub>s</sub>* : K in soil solution.
- Available K* : The K taken up by plants or K extracted by chemical methods that aim to mimic uptake by plants.
- K availability* : Reflects a complex of interdependent soil and plant processes that release the K that is taken up by plants. It is difficult to quantify.
- K releasing power (K release)* : Release of K from *K<sub>nex</sub>/reserve* form to *K<sub>ex</sub>* and *K<sub>s</sub>* forms.  
Any chemical method that determines total "available K" is a measure of K releasing power.
- K<sub>ex</sub> releasing power (K<sub>ex</sub> release)* : K extracted by chemical methods that measure soil *K<sub>s</sub>* and *K<sub>ex</sub>* forms e.g.,  $\text{NH}_4\text{OAc-K}_{\text{ex}}$ , QTK (also  $\text{NH}_4\text{OAc}$ -extractable),  $\text{CaCl}_2\text{-K}_{\text{ex}}$ , resin K etc.
- K<sub>nex</sub> releasing power (K<sub>nex</sub> release)* : K extracted by chemical methods believed to measure soil *K<sub>nex</sub>* of different solubility e.g, nitric



- acid K ( $\text{HNO}_3\text{-K}$ ), resin K etc.
- K<sub>ex</sub> plus K<sub>nex</sub> releasing power* : K extracted by chemical methods that measure soil  $K_{\text{ex}}$  and  $K_{\text{nex}}$  e.g,  $\text{HNO}_3\text{-K}$  (acid-extractable K), NaTPB K etc.
- K fixation* : Reverse of K release.
- It is the phenomenon by which the "available K" becomes unavailable due to fixation by clay minerals and can not be easily extracted by methods used to assess "*K<sub>ex</sub> release*."
- K supplying power (K supply)* : Supply of K to plants. Any biological method e.g., a ryegrass pot trial, that determines "available K" is a measure of K supplying power.
- K<sub>ex</sub> supplying power (K<sub>ex</sub> supply)* : Total K uptake minus  $K_{\text{nex}}$  uptake.
- K<sub>nex</sub> supplying power (K<sub>nex</sub> supply)* :  $K_{\text{nex}}$  uptake calculated from total K uptake minus fall in  $\text{NH}_4\text{OAc}$  extractable  $K_{\text{ex}}$ .
- K losses* : The predicted amount of K lost from a farming system by leaching, product removal etc.
- Soil K supply (Soil K gain)* : The predicted amount of total K supplied to a farming system. It constitutes soil  $K_{\text{ex}}$  supply and soil  $K_{\text{nex}}$  supply, but may or may not include fertilizer K depending on the context in which the term is used.

## TERMS USED WHILE REFERRING TO THE METHODS THAT DETERMINE K RELEASING POWER

- K<sub>c</sub>* : K extracted by boiling  $\text{HNO}_3$ . It is a measure of difficultly soluble soil  $K_{\text{nex}}$ . It is analogous to *constant rate K*.
- K<sub>ex</sub>* : K extracted by ammonium acetate ( $\text{NH}_4\text{OAc}$ ). It either measures soil  $K_{\text{ex}}$  plus  $K_s$  or  $K_{\text{ex}}$  alone.

<i>Threshold K level</i>	:	Critical K concentration in the equilibrated soil solution below which K release from $K_{\text{nex}}$ sources is initiated.
<i>Solution K</i>	:	K measured in equilibrated 0.01 M $\text{CaCl}_2$ solution.
$K_T$	:	K desorbed in $\text{CaCl}_2$ solution plus K extracted with $\text{NH}_4\text{OAc}$ .
$AR^k$	:	K-Ca activity ratio in equilibrated soil solution.
$K_G$	:	Gapon constant. This gives a measure of relative tightness of binding of $\text{K}^+$ in relation to other cations.
<i>QTK</i>	:	Quick test K. This measures approximately 80 % of the soil $K_{\text{ex}}$ plus $K_{\text{v}}$ .
<i>NaTPB K</i>	:	K extracted by sodium tetraphenyl boron (NaTPB) reagent. This reagent measures soil $K_{\text{ex}}$ and $K_{\text{nex}}$ .
<i>Resin K</i>	:	K extracted by a mixed cation and anion resin membrane. In Chapter 6 it was used to measure soil $K_{\text{ex}}$ plus $K_{\text{v}}$ .
<i>Acid-extractable K</i>	:	K extracted by boiling with 1 M $\text{HNO}_3$ . It is a measure of soil $K_{\text{ex}}$ and easily soluble fraction of soil $K_{\text{nex}}$ .
<i>Step K</i>	:	A measure of soil $K_{\text{nex}}$ obtained by the difference between acid-extractable K and $K_{\text{ex}}$ . It is therefore a computed value.
<i>QSK</i>	:	Quick step K. This is a measure of soil $K_{\text{nex}}$ obtained by the difference between acid-extractable K and QTK. It is also a computed value.
<b>OTHERS</b>		
**	:	Significant at $P < 0.05$
*	:	Significant at $P < 0.01$
LSD	:	Least-squares difference
NS	:	Non significant
C.V	:	Coefficient of variation

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# CHAPTER 1

## INTRODUCTION

### 1.1 THE PURPOSE OF THE STUDY

Potassium (K) is a major essential nutrient required for pasture and crop production in New Zealand. Not only is it taken up by plants in higher amounts than other cationic nutrients but also acts as a chemical traffic controller, regulating the movement of other nutrients in the plant system. Thus where a reduction in the supply of K from the soil is likely to limit plant growth and this reduction is of economic importance, K fertilizer application is undoubtedly warranted.

There has been an increasing demand for K fertilizers in New Zealand over the last two decades due primarily to the demands of increasing production levels under conventional farming, and the increasing area of soils used for more intensive production such as dairying, arable and horticultural crops. It has been calculated that soil K reserves are being depleted at an annual rate of approximately 226,000 tonnes, which is equivalent to an average loss rate of  $11 \text{ kg K ha}^{-1} \text{ yr}^{-1}$  over 20.5 million ha (White, 1991). Hence, there is good reason for farmers and growers to be concerned about the future sustainability of K reserves in the soils of New Zealand.

During 1992-1993, New Zealand imported 214,284 tonnes K fertilizers to the value of \$ 57 million (Imports Monthly, June 1993). This was \$ 24 million more than the country spent on K fertilizers in 1985-86 when an average of 155,000 tonnes K fertilizers, worth \$ 33 million, was imported into the country (Williams, 1988). Importation is expensive to both the farmer and to the nation and, therefore, it is necessary to ensure rational and efficient use of K fertilizers.

Currently, in New Zealand, the potassium fertilizer requirement for any pastoral farming system can be estimated using the model developed by Cornforth and Sinclair

(1984). This model, called the "Computerised Fertilizer Advisory Service model" (CFAS model), takes into account the annual gains (supply) and losses of K that occur for an individual farm. The difference between the estimated supply and loss is the amount of fertilizer K that should be applied to the farm with the objective of maintaining productivity at the existing stock rate.

The usefulness of the CFAS model depends on its accuracy in estimating K supply and loss. Williams (1988) addressed the matter of K loss and presented an improved method for its estimation in dairy farming. This current study addresses the K supply component of the CFAS model.

In the CFAS model the soil K supply is assessed partly by a soil test and partly by an assigned value for long term K supply. The soil test (quick test K, QTK) measures the solution ( $K_s$ ) and a proportion of the exchangeable ( $K_{ex}$ ) pool, and the assigned value for long term K supply (reserve K,  $K_c$ ) is an estimate of the non-exchangeable ( $K_{nex}$ ) which will become available annually. These values (low, 0.10; medium, 0.30; and high, 0.70 meq %) are assigned on the basis of soil genetic group. As a consequence, while the soils that belong to a particular soil genetic group or subgroup may have different QTK levels (which are highly variable) they are presently all deemed to supply similar amounts of  $K_{nex}$ .

To date few studies have been conducted to evaluate the accuracy of using the exchangeable (QTK) and non-exchangeable K ( $K_c$ ) parameters of the soil supply component of the model to estimate annual soil K supply. There is circumstantial evidence (Williams *et al.*, 1986; Williams *et al.*, 1990) that the model underestimates the soil K supply for soils with low quick test values but which contain K reserves rated as "medium". For soils of this type, the supply of K from non-exchangeable K sources is often sufficient to balance the K losses. An example of this situation is the Massey University No. 4 dairy farm, which is on a yellow-grey earth soil (low QTK and medium  $K_c$  soil). Over a period of years there was little indication of a depletion of the quick test values on this farm despite no added K fertilizers (M.J. Hedley, pers. comm.), and there has been little or no measurable response to K fertilizer by pasture

(P.E.H. Gregg, pers. comm.) yet the CFAS model estimates that K fertilizer is required.

Studies on the K status of New Zealand soils have so far dealt mostly with a variety of genetic soil groups covering a wide range of reserve K levels. Few attempts have been made to assess the K status of soils within a specific genetic group.

The purpose of this study is to gain a better understanding of the non-exchangeable K supply of yellow-grey earths and related soils, with the expectation that the information gained can be used to address some of the problems identified above.

## 1.2 THE STRUCTURE OF THE STUDY

The thesis comprises of 10 chapters.

Chapters 2 and 3 present a review of literature, and the common methods and methodology used in the thesis, respectively.

The first major objective of the study aims to test the hypothesis that soils within a given soil group, and hence with a single assigned value for the supply of  $K_{nex}$ , do in fact supply similar amounts of  $K_{nex}$  for plants. The glasshouse experiment described in Chapter 4 addresses this objective. In Chapter 5 an attempt is made to explain the variations in the  $K_{nex}$  supply of the soils used in the glasshouse experiment. A laboratory experiment based on the "threshold K level" concept of Datta and Sastry (1991) is described.

In Chapter 6, K extracted by different chemical methods is correlated with the K taken up by plants in the pot experiment (Chapter 4). Here the objective is to determine the most suitable K extraction method. Once it is demonstrated that a particular method is most suitable, that method is used to assist in determining the supply of  $K_{nex}$  from the sand, silt and clay separates. Chapter 7 addresses this issue and describes an "agar pot trial" that is carried out.

In Chapter 8 the K-bearing mineral contents of the soils obtained by mineralogical studies are considered in relation to the  $K_{\text{ex}}$  supply. This chapter is sequential upon the information presented in Chapters 2, 4, 6, and 7.

In Chapter 9 some practical implications of the variations in the soil K supply parameter of the CFAS model are addressed.

In Chapter 10 the overall results of the study are assessed and summarised.



## CHAPTER 2

### REVIEW OF LITERATURE

#### 2.1 INTRODUCTION

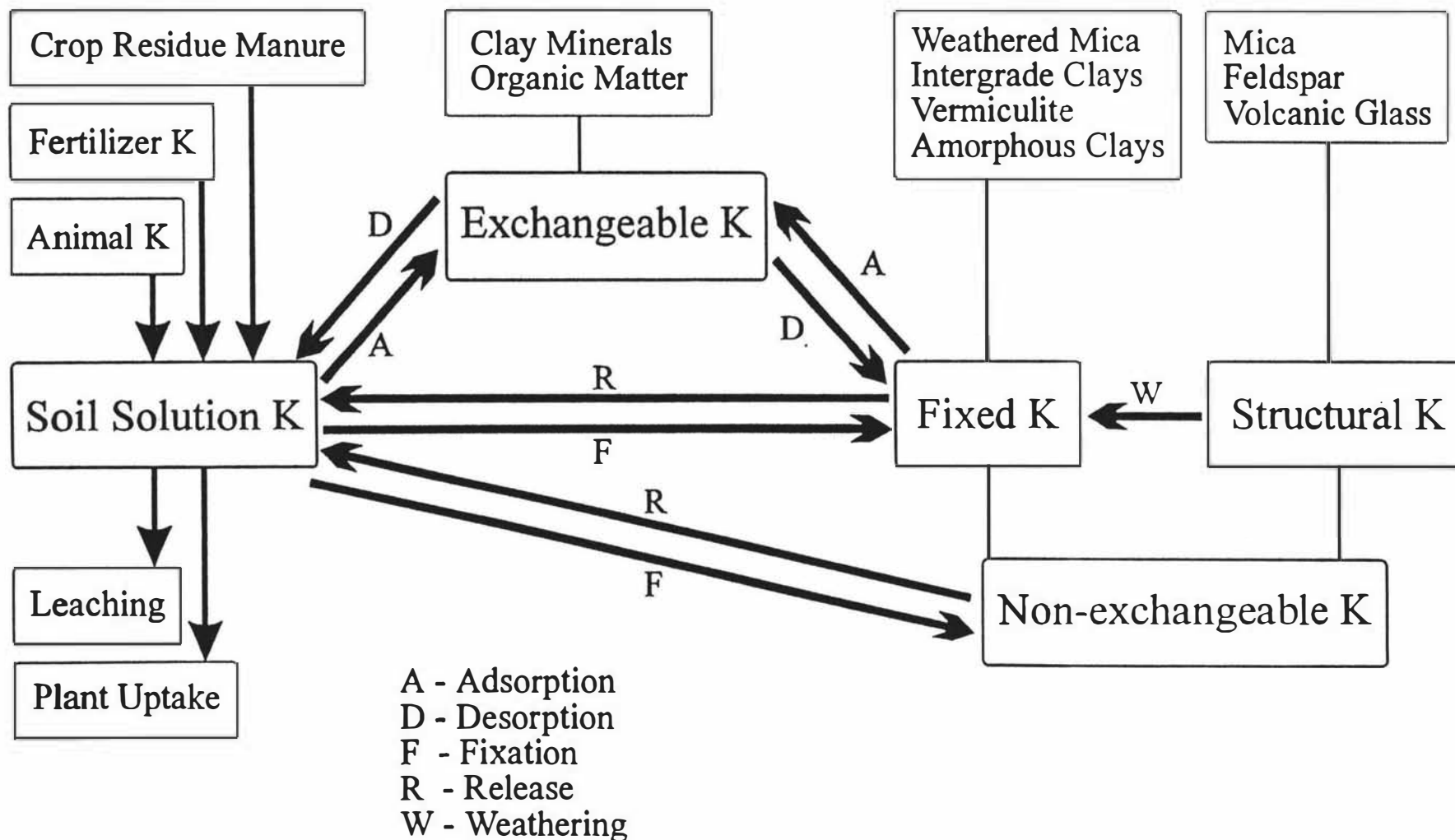
Potassium was recognised as an essential nutrient for plant growth by von Liebig (1840). Since then it has been studied extensively in both soils and plants and comprehensively reviewed by Reitemeier (1951), Arnold (1960 and 1962), Rich (1968), Metson (1980), Lee and Metson (1981), Sparks and Huang (1985), and Sparks (1987). Given the vast amount of literature available it is not the intention of the present review to cover all the information. Rather this review attempts to provide the reader with a general background to the different forms of soil K and the dynamic equilibria between them, the release and fixation of K by soil components, the methods of assessing K releasing power and K supplying power, the concepts for making K fertilizer recommendations, and the method of predicting the K fertilizer requirements of New Zealand pastures and crops.

#### 2.2 FORMS OF SOIL K

Potassium exists in four forms in soil (Fig. 2.1). In order of increasing availability to plants these forms are structural, fixed, exchangeable, and solution K (Sparks, 1987). Organically bound K is relatively unimportant in mineral soils. The boundaries for the mineral forms are arbitrary and the amount of K available in each form at a given time depends on many factors including plant K uptake, fertilizer additions, crop and leaching losses and soil processes. Thus the amount of K in each form should be related to the method of determination (Grimme, 1985).

The nature of these forms has been established using a variety of chemical and instrumental techniques (Sparks, 1980; Martin and Sparks, 1985), but in the field distinct boundaries do not exist (Sharpley, 1990).

**Fig. 2.1 The Dynamic Equilibria Between the Forms of Soil Potassium**



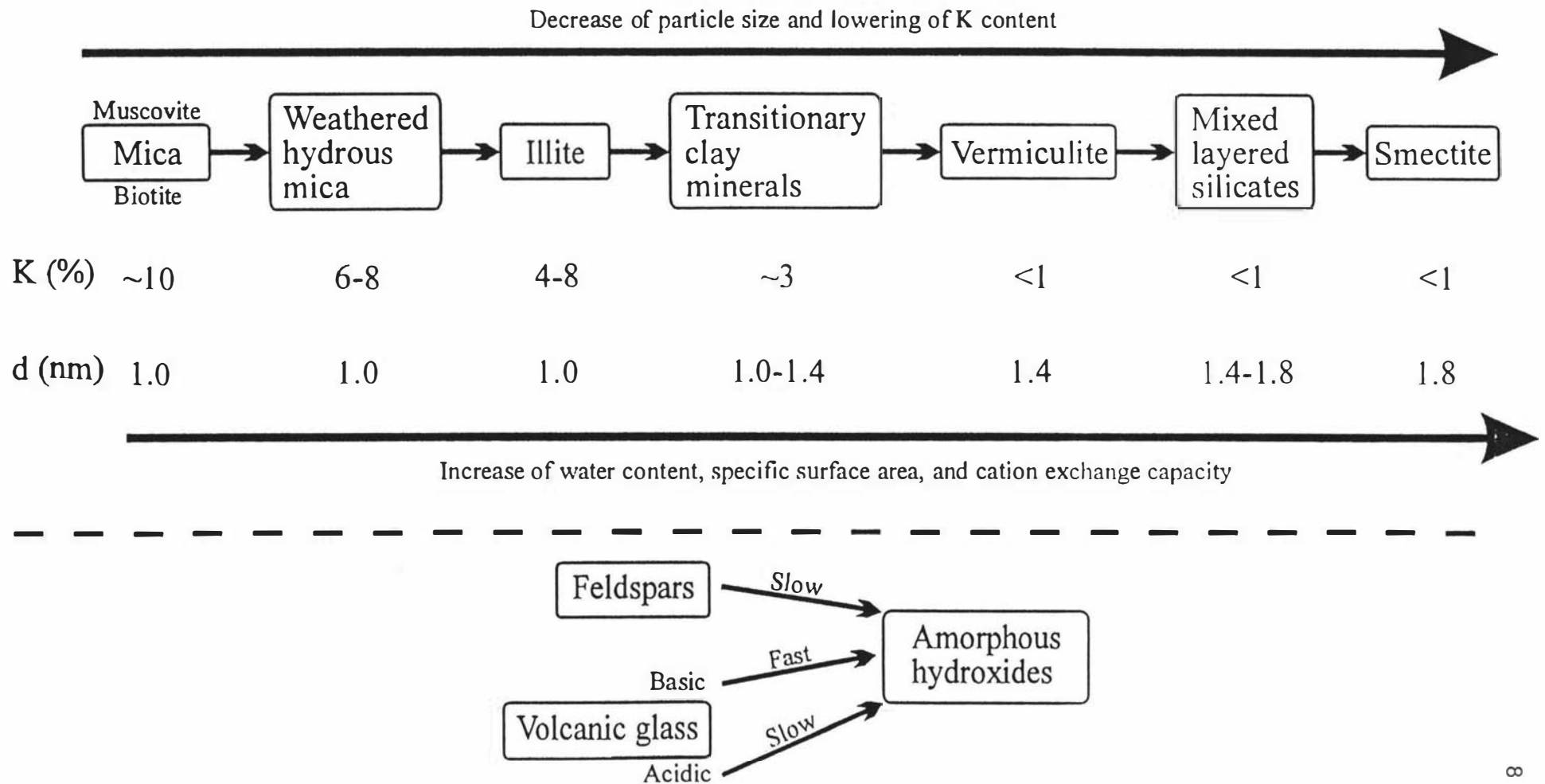
### 2.2.1 Structural K

Structural K is variously called mineral K, unweathered K, native K, matrix K, or inert K. It constitutes the bulk of the total K in most soils (Metson, 1980), the amount depends on the K composition of parent rocks and the stage of development of soils (Sparks and Huang, 1985). Structural K is bonded covalently within the crystal structure of the K bearing soil primary minerals such as mica, feldspar and volcanic glass (Schroeder, 1974; Tisdale *et al.*, 1985). These minerals are found principally in coarse size fractions (sands and silts) of soils (Metson, 1980). When physically and chemically altered (either by edge, or wedge/layer or surface weathering) secondary layer silicates are formed, some of which may have K present in the crystal structure.

Micas, commonly muscovite and biotite, are layered minerals of silica and alumina that contain  $K^+$  ions bonded to oxygen ions between the layers. Feldspars, including orthoclase and microcline, consist of a three dimensional honeycomb framework of linked silica and alumina with K acting as a balancing cation heterogeneously dispersed throughout the structure (Sparks, 1987). The composition of volcanic glass is often similar to feldspars but the structure is disordered and amorphous to x-rays. In New Zealand, micaceous minerals are mainly found in the clay fractions of brown-grey earths, yellow-grey earths, and the less weathered yellow-brown earths, feldspars are found in the sand and silt fractions of most soils, and volcanic glass mainly in the yellow-brown loam (basic volcanic glass) and yellow-brown pumice (acidic volcanic glass) soils (Fieldes and Swindale, 1954).

The K in the structures of these minerals is not immediately available for plant growth, but becomes available as a result of weathering. The general sequence of weathering of K-bearing primary minerals in soils is depicted in Fig. 2.2 and has been described by Tributh (1987). A similar sequence was also proposed by Fieldes and Swindale (1954) for the zonal soils of New Zealand. Weathering of micas results in the formation of illite, vermiculite, smectite, and transitional clay minerals. Feldspars and volcanic glass weather to X-ray amorphous hydroxides together with clay minerals such as halloysite (Kirkman, 1981).

Fig. 2.2 The Dynamics of Weathering of Primary Minerals



During the process of weathering the size of particles is reduced, K is depleted (from about 10 % in micas to less than 1 % in smectite) and the inter lattice spacing increases from 1.0 nm (micas) to 1.8 nm (smectites). Clay mineral formation may not always be in the same sequence as shown in Fig. 2.2 since soil conditions may favour the formation of one mineral over another. For example, transformation of illite to smectite is favoured under conditions of high pH, whereas at lower pH values interstratified minerals are favoured (Tributh *et al.*, 1987).

In New Zealand soils, the dominance of either micaceous minerals, or smectite, or 1:1 kaolin is influenced by the stage of weathering as well as inheritance from the parent materials. For example, the least weathered zonal soils (brown-grey earths) contain weakly-hydrated mica, illite, clay-vermiculite, and amorphous hydrous oxides of Al and Fe (Fieldes, 1968). With increased weathering and leaching, 2:1 clays are transformed to K-depleted clay vermiculite, and then to 1:1 minerals (metahalloysite and kaolinite). Thus in podzols and the podzolized yellow-brown earths, kaolinite and secondary silica are the main clay-size minerals (Fieldes and Taylor, 1961). On the other hand, the mineralogical features of the intrazonal soils (e.g., yellow-brown pumice soils, yellow-brown loams, red loams, brown loams) are largely inherited from the parent materials (rhyolitic or andesitic or mixed tephra, or scoriaceous basalt or flow basalt), modified by soil development (Fieldes and Taylor, 1961) and hence contain either allophane, mixed amorphous hydrous oxides, hydrous feldspars, metahalloysite, Fe oxides, crystalline oxides, or kaolinite. Layer silicates with 2:1 structure are either low or absent in these soils.

The 2:1 micaceous minerals are predominant in controlling the relationship between forms of K. Not all New Zealand soils, however, are dominated by these minerals. For example, the more strongly weathered and leached 'zonal' soils, and the 'intrazonal' soils derived from parent materials of volcanic origin with low mica content all have low K status and hence may be K deficient (Lee and Metson, 1981) for pasture or crop growth.

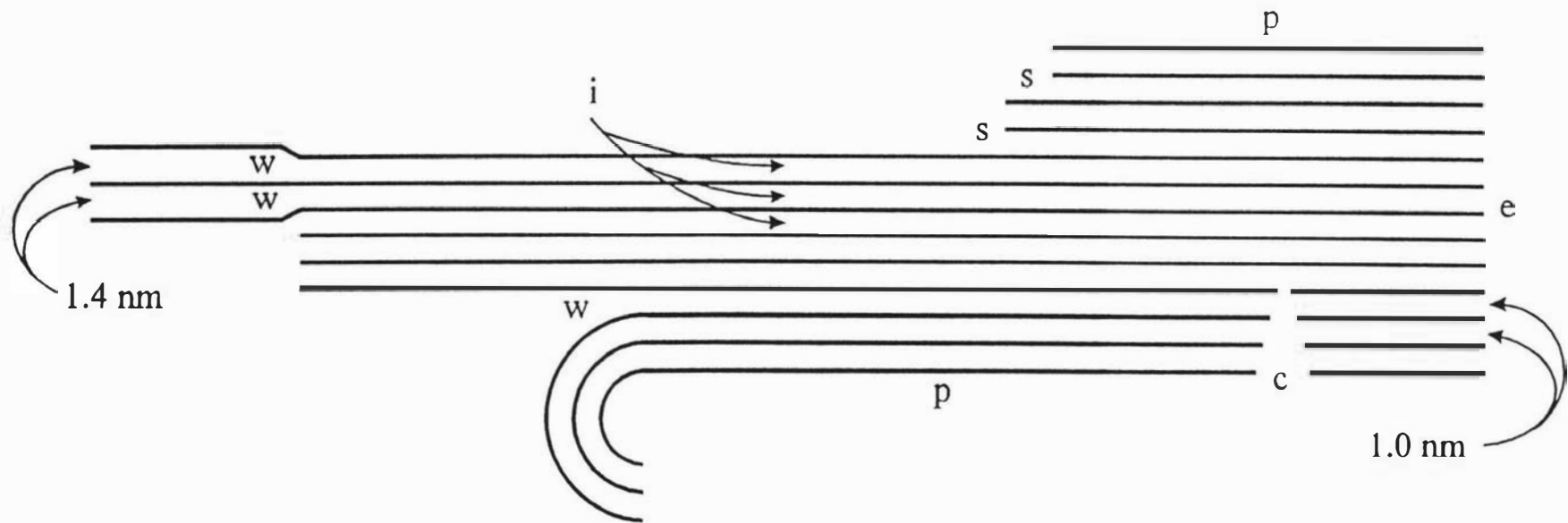
### 2.2.2 Fixed K

Fixed K has been defined as that fraction of soil K not bonded covalently within the crystal structure but rather found between adjacent 2:1 layers (bridging them by electrostatic bonds) of weathered micaceous minerals (Sparks and Huang, 1985; Martin and Sparks, 1985).

Due to the affinity of  $K^+$  for clay surfaces, several types of adsorption (exchange) sites for K on layered clay minerals (Fig. 2.3) have been postulated (Mengel and Kirkby, 1987; Goulding, 1987). Those on planar surfaces (p-position) have low  $K^+$  selectivity (non-specific), those on edge (e-), wedge (w-), step (s-) and crack (c-) adsorption positions have medium  $K^+$  selectivity (medium-specific), and those at interlayer sites (i-position) have high  $K^+$  selectivity (high-specific). The K present in the e-, w-, s-, and c- positions (Fig. 2.3) can be referred to as fixed K. The K in the i- positions of clay sized (weathered) micas and the K in amorphous clays can be regarded as native or strongly fixed K due to the position deep in the structure of the clay mineral. The differences in the mechanisms by which K is held at adsorption sites of the mica-like group of minerals (hydrous mica, illite, and vermiculite), and the smectite/kaolinite group are well documented (Bar *et al.*, 1987).

The amount of fixed K in soil at any given time depends on the particle size distribution, types and amounts of the clay minerals, and addition and removal of K. While addition of K to soils containing K depleted interlayer sites (e.g., vermiculite) results in strong K adsorption (fixation), removal of K from the soil by either plant uptake, leaching or microbial utilisation could result in release of K from any of the sites holding this form of K. This fixed K along with the native or strongly-fixed K, forms the main K reserve and buffer of the pedosphere and is generally not removed by extractants used to determine exchangeable K ( $K_{ex}$ ). It is therefore known as the "non-exchangeable K" ( $K_{nec}$ ) or "reserve K". Soils containing 1:1 clay minerals contain less  $K_{nec}$  due to the absence of K-specific sites in 1:1 clay minerals and hence all the  $K_{nec}$  is in the unweathered minerals (structural K). Thus all soils which contain either structural K, or fixed K, or both, can be regarded as containing  $K_{nec}$ . The basic

**Fig. 2.3 Model of a 2:1 layer-silicate clay showing 1.0 and 1.4 nm layers and planar (p), edge (e), interlayer (i), wedge (w), crack (c), and step (s) exchange sites (Goulding, 1987)**



difference between fixed K and structural K is that the release of fixed K is reversible whereas the release of structural K is irreversible.

From the above discussion it is concluded that exchangeable K and fixed K are found predominantly in the clay fraction and that structural K is found mostly in the unweathered primary minerals of the sand and silt fraction.

### 2.2.3 Exchangeable K ( $K_{ex}$ )

Exchangeable K ( $K_{ex}$ ) is the K sorbed at exchange sites, mainly on clays and humic colloids. In clays,  $K_{ex}$  is held at non specific adsorption sites (p- and e-positions) by bonds of varying strengths. Usually the contribution of  $K_{ex}$  to the total K content of soils is below 2 % i.e., between 10 and 400 ppm (Schroeder, 1974). In the major dairy farming soils of New Zealand  $K_{ex}$  levels (measured by the  $NH_4OAc$  method) account for between 1 and 5 % of the total soil K content (Williams, 1988).

For all soils, especially those that contain significant amounts of micaceous minerals,  $K_{ex}$  will be in dynamic equilibrium with the fixed K and also in equilibrium with K in solution ( $K_s$ ).

### 2.2.4 Soil solution K ( $K_s$ )

The K in the soil solution is immediately available for plant growth, and depletion in  $K_s$  below a certain level results in a rapid replenishment from  $K_{ex}$ . Thus  $K_s$  equilibrates with  $K_{ex}$  and the two forms are closely interdependent.

## 2.3 POTASSIUM EQUILIBRIA IN SOILS

Equilibria exist between the forms of K in soils. An equilibrium is reached and said to be dynamic when the rate of the forward reaction (fixation or adsorption in Fig. 2.1) is equal to that of the backward reaction (release). Equilibria appear to favour solution K. When the K in equilibrium soil solution is depleted the rate of its replenishment



(intensity) depends on the clay composition and the magnitude of release (quantity) depends on the clay content and humus that acts as buffering agent (McLean, 1978). The equilibria are therefore more dynamic in soils which contain significant amounts of 2:1 layered silicate minerals.

When the concentration of  $K_s$  is lowered it is rapidly replenished from the  $K_{ex}$  form, which in turn is more slowly replenished from fixed and/or structural forms ( $K_{ncx}$  or reserve K). The equilibrium between solution and  $K_{ex}$  is controlled to a large extent by the degree of K bond strength of the adsorption sites in the p- positions. For example, the adsorption sites of 2:1 clay minerals have high K bond strength (i.e., they bind K strongly) and that of organic matter and kaolinite (a 1:1 mineral) have low K bond strength (Mengel and Kirkby, 1987). On the other hand when excess K is added to the  $K_s$  to  $K_{ex}$  equilibrium the  $K_{ex}$  component tends to remain the same thus the added K tends to move into the  $K_{ncx}$  pool. The equilibrium system is therefore dependent on the operation of two processes viz, K release and K fixation.

#### **2.4 RELEASE OF K FROM PRIMARY (STRUCTURAL K) AND SECONDARY (FIXED AND EXCHANGEABLE K FORMS) MINERALS IN SOILS**

Release of K from structural forms to either fixed, exchangeable or soluble forms in soil is irreversible as far as K-bearing primary minerals, such as feldspars and volcanic glass, are concerned. Most of the K released from the primary minerals in the weathering process is adsorbed by the secondary clay minerals.

Release of K from feldspars initially proceeds rapidly at the surface, but as the silica-alumina residual layer increases in thickness the rate of release of K from deeper in the mineral is reduced and finally prevented (Correns, 1963; Rasmussen, 1972). K release from feldspars also involves lattice destruction (Robert, 1986). Feldspars, however, occur most commonly in the silt and sand fractions of soils and are therefore less important sources of K than micas.

The rate of release of K from acidic glasses is considered to be low, whereas it is high from basic glasses, as in young soils from basalt (Metson, 1968a and 1968b). In New Zealand, volcanic glasses are the principal K bearing primary minerals in the yellow-brown pumice soils from rhyolitic ash and pumice.

Structural K release from primary micas on the other hand is not necessarily completely irreversible. This is because weathering of primary micas results in transformations in the silicate layers often accompanied by a decrease in particle size and also by an expansion of the b-axis. As a consequence, 2:1 weathered micaceous minerals with different adsorption (exchange) sites (Fig. 2.3) are formed. These sites control the relationship between the forms of K and enable clay minerals to exhibit varying degrees of K fixation and release.

Fixed K in the secondary clay minerals (e.g., weathered mica) is also vulnerable to release by further weathering. The release depends on the K concentration in the bathing soil solution, each mineral having a different critical concentration below which release occurs (Talibudeen, 1975). The release occurs basically by an exchange process involving hydrated  $\text{Na}^+$ ,  $\text{Mg}^{++}$ , and  $\text{Ca}^{++}$  which are larger in size than  $\text{K}^+$  followed by partial expansion and dissolution of silicate layers (von Reichenbach, 1972; Martin and Sparks, 1985; Mengel and Kirkby, 1987). The replacing ions enter the unexpanded interlayers, which results in the formation of frayed edge or wedge zones (typical of weathering micas) which favour diffusion of K out of the mineral to either exchange sites on the outer parts of the clay particles or directly to the soil solution. Rausell-Colom *et al.* (1965) and Scott (1968) have also presented evidence for very slow solid state diffusion of non-hydrated  $\text{K}_{\text{ncx}}$  ions out of the interlayer space and simultaneous inward diffusion of exchanging cations.

The proportion of wedge zones decreases in the order micas > illite > vermiculite > smectite (Arifin *et al.*, 1973). This reflects the decreasing proportion of K in the i- and w- positions in these minerals. The amount and the release of fixed K in soils therefore depends on the clay types present and the rate of K release from them.

The rate of release of fixed K is, however, a diffusion controlled process characterised by a linear relationship between the percent of K released versus the square root of time (Feigenbaum *et al.*, 1981; Martin and Sparks, 1985; Sparks, 1985; Dhillon *et al.*, 1989). The difference in K concentration between the newly-mobile, just-released K and that in the external solution provides the driving force for this diffusion (Quirk and Chute, 1968; Martin and Sparks, 1985).

## 2.5 POTASSIUM FIXATION

The reverse of release i.e., the reverse of weathering, during which the larger cation species are replaced from w-positions by  $K^+$ , is called fixation. This occurs in the K-specific binding sites (K-selective sites) of the interlayer zone of the K-depleted 2:1 clay minerals. The  $K^+$  ions are geometrically and ionically entrapped in the di-trigonal facing holes of the interlayer oxygens between the unit cells of expanding 2:1 layer silicates (Beckett and Nafady, 1967; Arifin *et al.*, 1973). The entrapment causes the collapse of the layer structure to the 1.0-1.2 nm d(001) spacing. For example, when Ca-saturated smectite or vermiculite is treated with K, the d(001) spacings collapse to 1.2 nm and 1.0 nm, respectively (Sawhney, 1969). This type of fixation may be visualised as an ion exchange reaction.

The second fixation mechanism, which is relatively unimportant, is considered to happen via formation of insoluble K compounds, especially aluminosilicates (Shaviv *et al.*, 1985). At high pH K may precipitate with alumina and silicates (Volk, 1938).

The clay type is considered to be the dominant factor that determines the course of fixation. In general, soils containing micas, hydrous micas, or vermiculites have the highest fixation capacities, while smectitic and kaolinitic soils have low capacities (Shaviv *et al.*, 1985). Differences in the K fixation properties of soils also arise due to the presence or absence of wedge zones in the weathered micaceous minerals. The effect of wedge zones in K fixation is determined by their position and number in the 2:1 clay minerals (Arifin *et al.*, 1973). Fixation would be less effective if the wedge zone is located near the edge of the particle and more effective if penetrated deep within

the particle. The number of wedge zones would diminish according to the weathering sequence in the order micas > illite > vermiculite > smectite as mentioned earlier.

Assessment of K fixation in heterogenous soils is more complex than the above considerations because soils may contain numerous types of K-depleted and partially expanded clay minerals of varying particle size and crystallinity, which have different adsorption characteristics. As Martin and Sparks (1985) pointed out, it may be logical to assume that if fixation takes place, K release also occurs, but the reverse may not always be true.

It is doubtful if K fixation in the disordered micas (weathered / expanded / mixed / interstratified) results in complete reversion of the mineral phase to pedogenic mica having 1.0 nm basal spacing (Bertsch and Thomas, 1985; Tributh, 1987). Arifin *et al* (1973) suggested that reorganisation is brought about by progressive entrapment of  $K^+$  ions in the selective adsorption sites of the wedge zones of the disordered micas. As a result, the silicate layers progressively collapse and rearrange to a mica-like structure with increased entrapment of  $K^+$  ions. They pointed out that the ease of reconstitution of the mica-like lattice by K fixation would be determined by the availability of wedge zones, the degree of crystallinity, and the interlayer charge density. Intensive weathering may result in fewer wedge zones, less crystallinity, and lower interlayer charge density of micas.

In summary K release and fixation in soils is chiefly a function of mineralogy i.e., the amounts and types of primary and secondary minerals present. Soils that are high in kaolinite and smectite release only small quantities of  $K_{nex}$  whereas soils containing mica-like and vermiculite minerals release substantial amounts of  $K_{nex}$  to plants. The minerals that determine whether K is released or fixed have been listed by Rich (1972) and Goulding (1987). Since K release and K fixation fundamentally involve ion exchange reactions, the factors that influence one process also influence the other. These factors have been reviewed by Rich (1972), Sparks and Huang (1985), Martin and Sparks (1985), and Goulding (1987) and include wetting and drying, freezing and thawing, plant roots, protonation, manuring, soil structure, rainfall and temperature.

## 2.6 PLANT AVAILABILITY OF K IN RELATION TO RELEASE/FIXATION PROCESSES

With respect to soil-plant relationships, a number of vague terms have been used liberally in the literature. Pertinent examples include available K, K availability, K releasing power, and K supplying power. "Available K" (meaning quantity) is meaningful only if either the time during which it can be made available to plants or the chemical method by which it is determined is stated because all the forms of K are eventually plant available.

"Potassium availability", as the name implies, describes a complex situation and denotes a quality dependent on soil properties as well as plant characteristics (Grimme, 1985). It reflects the overall "availability" of K to plants. Where "availability" is poor, K uptake by crop or pasture is also low and unsatisfactory yields are obtained. It therefore includes other factors in addition to the "available K". Andres (1990) listed a number of site factors on which the availability of soil K for plant uptake depends.

The soil factors that influence K availability include factors that control K flux rates/K diffusion viz, temperature, water content, tortuosity, and K concentration in the soil solution, factors that influence exchange equilibria viz, amounts and proportions of K in relation to other cations, K buffering capacity, the rate of K release from  $K_{\text{oc}}$  to solution form, and K fixation (Haby *et al.*, 1990). The soil factors also include soil solution parameters and plant water use related to mass flow. Plant factors include plant type and genetics, age, K requirement, transpiration rate, root morphology and growth rate, K absorption mechanism of the root (Haby *et al.*, 1990). K availability therefore is difficult to quantify and available K is only one of the many factors contributing to K availability under field conditions. Its quantity is dependent on both soil and plant factors and a single clear-cut value for K availability is not possible.

"Potassium releasing power" refers to the change of  $K_{\text{oc}}$  to  $K_{\text{ex}}$  and  $K_s$ , and the release of  $K_{\text{ex}}$  to  $K_s$ . It denotes the total availability from the soil, not the total uptake of K, because the entire amount of K that was released may not be used by the plants (some

may be lost by leaching and/or by simultaneous fixation by K-specific sites in the weathered micaceous minerals). Hence any chemical method denoting "available K" would reflect the K releasing power of soils. On the other hand any biological method denoting "available K" reflects "K supplying power". Thus K supplying power could be equated to the actual uptake of K by the growing plants (Pearson, 1952; Ramanathan and Krishnamoorthy, 1982). Plant growth studies on available K (actual uptake of K by plants) are really about the K supplying power of soil and chemical extractions are about K releasing power.

Consequently, with respect to plant performance (reflecting K supplying power), it is not the total amount of K that can be released but rather the rate of release and the K concentration maintained in the soil solution at the root zone that is important. Both of these must be high enough to support good plant growth and to prevent K deficiency symptoms. They are influenced not only by exchange processes between solid (K-bearing minerals) and liquid (soil solution) phases, but also by transportation of water towards the roots. Furthermore, when the level of K in the soil solution is low, release from  $K_{ex}$  will occur and when it is high the reverse (fixation) is true (section 2.3). This is due to the dynamic equilibria that exist between the various forms of K (Martin and Sparks, 1985), which indicate soil minerals can function both as K sources and K sinks. Plant root uptake of K disturbs the dynamic equilibria and favours the flux of K towards the roots.

Significant increases of K concentration in the soil solution will occur only after the K selective adsorption sites have been saturated with K. There are many examples where K fertilization did not have a positive effect on yield (Richards *et al.*, 1988) because normal application rates did not raise the K concentration in the soil solution by a significant amount.

Potassium availability to plants is therefore mainly a function of the K diffusion flux that a soil can maintain towards the plant roots (Barber, 1962; Grimme, 1974; Kuchenbuch, 1987). Usual K levels in soil solution are inadequate to supply sufficient K by diffusion flux. A sufficiently high flux rate of K, however, is only attained and

sustained by a sufficiently high concentration of solution K backed up by either high quantities of  $K_{ex}$  and/or  $K_{nex}$  or by the addition of K fertilizers.

## 2.7 METHODS OF ASSESSING PLANT AVAILABLE K

Plant available K can be assessed either by plant growth studies or by simple chemical extraction methods or a combination of both procedures. When assessed by plant K uptake studies, it can be termed "K supplying power" whereas by extracting the soil with one or more extractants, a chemical index of available K (K releasing power) is achieved (section 2.6). The uptake of K by plants, however, is the true index of plant available K.

Consequently, while "plant available K" can be equated to the K supplying power of the soil, it can only be related to the K releasing power. Thus both K releasing power and K supplying power are measures of the ability of a soil to supply K to plants, but as indicated in section 2.6 they have different meanings. The reliability of K releasing power as an index of plant available K depends on how closely its value, in absolute terms, approaches the actual amount of K required or taken up by plants (K supplying power).

The annual K uptake of an average grass-clover pasture in New Zealand was estimated to be in the range of 225-280 kg ha<sup>-1</sup> (During, 1984). Unfortunately none of the existing methods of measuring K releasing power match these levels of K uptake because extraction of K by reported chemical methods does not mimic extraction by plants. Soil chemical methods operate by different mechanisms. For example, K uptake during plant growth is a dynamic process with periods of K depletion in the root zones and release of  $K_{nex}$  to both  $K_{ex}$  and solution forms by K-bearing soil minerals. The situation is further complicated in grazed pastures where K is recycled (redistributed) at a faster rate than under cropping. On the other hand, methods used for measuring K releasing power are mostly based on equilibration processes. Furthermore, they do not directly account for the soil processes and the influence of soil, site, and climate which control K availability. Hence any chemical procedure to

be used as an index of K supplying power, though not exactly equating to K uptake, must at least provide a good relationship (correlation) between test results and the actual K uptake during the growing season for a specific crop (Haby *et al.*, 1990).

### 2.7.1 Methods for assessing K supplying power

Methods used to study soil K supplying power are mostly biological and adopt exhaustive cropping experiments either in the field or in pots. They involve growing plants to K exhaustion, and measuring cumulative K uptake to get a direct measure of K supplying power. To get additional information they are often conducted in association with chemical extraction methods (mainly the  $\text{NH}_4\text{OAc}$  method of measuring  $K_{\text{ex}}$ ). For example, the K supplying power (K uptake) can be apportioned into two categories based on depletion of  $K_{\text{ex}}$  due to cropping. The categories are  $K_{\text{ex}}$  supplying power ( $K_{\text{ex}}$  uptake) and  $K_{\text{nex}}$  supplying power ( $K_{\text{nex}}$ ) and they reflect K uptake from soil  $K_{\text{ex}}$  and soil  $K_{\text{nex}}$  sources, respectively. The  $K_{\text{nex}}$  supplying power is calculated as the difference between the  $K_{\text{ex}}$  releasing power ( $\text{NH}_4\text{OAc}$  extractable K) plus added fertilizer K at the start of the experiment, and plant uptake plus the  $K_{\text{ex}}$  releasing power at any time period within the experiment (Grissinger and Jeffries, 1957; Tabatabai and Hanway, 1969; During and Campkin, 1980; Havlin and Westfall, 1985; Richards *et al.*, 1988; Tarafdar and Mukhopadhyay, 1989; Badraoui *et al.*, 1992; Portela, 1993).

A positive value of  $K_{\text{nex}}$  supplying power in a field experiment indicates a source of K ( $K_{\text{nex}}$ , and/or  $K_{\text{ex}}$  below the sampling depth) for plants while a negative value indicates that there is a sink for K (fixation, leaching, or runoff). In a pot experiment, however, the only probable source and sink is the  $K_{\text{nex}}$  (reserve K). Therefore, if the  $K_{\text{nex}}$  supplying power is positive, K release has occurred and if negative, K fixation has taken place.

There are important environmental differences between plants growing in the field and in pots (Arnold and Close, 1961; Arnold, 1970; Feigenbaum and Kafkafi, 1972; Goulding, 1987; Johnston and Goulding, 1990; Portela, 1993). These differences account for the divergence between the K supplying power as measured in the field and



that measured in the pot, and they indicate that results from pot experiments are difficult to relate to the field situation. Arnold (1970), however, rightly criticised the use of pot trials for other than soil comparative purposes, on the ground that the intensity of soil exploration was great (10-20 times that under field conditions) and that K was depleted to very low exchangeable K levels which were irrelevant under field conditions. Weber and Grimme (1986) suggested that one year of intensive cropping with ryegrass was approximately equivalent to 10-15 years of normal cropping in the field. Despite these reservations the pot trial technique is widely used because it is controlled and very useful for comparing soils under standardized environmental conditions.

The standard methods of pot culture are Chaminade, Stanford and DeMent, and Neubauer (Goulding, 1987). Culture vessel techniques using agar-gel are becoming popular for measuring K supplying power at rhizosphere scale of investigation (Kuchenbuch and Jungk, 1982; Hinsinger *et al.*, 1992; Hinsinger *et al.*, 1993; Hinsinger and Jaillard, 1993). The K supplying power ( $K_{ex}$  and  $K_{nex}$ ) of a soil may, however, vary in magnitude depending on the pot trial technique used. The two important factors that contribute to this variation are: (i) soil to plant ratio, and (ii) cropping period.

Both field (Lee and Metson, 1977; During and Campkin, 1980) and pot (Haylock, 1956b; Campkin, 1972; Lee and Gibson, 1974; During and Duganzich, 1979; Jackson and During, 1979; Jackson, 1985) trials have been used to assess the K supplying power of New Zealand soils. The K supplying power to a lucerne crop over 3 years in a field trial on a soil from the Spring Creek series (flood-banded fine alluvium derived from greywacke) was reported to be 571 kg K ha<sup>-1</sup> (Lee and Metson, 1977). This would be considered a high value for this region. Data from the first year of a national series of K trials on pastures (Campkin, 1983) revealed that the K supplying power of some YGE soils in the South Island (Christchurch and Timaru regions) ranged from 92 to 282 kg ha<sup>-1</sup>. In contrast, During and Campkin (1980) measured the K supplying power of some North Island soils derived from volcanic and sedimentary parent materials and identified the sources and sinks of  $K_{nex}$ . The  $K_{nex}$  supply to

ryegrass ( $K_{\text{nex}}$  supplying power) in this study was as high as  $500 \text{ kg ha}^{-1} \text{ yr}^{-1}$  with a more usual rate of supply of  $200\text{-}300 \text{ kg ha}^{-1} \text{ yr}^{-1}$ . It is inferred that there is a wide range of K supplying power of New Zealand soils.

Potassium supply measured by pot trial methods is more often used as a tool to compare K supplying abilities of different soils and to further evaluate soil chemical methods for assessing K releasing power. The choice of the method (field or pot) for measuring K supplying power therefore depends on the objective of the research.

### 2.7.2 Methods for assessing K releasing power

In contrast to the methods used to assess K supply, which depend on the growth of plants, the assessment of K releasing power is based on chemical extraction methods, several of which form the basis of soil testing methods. Extraction methods depend on the solubility of soil K in different reagents including water, salt solutions or mixed salt solutions, organic and inorganic acids of varying strengths and temperature. Depending upon the activity of the extractants and the method, the amount of K extracted is variable. For example, strong acids extract a greater proportion of soil K than weak acids and  $\text{NH}_4^+$  containing extractants (Metson, 1980; McLean and Watson, 1985).

Although comprehensive reviews on the methods of K releasing power have been carried out by numerous investigators (Doll and Lucas, 1973; Grimme and Nemeth, 1979; McLean and Watson, 1985; Martin and Sparks, 1985; and Goulding, 1987), they were inadequate in categorising these methods based on the form of soil K that is measured. Goulding (1987) discussed the most widely used and/or useful methods in relation to their advantages and disadvantages.

#### 2.7.2.1 *Methods for assessing $K_{\text{ex}}$ releasing power*

Methods for assessing  $K_{\text{ex}}$  are based on the use of cations such as  $\text{NH}_4^+$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ , and  $\text{Na}^+$  which replace  $\text{K}^+$  on soil exchange sites (p- and e-). They also measure  $\text{K}^+$  in the soil solution. Of all the methods, the M  $\text{NH}_4\text{OAc}$  (pH 7) procedure

has been most widely used. James and Weaver (1975) outlined the basis for  $\text{NH}_4\text{OAc}$  becoming the classical procedure for determining  $K_{\text{ex}}$  but Goulding (1987) warned that "the use of this reagent may diminish with wider availability of instrumental techniques in which the acetate ion interferes with detection".

There are reports that  $\text{NH}_4\text{OAc}$  "overestimates" the amount of K that is truly present at the exchange sites (p- and e-) of base-saturated soils with appreciable amounts of vermiculite (Martin and Sparks, 1983; Richards *et al.*, 1988; Richards and Bates, 1989; Simard *et al.*, 1989). This "overestimation" of  $K_{\text{ex}}$  by  $\text{NH}_4\text{OAc}$  is in relation to a comparison with  $K_{\text{ex}}$  release measured by a Ca salt, and in fact is a result of the smaller  $\text{NH}_4^+$  ions exchanging with K located at both the soil exchange (non-specific) and fixed (specific/wedge) sites whereas  $\text{Ca}^{++}$  replaces K at non-specific sites only.

"Overestimation" is probably not the best word in the above context because no two methods of assessing  $K_{\text{ex}}$  releasing power can be comparable in absolute terms. Rather,  $K_{\text{ex}}$  released by  $\text{NH}_4\text{OAc}$  is better referred to as " $\text{NH}_4\text{OAc}$  extractable  $K_{\text{ex}}$ " and that released by Ca salts as "Ca extractable  $K_{\text{ex}}$ ". Thus "K releasing power" is best considered as being specific to the extractant and the technique.

Dilute solutions of strong acids such as 0.1 M  $\text{HNO}_3$  have been used as an alternative for assessing  $K_{\text{ex}}$  releasing power (Haylock, 1956a) but the  $\text{H}^+$  ion may displace more K than is truly exchangeable.

#### 2.7.2.2 *Methods for assessing $K_{\text{ex}}$ plus $K_{\text{nex}}$ releasing power*

There are methods that are used as a single measure of K status that include both  $K_{\text{ex}}$  and  $K_{\text{nex}}$  forms and use only one extractant. They involve either treating the soil with acid e.g., boiling with M  $\text{HNO}_3$ , continuous leaching with 0.01 M HCl, or with a salt precipitant (sodium tetraphenyl boron, NaTPB). Of these, single extraction with boiling nitric acid is used widely (Pratt, 1951; Grissinger and Jeffries, 1957; Campkin, 1972; Wood and Schroeder, 1992).

In New Zealand  $K_{ex}$  plus  $K_{necx}$  releasing power has been assessed for a wide range of soils using both  $HNO_3$  (Campkin, 1972) and NaTPB (Jackson, 1985; Williams *et al.*, 1986). Jackson (1985) gave a list of workers who used NaTPB extensively in both clay mineralogical and agronomical studies.

### 2.7.2.3 *Methods for assessing $K_{necx}$ releasing power*

Methods of assessing only  $K_{necx}$  releasing power involve more than one determination. The computation method, subtracting the  $K_{ex}$  release from the K extracted by strong acids, usually M  $HNO_3$ , is the most popular. Thus a minimum of two measurements (one to measure  $K_{ex}$  release and another to measure  $K_{ex}$  plus  $K_{necx}$  release) are made before computation.

Several workers have proposed methods to calculate the amount of  $K_{necx}$  released (Pratt, 1952; Haylock, 1956a; Metson *et al.*, 1956; Campkin, 1972; Hay *et al.*, 1976; Knudsen *et al.*, 1982; Al-kanani *et al.*, 1984; Richards and Bates, 1988; Richards and Bates, 1989; Simard *et al.*, 1989). The methods differ in the methodology used to measure  $K_{ex}$  releasing power and in the methodology to extract K by  $HNO_3$ . For example Pratt (1952) measured  $K_{ex}$  by a leaching solution (acetate salt of  $NH_4$  and Mg) and subtracted this value from the K extracted by  $HNO_3$ . The methods of Haylock (1956a) and Metson *et al.* (1956) were similar in that five successive  $HNO_3$  extractions were used to extract  $K_{necx}$  but differ in the methods used to remove  $K_{ex}$ . The former used 0.1 M  $HNO_3$  to remove  $K_{ex}$  but did not use this value in computing the amount of  $K_{necx}$  release. The latter used  $NH_4OAc$  to measure  $K_{ex}$  and used this in the calculations. Both these methods, however, are based on similar formulae to calculate the  $K_{necx}$  released, even though the amount released varied according to inclusion or exclusion of  $K_{ex}$  release in the formulae.

The  $K_{necx}$  determined by computation methods is variously called step K (Haylock, 1956a; McLean, 1961; Campkin, 1972; Richards and Bates, 1988),  $K_{int}$  (Hay, 1971; Hay *et al.*, 1976), Delta K (Metson *et al.*, 1956), wedge K ((Richards and Bates, 1989),  $K_{df}$  (Liu and Bates, 1990) or simply non-exchangeable K (Knudsen *et al.*, 1982).

For convenience, this will be called "step K" in this study. Unfortunately the existing computational methods are tedious and involve additional measurements and/or sequential extractions. The easiest method to use is the  $K_{int}$  method described by Hay (1971), and Hay *et al.* (1976). The  $K_{int}$  is the K extracted by boiling 1 M  $HNO_3$  (1:100 soil to acid ratio) together with the K included in one further washing with the acid minus the  $K_{ex}$  value (measured by  $NH_4OAc$ ). A simpler method would be to eliminate the washing step of Hay's method because this merely extracts additional readily soluble K.

A further extension of the step K method led to the development of yet another method of  $K_{nex}$  determination called the  $K_c$ /reserve K method (Metson *et al.*, 1956; Metson, 1968a) or the constant rate K (Haylock, 1956a; Richards and Bates, 1988). Blakemore *et al.* (1987) standardised this method. All the  $K_{ex}$  (which can be measured by  $NH_4OAc$  method) and the more accessible  $K_{nex}$  (which can be measured by step K method) is removed before the  $K_c$  value is determined. Thus while step K gives the actual amount of the more soluble  $K_{nex}$  released (short/medium term)  $K_c$  measures the rate of release of difficultly soluble K from  $K_{nex}$  sources in the long term (Metson, 1980).

In New Zealand, the  $K_c$  method of assessing  $K_{nex}$  releasing power is used widely. It was developed as a guide to measure the long term rate of release of K from soil  $K_{nex}$ , but not to measure the absolute amount of  $K_{nex}$  (Metson, 1980; Lee, 1984). This  $K_c$  measurement is meaningful because it reflects the soil mineralogy and gives an indication of the potential  $K_{nex}$  release that is inherent in the soil (Lee, 1984). Thus  $K_c$  levels are expected to decrease with increasing K depletion of micaceous clays and decrease even further with the predominance of 1:1 layer and oxide clays (Metson and Lee, 1977; Metson, 1980).

The  $K_{nex}$  releasing power of New Zealand soils, as measured by the  $K_c$  method, ranges from virtually zero to 31.2 mg 100 g soil<sup>-1</sup> (Metson, 1968b) and was categorised as being low, medium, or high (Metson, 1980; Lee and Metson, 1981; Campkin, 1985). This categorisation was based on the  $K_c$  measurements of selected undeveloped soils that broadly represented various New Zealand genetic groups, followed by an arbitrary

descriptive rating (Metson, 1980; Campkin, 1985). The numerical limits used to define the  $K_c$  categories by Metson (1980) are, however, different to those used by Campkin (1985).

Lee and Metson (1981) summarised the extensive information of Metson (1980) on the  $K_{n\text{ex}}$  releasing power ( $K_c$  method) of New Zealand genetic soil groups. Thus the YGE soils in the North Island region were rated "medium  $K_c$ " and their counterparts in the South Island rated "high  $K_c$ " with respect to their  $K_{n\text{ex}}$  releasing power (Cornforth and Sinclair, 1984; Campkin, 1985). This rating, however, was not based on  $K_c$  values of all the soils within the YGE group of respective Islands, but on selected soils that were believed to give a reasonable coverage of this genetic group. Nevertheless, a variation in the extent of  $K_{n\text{ex}}$  release (step K method or  $K_c$  method) would be expected within the soils of both the Islands due to the mineralogy being variable through differences in soil forming factors within each regional YGE group.

In New Zealand, information on  $K_{n\text{ex}}$  releasing power as measured by the step K method is not as extensively used as information based on the  $K_c$  method of measuring  $K_{n\text{ex}}$  release. Like  $K_c$ , step K values showed wide variations according to genetic soil groups (Metson, 1968b). Haylock (1956a) used step K as a method for detection of K deficient (responsive) and K non-deficient (non-responsive) soils. Metson *et al.* (1956), Haylock (1956a and 1956b), Campkin (1972), Lee and Gibson (1974), and Hay *et al.* (1976) appear to be the only workers to have reported the short term  $K_{n\text{ex}}$  releasing power (measured by step K) in New Zealand soils.

#### 2.7.2.4 *Additional methods for assessing both $K_{\text{ex}}$ and $K_{n\text{ex}}$ releasing power*

These methods were developed principally as tools for understanding exchange processes in soils. They include exchange isotherms (Goulding, 1983; Goulding, 1986; Elkhatib and Hem, 1988), quantity/intensity (Q/I) relationships (Beckett, 1964; Lee, 1973; During and Duganzich, 1979; Sparks and Huang, 1985; Haby *et al.*, 1990; Cervantes and Hanson, 1991; Herlihy, 1992), electro-ultrafiltration (EUF) (Nemeth, 1982; Sparks, 1987; Haby *et al.*, 1990; Herlihy, 1992; Liu *et al.*, 1992), and cation

exchange resins (Lee and Gibson, 1974; Talibudeen *et al.*, 1978; Martin and Sparks, 1983; Havlin and Westfall, 1985). Apart from measuring both  $K_{ex}$  and  $K_{nex}$ , they also measure the concentration or activity of K in the soil solution. The  $K_{nex}$  is, however, indirectly measured as the buffering capacity in some of these methods (e.g., Q/I and EUF).

Cation exchange resins have been employed to investigate K release from soil clay minerals, especially for evaluating kinetics of  $K_{nex}$  release using different rate equations (Martin and Sparks, 1983). The end results of these kinetic studies (e.g.,  $K_{ex}$  and  $K_{nex}$  release rate coefficient) indicate the rate of  $K_{nex}$  release (low or high) as well as the mechanism of release (which is invariably by diffusion-controlled exchange).

While single equilibrium extractions with cation ( $Ca^{++}$  or  $Na^+$ ) saturated resins are satisfactory for measuring  $K_{ex}$  release power alone, multiple extractions are necessary to build up K release curves that can differentiate  $K_{ex}$  (immediate) and  $K_{nex}$  (short and long term) releasing powers (Talibudeen *et al.*, 1978; Havlin and Westfall, 1985).

All these methods, however, are deemed to be of little use for practical predictions of K releasing power (Sparks, 1987) because they are expensive and time consuming.

The so-called "universal extractants" (Jones, 1990; Grzebisz and Oertli, 1993) that measure either  $K_{ex}$  (e.g.,  $CaCl_2$ ) or  $K_{ex}$  plus  $K_{nex}$  (e.g., Mehlich 3) can also be categorised under the additional methods for assessing both  $K_{ex}$  and  $K_{nex}$  releasing power.

### **2.7.3 Relationship between K releasing power and K supplying power**

While the above methods of K release give an empirical measure of the likely release of K, their utility under practical field situations would be enhanced if a close relationship could be established between K releasing power and K supplying power of soils. The methods, however, provide little information on the rate at which the soil supplies K to the plants.

The success of any chemical method for evaluating K release depends on the ability to measure  $K_{\text{dex}}$ , not  $K_{\text{ex}}$ . This is because plants take up K not only from the  $K_{\text{ex}}$  form but also from the  $K_{\text{dex}}$  form, the amounts varying considerably between soils as well as between plant species (Lee and Metson, 1977; Memon *et al.*, 1988). Moreover, all the chemical methods measure more or less similar amounts of soil  $K_{\text{ex}}$  but varying amounts of  $K_{\text{dex}}$ . The varying amounts of measured  $K_{\text{dex}}$  are due to varying strengths of the acid, acid to soil ratios, and boiling times used to assess  $K_{\text{dex}}$  release.

A great deal of effort has been expended in searching for the method of evaluating K releasing power that most closely approaches K uptake by plants. A linear relationship between K uptake (y-axis) against any method of measuring K releasing power (x-axis) that gives the smallest y-intercept value, and a slope near unity signifying the quantities of K removed, and is more nearly equivalent to K uptake (crop removal) would be best suited to predicting the K supplying power (Garman, 1957). Thus far no one method meets these criteria. The next best way to evaluate the credibility of the methods that measure K release for determining K supplying power is based on the correlation coefficient ( $r$ ) or percent prediction ( $R^2$ ) between K release and K supply. If the correlation is high for a particular method of assessing K release it might be expected that the method predicts the trend in the K supplying power of soils but its use should be limited to that range of validity for which it has been adequately tested. In situations where several methods proved to be equally satisfactory, Oertli (1990) suggested that the most efficient one should be chosen.

The neutral molar  $\text{NH}_4\text{OAc}$  method of assessing K release is widely used as an index of K release for predicting the K supply of soils. It is, however, more successful for soils where  $K_{\text{dex}}$  release is insignificant i.e., where  $K_{\text{ex}}$  is the major source of K available to plants (e.g., volcanic ash soils). For example, in soils dominated by kaolinitic, smectitic, or amorphous minerals any method of measuring  $K_{\text{ex}}$  releasing power (including the  $\text{NH}_4\text{OAc}$  method) may well reflect the K supplying power (Sharpley, 1989). This is because such soils contain very little K in the  $K_{\text{dex}}$  form compared to micaceous soils which contain copious amounts of K in the  $K_{\text{dex}}$  form. Since the ability of the plants to take up K from these forms (i.e.,  $K_{\text{dex}}$  supplying



power) is well documented (section 2.7.1), methods which assess  $K_{ex}$  release frequently fail to predict the K supplying power in these types of soils.

The so-called "non-micaceous soils" (e.g., kaolinitic soils) frequently contain either small amounts of K selective material (e.g., illite or interstratified minerals) in the clay fraction (Poss *et al.*, 1991) or varying amounts of K bearing minerals in the coarser fractions thus contributing to  $K_{dex}$  supply which may be insignificant compared to  $K_{ex}$  supply.

Thus in soils with either micaceous or non-micaceous minerals, a chemical method that measures  $K_{ex}$  plus  $K_{dex}$  forms, or methods that individually assess  $K_{ex}$  and  $K_{dex}$  releasing powers might better predict the K supplying power of soils than the methods of  $K_{ex}$  release alone.

The  $NH_4OAc$  method of  $K_{ex}$  determination has been found to be a poor indicator of the K supplying power for many New Zealand soils because a significant proportion of K extracted by pasture plants and crops is derived from  $K_{dex}$  sources (Haylock, 1956b; Williams *et al.*, 1986; Jackson, 1985). Thus the pot trial data of Campkin (1972), Hay *et al.* (1976), and Jackson (1985) indicated that the methods of K release that measure both  $K_{ex}$  plus  $K_{dex}$  forms better predict the K supply than the  $NH_4OAc$  method alone.

The methods available for  $K_{dex}$  determination (step K,  $K_c$ , or the resin K method) appear to adequately predict the  $K_{dex}$  supplying power of New Zealand soils according to Campkin (1972), and Hay *et al.* (1976). This evidence was based on pot trial studies using soils of several genetic groups which varied widely in  $K_c$  with ryegrass as the test plant. Lee and Gibson (1974), however, reported that the step K method is superior to  $K_c$  and resin K methods for the prediction of K uptake by ryegrass in separate pot trial study. Furthermore, the  $K_c$  test has been shown to be poorly correlated with plant uptake of soil K (Jackson, 1985).

Since the  $K_c$  method was designed principally as a tool to understand and interpret the weatherability and the clay mineral suites of soil groups it may not be justifiable to use

this method as an index of short or medium term  $K_{\text{dex}}$  supplying power.

From the above discussion it is possible that the chemical methods of assessing  $K_{\text{ex}}$  release (e.g.,  $\text{NH}_4\text{OAc}$ ), short term  $K_{\text{dex}}$  release (step K), and long term  $K_{\text{dex}}$  release ( $K_c$ ) may give a first approximation of immediate, short to medium term, and long term K supplying power, respectively.

## 2.8 CONCEPTS FOR MAKING K FERTILIZER RECOMMENDATIONS

From the previous sections (sections 2.6 and 2.7) it is evident that the methods of evaluating K release aim to better predict the K supplying power (K uptake) of New Zealand soils. Any method that gives a satisfactory prediction therefore has potential as a soil test (an index of soil K supply) for making K fertilizer recommendations. Hence, when referring to fertilizer strategies in this section, K release and K supply are one and the same.

Soil testing procedures should be calibrated against plant growth trials using different rates of K to assess the extent of K responsiveness. Soil testing, however, is not the only essential consideration in estimating nutrient requirements for maximum yields of crops or pastures.

The methods for making K fertilizer recommendations make use of either (a) soil K gains to the system (a component of K input that can be quantified by release/supply), (b) soil K loss from the system (output), (c) both of these, or (d) neither of these. The major K losses (crop or animal product removal, leaching, and fixation) and K gains (soil K supply either by added K fertilizers or by release of K from K reserves) have been dealt with in detail by Campkin (1985), Williams (1988), Williams *et al.* (1990), and Spiess and Besson (1992).

### **2.8.1 Method that does not directly quantify either soil K gains (release/supply) or soil K losses**

This method was the basis of K fertilizer requirements in New Zealand before the introduction of the existing method (sections 2.8.4 and 2.9) and is based on the responsiveness of pasture yield to fertilizer K in field trials for a specific soil. A typical response curve is presented in Fig. 2.4 where dry matter yields at varying rates of K fertilizer are compared with a control where no K is applied and relative yield (a measure of responsiveness) obtained. The rate of K fertilizer corresponding to 90 % maximum yield in the curve is taken as the amount of K fertilizer to be added to attain that level of production. Hence it may be called a "yield maintenance model".

Using this method varying levels of K fertilizer rates have been recommended for various New Zealand soil types in the past. For example, O'Connor *et al.* (1973) and Scott (1977) found no necessity for K fertilizer to achieve 90 % maximum pasture yields in the trials studied. In contrast 50-100 kg K ha<sup>-1</sup> was required to attain 90 % maximum yield (Smith *et al.*, 1978; Weeda, 1979; Morton, 1981; O'Connor and Feyter, 1980) in the pastures they studied.

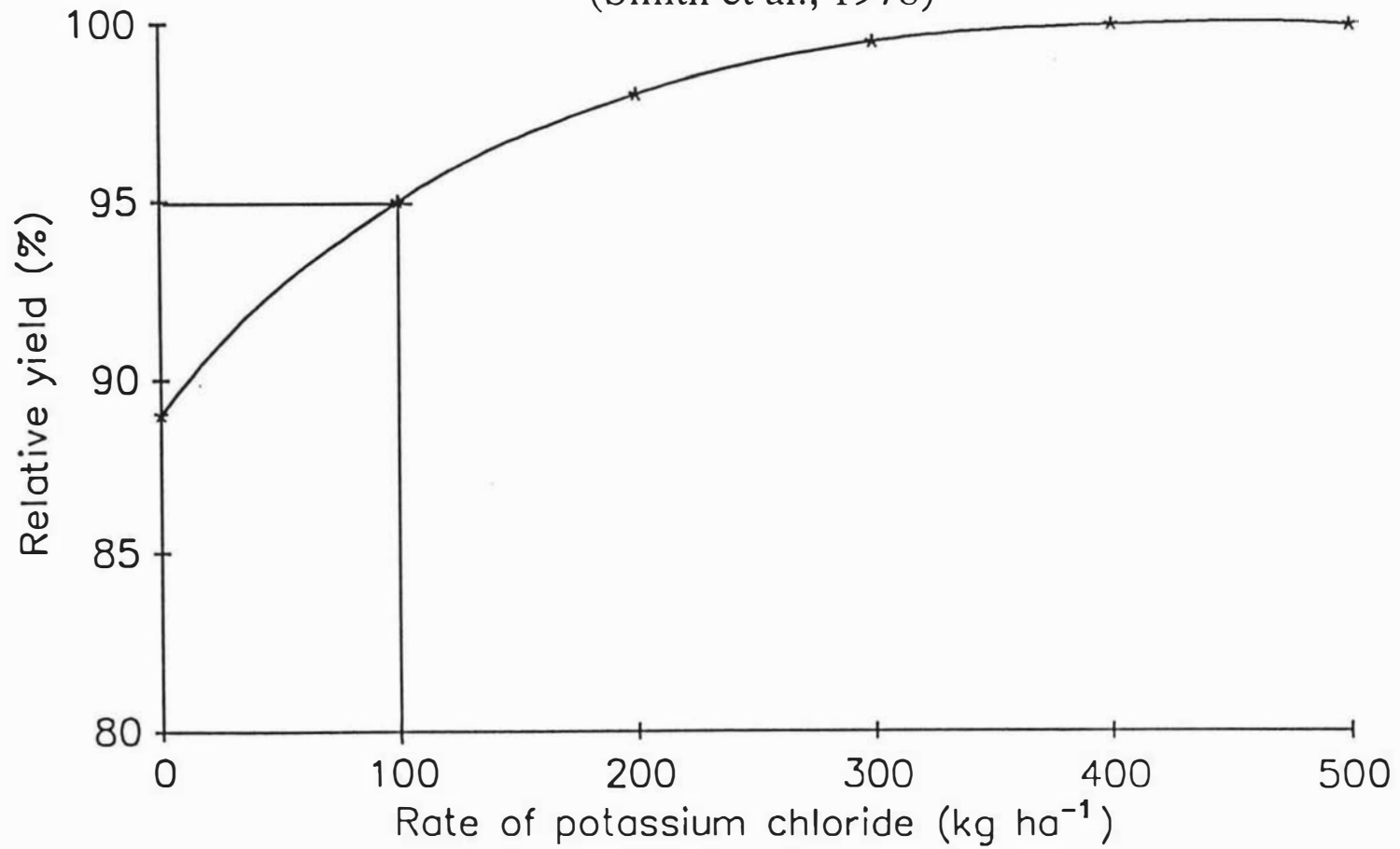
A major disadvantage of this method is that a separate response curve must be established for each soil type and farming system and over a period of years. Moreover, this method does not directly accommodate either the soil K supply (gains) or the soil K losses. As a result, changes in the soil K levels (release) could not be monitored and consequently the response curve could become less and less valid in subsequent years.

### **2.8.2 Method that directly quantifies only the soil K gains (release/supply)**

This method of making K fertilizer recommendations make use of soil K gains in terms of K released by soil and hence may be referred to as the "soil K supply model".

A typical example is that of McLean *et al.* (1982) and McLean and Watson (1985)

Fig. 2.4 Dry matter response to K fertiliser  
(Smith et al., 1978)



which is based on the sufficiency (desirable) level ( $K_{SL}$ ) and existing level ( $K_{EL}$ ) of soil nutrient (Fig. 2.5). A sufficiency level is the amount of K in soil (usually measured as  $K_{cx}$ ) that is required for production of 100 % maximum possible yield. This is obtained from a response curve similar to Fig. 2.4, with the exception that the ordinate on the x-axis is a measure of K supply to the system (measured by  $K_{cx}$  releasing power). Moreover, unlike the previous method (section 2.8.1) the response curve in this method was established for a wide range of soils (with varying K levels) and can be valid for a number of years.

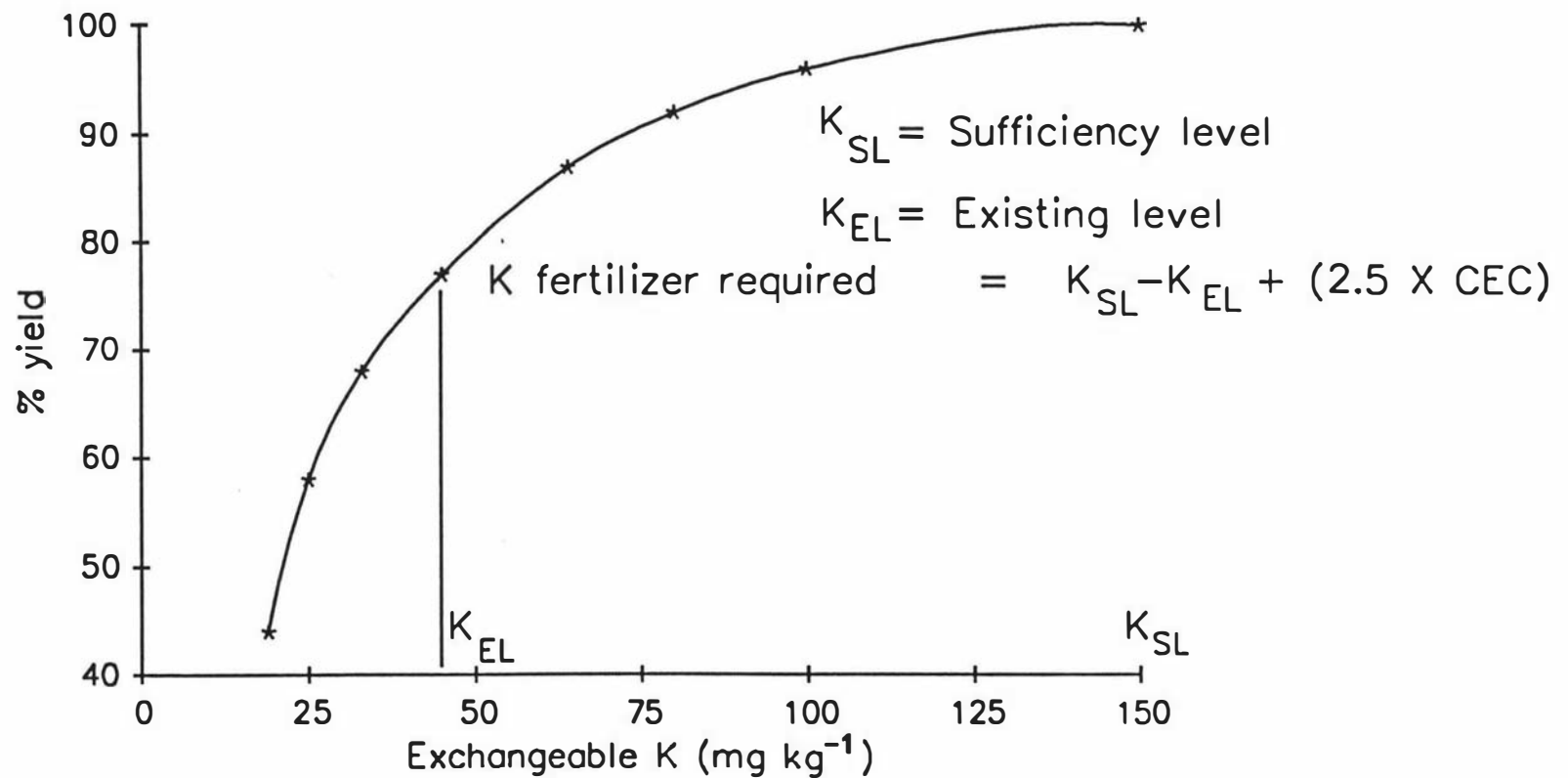
Yet another example of the methods that make use of soil K gains is the "K number calculation method" that is being used in the Netherlands (Novozamsky and Houba, 1987). This method involves measuring  $K_{cx}$  plus  $K_{nex}$  release (using 0.1 M HCl), and using different empirical formulae to calculate the K number. Fertilizer K requirements are calculated for different soil types and farming systems.

The above examples of estimating K fertilizer requirements also necessitate additional measurements and modifying factors such as CEC, organic matter, pH, fixation factors, correction factors thus indicating the importance of factors other than soil testing methods for accurately estimating soil K gains. For example, McLean's method adjusts the fertilizer K recommendation by taking into account the CEC and fixation factors specific to various groups of soils (McLean *et al.*, 1982; McLean and Watson, 1985).

### **2.8.3 Method that directly quantifies only the K losses**

This method does not take account of the soil K gains for estimating K fertilizer requirements, but only the K losses from the system. Thus a quantity of K is added to replace the amount lost (by crop removal, leaching loss, fixation, loss from animal products, etc.). Commercial laboratories in the US use this approach in conjunction with soil information (cation ratios) to estimate K fertilizer requirements (Olson *et al.*, 1982). It may also be referred to as the "sustainable model" or "soil K maintenance model" or "non-depletive model" or even "K loss model" because the soil K gains (K release) are not calculated to offset the K losses, thus enabling maintenance of the soil

Fig. 2.5 Schematics of computation of fertilizer K to reach near-maximum yields on individual soils (McLean and Watson, 1985)



K levels in the system.

The major disadvantage of this method is that it does not take into account economics. Where the K supplying power of soils is adequate for near maximum yields (Olson *et al.*, 1982), unnecessary expenditure on high K reserve soils will be incurred. Olson *et al.* (1982), pointed out that a system is said to be truly sustainable only if it is non-depletive and therefore this approach has merit.

#### 2.8.4 Method that directly quantifies both soil K supply (gains) and soil K losses

This method makes use of a balance sheet of the inputs and outputs of the K cycle in a farming system. The difference between the two is used as an estimate of K fertilizer requirement for that particular system (Adams and McAllister, 1975; Middleton and Smith, 1978; Campkin, 1985; Villemin, 1987). For example, fertilizer advice in France (Villemin, 1987) takes into account the K losses (crop removal, leaching, and fixation) and K gains (difference between the existing determined level and the established sufficiency level).

Theoretically this appears to be the best method available for making K fertilizer recommendations from a planning point of view because it considers both K gains and K losses from the system - hence the name "mass balance model". The success of the method, however, depends on the efficacy of the methods of evaluating soil K release (soil testing methods) as a means for predicting the K supplying power (to quantify K gain), and on the efficacy of predicting K losses from the system.

Since the soil K supply is used to offset the K losses, this model overall is also depletive in nature, ultimately tending to deplete soil K reserves. It is not as depletive as the "soil K supply model" (section 2.8.2) since it takes into account the soil K losses. On the other hand it is not as sustainable (non-depletive) as the "K loss model" (section 2.8.3) since it considers the soil K supply as well and is therefore depletive.

Campkin (1985) developed this concept to calculate maintenance K requirements for grazed pastures in New Zealand. A slightly modified version of the Campkin model is currently being used in New Zealand by AgResearch as the Computerized Fertilizer Advisory Services (CFAS) for K fertilizer recommendations (Cornforth and Sinclair, 1984). The following section reviews this method of recommending K fertilizers for New Zealand pastures.

## 2.9 THE CFAS MODEL FOR CALCULATING K FERTILIZER REQUIREMENTS

Basically the model assumes that the flow of potassium through the plant available pool is steady state and plant/animal K requirements can be sustained if K losses from the system are replenished (Campkin, 1985). The fertilizer K requirement is the difference between losses of K (leaching and harvested produce) and gains of K to the cycling pool from the weathering of soil minerals. The inputs of K (K gains) from rainfall and irrigation water are considered negligible.

A detailed explanation of the mass balance model and the derivation of the equation is provided by Campkin (1985). The original equation developed by Campkin is:

$$\text{K fertilizer requirement (kg ha}^{-1} \text{ yr}^{-1}) = \text{K losses} - \text{soil K supply (K gains)}$$

$$\text{K losses} = [\text{SR} \times \text{ALF}] + [(\text{R} + \text{I} - \text{PE}) \times (\text{LF})]$$

$$\text{Soil K supply} = 10 (\text{QTK} - 3) + 100 (\text{K}_c)$$

where	SR	=	Stocking rate (stock unit ha <sup>-1</sup> )
	ALF	=	Animal K loss factor (kg K stock unit <sup>-1</sup> ) which includes K lost in meat/milk and K lost through transfer of excreta to unproductive areas
	R	=	Rainfall (mm)
	I	=	Irrigation (mm)
	PE	=	Potential evapotranspiration



- LF = Leaching factor (SR divided by 1250)
- 1250 = Drainage water K concentration and includes conversion from ppm to kg K ha<sup>-1</sup>
- QTK = Exchangeable K as measured as quick test K (QTK). This K is extracted by shaking for two minutes with 1 M ammonium acetate at a soil:solution ratio of 1:4 (Mountier *et al.*, 1966), expressed as parts per 250,000 of extracting solution.
- K<sub>c</sub> = K extracted by boiling with 1 M HNO<sub>3</sub> for 10 min at a soil:solution ratio of 1:12.5, expressed as meq % (Metson *et al.*, 1956; Blakemore *et al.*, 1987).

The animal and leaching losses of K in the mass balance equation have been dealt with in depth and tested under different situations by Williams (1988) and Williams *et al.* (1990). The accuracy of the K losses predicted by the model was appraised and refinements for the "K loss" component of the model have been suggested by Williams *et al.* (1990). It was concluded that the CFAS model tends to underestimate the K losses from the grazed dairy pastures via leaching by not allowing for the loss that occurs during preferential flow of urine through the soil profile (Williams *et al.*, 1990) and overestimates the losses of K through transfer to unproductive areas (Williams and Roberts, 1988; Williams *et al.*, 1990).

The K gains in the model are estimated empirically from the immediate (exchangeable K as measured by the quick test K (QTK), and long term (reserve K pool as measured by K<sub>c</sub>) K supplying capacity of the soil. Despite the widespread use of this model no information has been published on the accuracy of the predicted K gains to the system. The main reason for this is the scarcity of suitable information about K responsiveness in grazed pastures against which the soil K supply component of the model (K gains) can be validated. There is evidence, however, that the model underestimates the soil K supply in soils showing low QTK values but which contain medium or high amounts of K reserves (Williams *et al.*, 1986; Williams *et al.*, 1990). In these types of soils the release of K from non-exchangeable sources in the soil is often sufficient to meet the

K losses. Despite this the CFAS model predicts that K is required by these soils. In this situation a measure of  $K_{\text{ex}}$  release that will become plant available in the short term might be useful. The NaTPB test is currently used in the CFAS model on Recent soils to predict soil K supply (Cornforth and Sinclair, 1984).

Furthermore, the soil K supply parameter  $[10 \times (\text{QTK} - 3) + 100 \times K_c]$  lacks precision because of the problems associated with the accurate measurement of QTK and  $K_c$ . Variability in QTK values can have large effect on the K fertilizer requirement (White and Gregg, 1991). For a site with a true QTK value of 5, the range of measured QTK values was between 3 and 7. The fertilizer requirement for this site varied from 26-66 kg K ha<sup>-1</sup> and to be completely sure that sufficient K is applied, 66 kg K ha<sup>-1</sup> should be the requirement.

The reserve K ( $K_c$ ) is determined by sequential HNO<sub>3</sub> extraction (Blakemore *et al.*, 1987) and its magnitude and variability largely reflect the mineralogy of the soil. The CFAS model attempts to reduce this difficulty by using a range of values within low, medium or high  $K_c$  categories determined for different soil groups by HNO<sub>3</sub> extraction of undeveloped soils.

Thus all New Zealand genetic soil groups are categorised as having either low (0.1 meq %), medium (0.3 meq %), or high (0.7 meq %)  $K_c$  values (Campkin, 1985) despite mineralogical variability and variable development of the soils under pastoral farming. Therefore, for a specific soil type in a soil group, the assigned  $K_c$ , may be quite different to the actual  $K_c$ . For example, while the measured  $K_c$  values for 5 soils belonging to the YGE group in the South Island ranged from 0.30 to 0.76 meq % (Jackson, 1985), the assigned  $K_c$  for the soil group is 0.7 meq % (Campkin, 1985). Similarly, while the assigned  $K_c$  of the yellow-brown earth (YBE) soil group is 0.30 meq %, the measured  $K_c$  values of some soils in this group (Jackson, 1985) ranged from 0.17 to 0.76 meq %. Other examples of this variability are not uncommon in the New Zealand literature (Campkin, 1972; Lee and Gibson, 1974; Hay *et al.*, 1976; Jackson and During, 1979).

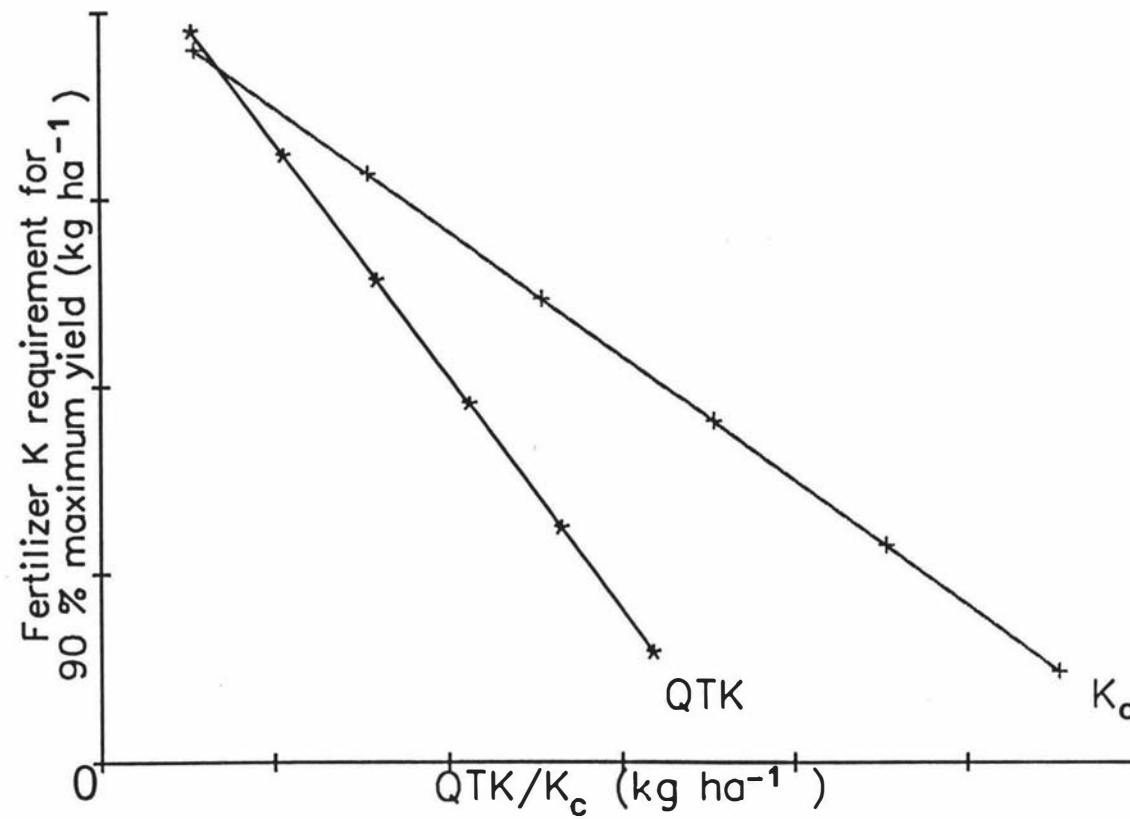
It is uncertain whether  $K_c$  values remain essentially constant despite declining K supply after several years of intensive agriculture, as no studies have been reported. Short term studies (less than 15 months) provided evidence to demonstrate that  $K_c$  values did not change as a result of cropping the soils with ryegrass (Haylock, 1956a; Lee and Gibson, 1974).

The soil K supply parameter of the mass balance equation includes two constants. The constant value 10 is 75 % of the approximate factor (13.6) used to convert QTK values to  $\text{kg K ha}^{-1}$ , and the constant value of 100 is approximately 40 % of the conversion factor (265) used to convert  $K_c$  ( $\text{HNO}_3$ -extractable K) from  $\text{meq \%}$  to  $\text{kg K ha}^{-1}$  assuming a bulk density of  $0.91 \text{ Mg m}^{-3}$  (Campkin, 1985). Thus 75 % of QTK above a value of 3 and 40 % of  $K_c$  (0.10, 0.30, or 0.70  $\text{meq \%}$ ) are used in the equation.

These percentages (constants) viz, 75 % and 40 % represent pasture utilisation efficiency of K from QTK and  $K_c$ , respectively, and were supposedly (Campkin, 1985) derived from the first year results of a series of "rate of K trials" conducted throughout New Zealand (Campkin, 1983) on 38 sites representing a wide range of soil groups. Unfortunately Campkin (1983) did not present detailed information on the percent utilisation of K by plants from either QTK or  $K_c$  and no subsequent evidence is presented in the literature. It appeared, however, that the following two step procedure might have been adopted by Campkin (1983) to arrive at the above percentages.

1. Responses in pasture yield (measured as relative yield) to increasing rates of fertilizer K were fitted to Mitscherlich growth curves for 38 sites i.e., response curves similar to Fig. 2.4 were obtained for 38 sites. Fertilizer K required to achieve 90 % maximum yield for all the 38 sites were thus obtained from these curves.
2. The values of the fertilizer K required ( $\text{kg ha}^{-1}$ ) to achieve 90 % maximum yield for all the sites were plotted against their respective  $K_c$  and QTK values ( $\text{kg ha}^{-1}$ ) and inverse linear relationships similar to Fig. 2.6 were obtained. The slopes of the regression line for QTK and  $K_c$  (-0.75 and -0.40, respectively) give the

Fig. 2.6 Theoretical relationship between fertilizer K required for 90 % maximum yields and both QTK and  $K_c$  values



equivalent reductions in the amount of K required to maintain the 90 % maximum yields per unit increase in QTK and  $K_c$  values.

The constraints on the K supply parameter of the mass balance equation are thus three-fold.

1. Soil QTK values have a high degree of variability (coefficient of variation is commonly 30 % or more (Edmeades et al., 1985) due mainly to the spatial variability of exchangeable K levels in pasture soils. A recent urine spot may have a QTK value greater than 22 in a paddock where the average QTK is 4 (M.J. Hedley, pers. comm.). Thus one-urine affected soil core in a bulked sample of 10 cores will raise the QTK by 1.6 units. A 1, 2, or 4 unit change in the QTK value changes the fertilizer recommendation by 10, 20, or 40 kg ha<sup>1</sup>.
2. The use of three values (low 0.1, medium 0.3, or high 0.7 meq %) for all New Zealand soils, while permitting simplification of the model, nevertheless may be well-removed from actual  $K_c$  values for a particular situation. A difference in  $K_c$  of 0.1 meq %, which equates to a change in predicted annual K supply of 10 kg K ha<sup>-1</sup>, is not uncommon.
3. The two constants (10 and 100) in the mass balance equation were derived using the results of only one year of field trials. Therefore the validity of these constants for all soils and for all pasture and cropping systems in New Zealand has yet to be confirmed in the published literature.

## CHAPTER 3

### GENERAL MATERIALS AND METHODS

#### 3.1 INTRODUCTION

In this chapter the materials and methods common to Chapters 4 to 9 are described. Methodology specific to each chapter is described in that chapter.

#### 3.2 SOILS

Nineteen soils were chosen to represent a range of yellow-grey earth and related soils from developed pasture and virgin (undeveloped) sites in the North Island and the South Island. These soils (Table 3.1) were sampled to a depth of 75 mm, air dried, and sieved (< 2 mm).

Detailed descriptions of these soils have been presented by New Zealand Soil Bureau (1968), Pollok (1975), Rijkse (1977), Cowie (1978), Campbell (1979), Bruce (1984), and A.S. Palmer (pers. comm.). A brief description of the soils chosen, together with the location of the sampling sites follows. Soils that are not YGE are noted (Table 3.1).

#### S1 Tokorangi sandy loam

Top soil (0-240 mm)	:	Dark greyish brown fine sandy loam; nut and crumb structure
Location of sampling	:	Porewa Road, road side cutting, Grid reference NZMS 260; R23, S23; 274213
Drainage	:	Moderately well drained
Site vegetation	:	Undeveloped pasture site
Mean annual rainfall	:	1000 mm
Parent material	:	Wind-blown sand
Sampling date	:	20-12-89

**Table 3.1 USDA, New Zealand Genetic (NZ genetic), and new New Zealand (New NZ) classification of soils used for the study**

Soil No.	Soil series	Region	Classification		
			USDA	NZ Genetic	New NZ
S1	Tokorangi	Rangitikei	Aquic Dystric Eutrochrept *	Central YGE	Typic perch-gley Pallic**
S2 & S3	Tokomaru	Manawatu	Typic Fragiaqualf	Central YGE	Argillic fragic perch-gley Pallic
S4	Milson	Manawatu	Typic Fragiaqualf	Central YGE	Argillic fragic perch-gley Pallic
S5 & S6	Marton	Rangitikei	Aeric Ochraqualf	Central YGE	Argillic perch-gley Pallic
S7	Halcombe	Manawatu	Aeric Haplaquept or Aquic Dystric Eutrochrept*	Central YGE	Mottled argillic Pallic
S8	Ohakea	Manawatu	Typic Ochraqualf	Central YGE	Typic perch-gley Pallic
S9	Raumi	Pohangina	Aquic Ustochrept*	Central YGE-YBE intergrade	Mottled sandy Brown Soil**
S10	Te Arakura	Manawatu	Aeric Haplaquept	Gley soil***	Typic orthic Gley
S11	Matapiro	Hawke's Bay	Typic Durustalf	Central YGE	Mottled duric Pallic
S12	Wharekaka	Wairarapa	Typic Fragiaqualf	Central YGE	Argillic fragic perch-gley Pallic
S13	Pirinoa	Wairarapa	Aeric Ochraqualf*	Central YGE-YBE intergrade	Argillic perch-gley Pallic or Typic perch-gley Pallic
S14 & S15	Timaru	South Canterbury	Ustic Fragiochrept	Southern YGE	Mottled fragic Pallic
S16 & S17	Claremont	South Canterbury	Aquic Fragiochrept	Southern YGE	Mottled fragic Pallic
S18 & S19	Opuha	South Canterbury	Aeric Fragiaquept	Southern YGE	Fragic perch-gley Pallic

\* Insufficient chemical data therefore USDA classification is uncertain

\*\* Insufficient chemical and physical data therefore new New Zealand classification is uncertain

\*\*\* Transition between gley recent soil and gleyed YGE

**S2 Tokomaru silt loam**

Top soil (0-210 mm)	:	Dark greyish brown silt loam; weakly to moderately developed nut structure; some fine brown mottles
Location of sampling	:	Clifton Terrace, Massey University, Grid reference NZMS 260; T24; 329883
Drainage	:	Poor
Site vegetation	:	Undeveloped pasture site
Mean annual rainfall	:	1020 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	7-11-89

**S3 Tokomaru silt loam**

Top soil (0-210 mm)	:	Dark greyish brown silt loam; weakly to moderately developed nut structure; some fine brown mottles
Location of sampling	:	Paddock No. 5, No. 4 dairy farm, Massey University, Grid reference NZMS 260; T24; 317828
Drainage	:	Poor
Site vegetation	:	Developed pasture site
Mean annual rainfall	:	1020 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	8-11-89

**S4 Milson silt loam**

Top soil (0-150 mm)	:	Dark greyish brown silt loam.
Location of sampling	:	Richardson's Line, road side cutting, Grid reference NZMS 260; T24; 364956
Drainage	:	Poorly to imperfectly drained
Site vegetation	:	Undeveloped pasture site
Mean annual rainfall	:	950 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	8-11-89



<b>S5</b>	<b>Marton silt loam</b>	
	Top soil (0-240 mm)	: Very dark grey silt loam; some hard concretions; nut and crumb structure.
	Location of sampling	: Kelvin Grove Road, road side cutting, Grid reference NZMS 260; T24; 364956
	Drainage	: Poorly to imperfectly drained
	Site vegetation	: Undeveloped pasture site
	Mean annual rainfall	: 1020 mm
	Parent material	: Quartzo-feldspathic loess
	Sampling date	: 8-11-89
<b>S6</b>	<b>Marton silt loam</b>	
	Top soil (0-240 mm)	: Very dark grey silt loam; some hard concretions; nut and crumb structure.
	Location of sampling	: Tony Heywood's property, Grid reference NZMS 260; R23, S23; 154187
	Drainage	: Poorly to imperfectly drained
	Site vegetation	: Cropped with malting barley (summer) and ryegrass (winter)
	Mean annual rainfall	: 1020 mm
	Parent material	: Quartzo-feldspathic loess
	Sampling date	: November 1989
<b>S7</b>	<b>Halcombe silt loam</b>	
	Top soil (0-170 mm)	: Very dark grey silt loam; nut and crumb structure
	Location of sampling	: Tuapaka Beef Unit, Grid reference NZMS 260; T24; 422929
	Drainage	: Poorly to imperfectly drained
	Site vegetation	: Developed pasture site
	Mean annual rainfall	: 1000 mm
	Parent material	: Quartzo-feldspathic loess and colluvium
	Sampling date	: 7-11-89
<b>S8</b>	<b>Ohakea silt loam</b>	
	Top soil (0-320 mm)	: Very dark grey silt loam; fine nut and blocky structure; few concretions
	Location of sampling	: Massey University, Grid reference

	Drainage	:	NZMS 260; T24; 324873
	Site vegetation	:	Poorly to imperfectly drained
	Mean annual rainfall	:	<b>Developed pasture site</b>
	Parent material	:	1000 mm
	Sampling date	:	Quartzo-feldspathic colluvium
		:	7-11-89
<b>S9</b>	<b>Raumai hill soil</b>		
	Top soil (0-150 mm)	:	Dark greyish brown sandy loam; friable; moderately developed fine and medium nut structure
	Location of sampling	:	Zig Zag Road, road side cutting, Grid reference NZMS 260; T23; 084447
	Drainage	:	Moderately well and well drained
	Site vegetation	:	<b>Undeveloped pasture site</b>
	Mean annual rainfall	:	1070 mm
	Parent material	:	Loose sandstone and greywacke gravels
	Sampling date	:	20-12-89
<b>S10</b>	<b>Te Arakura silt loam</b>		
	Top soil (0-200 mm)	:	Very dark grey brown silt loam; nut and crumb structure
	Location of sampling	:	Grid reference NZMS 260; S23; 157077
	Drainage	:	Imperfectly to poorly drained
	Site vegetation	:	<b>Cropped with barley</b>
	Mean annual rainfall	:	920 mm
	Parent material	:	Quartzo-feldspathic alluvium
	Sampling date	:	1-11-89
<b>S11</b>	<b>Matapiro silt loam</b>		
	Top soil (0-180 mm)	:	Very dark greyish brown friable silt loam; fine granular to nutty structure
	Location of sampling	:	Grid reference NZMS 260; U23; 083247
	Drainage	:	Poor
	Site vegetation	:	<b>Developed pasture site</b>
	Mean annual rainfall	:	800 mm
	Parent material	:	Quartzo-feldspathic loess and tephra
	Sampling date	:	November 1989

**S12 Wharekaka silt loam**

Top soil (0-150 mm)	:	Greyish brown silt loam when dry and very dark greyish brown when wet
Location of sampling	:	Type section, road side cutting between Greytown and Martinborough, Grid reference NZMS 260; S27; 162038
Drainage	:	Poor
Site vegetation	:	Developed pasture site
Mean annual rainfall	:	800 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	10-1-90

**S13 Pirinoa silt loam**

Top soil (0-180 mm)	:	Dark greyish brown friable silt loam.
Location of sampling	:	Road side cutting, Grid reference NZMS 260; S27;
Drainage	:	Imperfect
Site vegetation	:	Undeveloped pasture site
Mean annual rainfall	:	1100 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	10-1-90

**S14 Timaru silt loam**

Top soil (0-210 mm)	:	Very dark greyish brown silt loam; friable; moderately developed medium and fine nutty structure
Location of sampling	:	Grid reference NZMS 260; J39; 485635
Drainage	:	Poor
Site vegetation	:	Undeveloped virgin (forest)
Mean annual rainfall	:	615 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	November 1989

**S15 Timaru silt loam**

Top soil (0-210 mm)	:	Very dark greyish brown silt loam; friable; moderately developed
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Location of sampling	:	medium and fine nutty structure Grid reference NZMS 260; J39; 485635
Drainage	:	Poor
Site vegetation	:	<b>Developed pasture</b>
Mean annual rainfall	:	615 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	November 1989

#### **S16 Claremont silt loam**

Top soil (0-150 mm)	:	Dark greyish brown silt loam; friable; moderately developed crumb structure
Location of sampling	:	Grid reference NZMS 260; J38; 782665
Drainage	:	Poor
Site vegetation	:	<b>Undeveloped virgin (forest)</b>
Mean annual rainfall	:	835 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	November 1989

#### **S17 Claremont silt loam**

Top soil (0-150 mm)	:	Dark greyish brown silt loam; friable; moderately developed crumb structure
Location of sampling	:	Grid reference NZMS 260; J38; 782665
Drainage	:	Poor
Site vegetation	:	<b>Developed pasture</b>
Mean annual rainfall	:	835 mm
Parent material	:	Quartzo-feldspathic loess
Sampling date	:	November 1989

#### **S18 Opuha silt loam**

Top soil (0-250 mm)	:	Very dark greyish brown silt loam; firm; moderately developed cast granular and nutty structure
Location of sampling	:	Grid reference NZMS 260; J37; 825655
Drainage	:	Poor
Site vegetation	:	<b>Undeveloped virgin (forest)</b>
Mean annual rainfall	:	1125 mm
Parent material	:	Quartzo-feldspathic loess

Sampling date : November 1989

### **S19 Opuha silt loam**

Top soil (0-250 mm) : Very dark greyish brown silt loam; firm; moderately developed cast granular and nutty structure

Location of sampling : Grid reference NZMS260; J37; 825655

Drainage : Poor

Site vegetation : **Developed pasture**

Mean annual rainfall : 1125 mm

Parent material : Quartzo-feldspathic loess

Sampling date : November 1989

### **3.3 SOIL PROPERTIES**

Mechanical analyses and subsequent separation of soil separates (sand, silt, and clay) were performed by the sedimentation method of Jackson (1956) after peroxidation of the soils. Calgon was used as the dispersing agent. The results of particle size analysis are given in Table 3.2.

Soil pH values were measured in water (1:2.5 soil:water ratio), after equilibration for 16 h. Exchangeable cations were determined after leaching the soil with 1 M  $\text{NH}_4\text{OAc}$  at pH 7 (1:50 soil:solution ratio) in semi-microleaching tubes. Potassium (K) and sodium (Na) in the extract were measured using atomic emission spectrophotometry (AES), and calcium (Ca) and magnesium (Mg) by atomic absorption spectrophotometry (AAS). The organic carbon content of the soils was determined using a Leco Gravimetric Carbon Determinator (Tabatabai and Bremner, 1970). The results of these analyses are presented in Table 3.3.

Total K (Table 3.3) was determined after caustic soda (NaOH) fusion in a nickel crucible. 100 mg of soil were fused at red heat with 1.5 g of NaOH for 5 min, the melt taken up in deionised water and K determined by AES.

**Table 3.2 Particle size analyses of the soils**

Soil No.	Soil name	% Sand (63-2000 $\mu\text{m}$ )	% Silt (2-63 $\mu\text{m}$ )	% Clay ( $< 2 \mu\text{m}$ )
S1	Tokorangi	21.5	51.6	26.9
S2	Tokomaru (a)	9.7	66.4	24.0
S3	Tokomaru (b)	6.7	68.4	24.9
S4	Milson	8.8	66.7	24.5
S5	Marton (a)	9.0	67.6	23.4
S6	Marton (b)	16.4	57.5	26.1
S7	Halcombe	10.5	68.3	21.2
S8	Ohakea	9.5	64.0	26.5
S9	Raumai	67.2	23.8	9.0
S10	Te Arakura	27.2	49.8	22.5
S11	Matapiro	32.1	43.8	24.2
S12	Wharekaka	11.0	59.9	29.1
S13	Pirinoa	16.1	51.4	32.6
S14	Timaru (a)	5.5	73.5	21.0
S15	Timaru (b)	7.3	72.5	20.2
S16	Claremont (a)	8.6	68.8	22.6
S17	Claremont (b)	10.1	59.0	31.0
S18	Opuha (a)	18.0	37.8	44.2
S19	Opuha (b)	4.5	71.5	24.0

- (a) Undeveloped site  
(b) Developed site

Table 3.3 Some selected soil properties

Soil No.	Soil name	Total K (%)	pH	Organic carbon (%)	Exchangeable cations (mg 100 g soil <sup>-1</sup> )			
					K	Ca	Mg	Na
S1	Tokorangi	1.02	6.0	4.86	43.9	265.0	29.3	3.9
S2	Tokomaru (a)	0.97	5.6	5.58	25.7	92.8	26.2	7.8
S3	Tokomaru (b)	1.00	5.5	4.20	13.6	120.6	17.3	4.6
S4	Milson	1.01	5.3	4.19	55.4	130.8	23.4	5.8
S5	Marton (a)	1.31	5.7	3.63	9.7	64.4	16.3	9.0
S6	Marton (b)	1.00	5.8	3.06	8.9	195.8	15.5	7.4
S7	Halcombe	0.93	5.6	5.23	24.5	135.8	28.8	6.9
S8	Ohakea	1.08	5.6	4.45	21.4	151.2	22.0	5.8
S9	Raumai	1.49	5.3	1.14	6.4	40.4	28.8	2.8
S10	Te Arakura	1.00	6.1	4.68	8.2	291.8	19.2	3.9
S11	Matapiro	1.26	5.8	4.40	22.2	213.8	20.5	8.3
S12	Wharekaka	1.06	5.7	3.92	8.8	86.0	15.8	5.1
S13	Pirinoa	1.41	5.8	3.13	18.1	70.2	32.0	7.6
S14	Timaru (a)	1.13	6.2	4.59	71.3	222.8	20.4	4.6
S15	Timaru (b)	1.11	7.1	3.22	12.1	267.8	12.1	4.1
S16	Claremont (a)	1.05	4.5	4.51	34.4	81.6	11.5	5.8
S17	Claremont (b)	1.04	5.8	4.06	10.1	154.2	13.3	4.4
S18	Opuha (a)	1.15	5.3	5.54	31.7	194.8	34.8	3.7
S19	Opuha (b)	1.06	6.1	3.94	20.9	204.6	16.4	5.8

(a) Undeveloped site

(b) Developed site

## CHAPTER 4

# CHARACTERIZATION OF YGE SOILS BASED ON NON-EXCHANGEABLE K RELEASING AND SUPPLYING POWER

### 4.1 BACKGROUND

From Chapter 2 (sections 2.7.2.3 and 2.9) it is evident that  $K_c$  values have been used to categorise New Zealand soils into low, medium, and high  $K_{nex}$  supplying groups for two distinct reasons: (a) for field classification purposes (Metson, 1980) and (b) for K fertilizer recommendation purposes (Campkin, 1985). The numerical limits used to define the categories (low, medium, and high) are different for each purpose (Table 4.1).

It was also mentioned that all the yellow-grey earth (YGE) soils of the North Island are formed on more weathered parent materials. They are more strongly weathered than their southern counterparts, and are considered to have a medium reserve ( $K_{nex}$  release assessed by  $K_c$  method) of K (Table 4.2). YGE soils in the South Island, being less weathered, are considered to have high  $K_{nex}$  reserves. In the CFAS model, no consideration is given to any variation of  $K_{nex}$  release ( $K_c$ ) of the soils within each region. Any variation of  $K_{nex}$  release, apart from known differences between the YGE soils of North and South Island groups, would mean a variation in  $K_{nex}$  supply.

The  $K_{nex}$  supply can be measured by growing plants until  $K_{ex}$  is exhausted using any standard method of pot culture in conjunction with the method of assessing  $K_{ex}$  release. Alternatively it can be measured by growing plants in already  $K_{ex}$  depleted soils.

Any significant variation in  $K_{nex}$  supplying power within the soils of either the North or South Island regions would not only question the validity of the  $K_c$  method as a



**Table 4.1** Ranges of values used for  $K_{ex}$  and  $K_c$  to classify the K status of New Zealand soils for field classification (Metson, 1980) and fertilizer recommendation (Campkin, 1985) purposes

Classification (Ranking)	$K_{ex}$ (mg 100 g <sup>-1</sup> ) Metson (1980) and Blakemore <i>et al.</i> (1987)	$K_c$ (mg 100 g <sup>-1</sup> ) Metson (1980) and Blakemore <i>et al.</i> (1987)	$K_c$ (mg 100 g <sup>-1</sup> ) Campkin (1985)
Very High (VH)	> 46.8	> 19.5	-
High (H)	31.2 - 46.7	13.7 - 19.4	> 17.94 (Mean 27.3)
Medium (M)	19.5 - 31.1	7.8 - 13.6	8.19 - 17.55 (Mean 11.7)
Low (L)	11.7 - 19.4	3.9 - 7.7	< 8.19 (Mean 3.9)
Very Low (VL)	< 11.7	< 3.9	-

**Table 4.2**  $K_c$  values for the soils, and field classification (Metson, 1980) and classification for fertilizer recommendations (Campkin, 1985) based on the ranges given in Table 4.1

Soil No.	Soil name (see section 3.2)	AgResearch grouping*	Measured $K_c$ (mg $100\text{ g}^{-1}$ )	Classification using	
				Metson rating	Campkin rating
S1	Tokorangi	M	13.30	M	M
S2	Tokomaru (a)	M	8.89	M	M
S3	Tokomaru (b)	M	9.42	M	M
S4	Milson	M	7.88	M	L
S5	Marton (a)	M	7.84	M	L
S6	Marton (b)	M	8.18	M	L
S7	Halcombe	M	9.50	M	M
S8	Ohakea	M	10.11	M	M
S9	Raumai	M	17.33	H	M
S10	Te Arakura	M	15.65	H	M
S11	Matapiro	M	9.03	M	M
S12	Wharekaka	M	14.71	H	M
S13	Pirinoa	M	18.59	H	H
S14	Timaru (a)	H	16.79	H	M
S15	Timaru (b)	H	14.50	H	M
S16	Claremont (a)	H	13.30	M	M
S17	Claremont (b)	H	12.27	M	M
S18	Opuha (a)	H	17.50	H	M
S19	Opuha (b)	H	13.48	M	M

(a) Undeveloped site

(b) Developed site

\* Based on grouping of YGE and intergrade soils in the North Island as medium  $K_c$  soils and the South Island YGE soils as high  $K_c$  soils. S10 has some features associated with YGE soils and hence is considered a medium  $K_c$  soil

measure of  $K_{\text{nex}}$  release, but also its place in the CFAS model as a measure of  $K_{\text{nex}}$  supply. Since  $K_c$  values were obtained for the undeveloped sites (section 2.7.2.3) it would be curious if the  $K_{\text{nex}}$  supply varies markedly between developed and undeveloped sites on the same soil type.

Furthermore, the variations of  $K_c$  values within soils of each region, if any, will have implications to formulating K fertilizer recommendations, where currently a standard  $K_c$  value is used. This implies that K fertilizer requirements could either be under or over estimated for a particular soil. For example, a change in a  $K_c$  value of  $3.9 \text{ mg } 100 \text{ g}^{-1}$  is equivalent to a change in annual soil  $K_{\text{nex}}$  supply of  $10 \text{ kg ha}^{-1}$  (Campkin, 1985). This might lead to significant error in the CFAS model.

It should be noted, however, that  $K_c$  (measure of  $K_{\text{nex}}$  release) and plant  $K_{\text{nex}}$  uptake (measure of  $K_{\text{nex}}$  supply) are two different indices measuring soil  $K_{\text{nex}}$  (section 2.7).  $K_c$  is a chemical index, the estimation procedure, which ignores readily soluble  $K_{\text{ex}}$  and the more soluble portion of soil  $K_{\text{nex}}$ . Plant  $K_{\text{nex}}$  uptake is a biological index of soil  $K_{\text{nex}}$  that is obtained by subtracting the fall in soil  $K_{\text{ex}}$  level due to plant uptake.

The objectives of the study described in this chapter are:

1. To determine  $K_{\text{nex}}$  supplying power of a range of North and South Island YGE soils.
2. To relate  $K_{\text{nex}}$  supply with the  $K_c$  method of assessing  $K_{\text{nex}}$  release and evaluate  $K_c$  as a parameter in the CFAS model.
3. To evaluate K fertility status of a developed and an undeveloped site on the same soil type.

## 4.2 MATERIALS AND METHODS

### 4.2.1 Soils and chemical measurements

The soils used in this chapter were described in Chapter 3.

Exchangeable K was measured using the method described in Chapter 3.  $K_c$  was measured using the method of Blakemore *et al.* (1987).

#### 4.2.2 Artificial leaching technique

The objective of this treatment was to remove the soluble and exchangeable K from the soil samples and allow plants to use only K from the non-exchangeable pool. A 0.1 M calcium chloride solution was mixed with a 0.1 M magnesium chloride solution to obtain a Ca:Mg at an equivalent ratio of 4:1. The choice of this ratio of Ca and Mg was based on the approximate ratio of exchangeable Ca:Mg in these soils (Table 3.3). This solution was used to remove  $K_{ex}$  by leaching and the filtrate was discarded. The soil: solution ratio used was 1:25. The pH of the leaching solution was lowered to the mean pH of the soils (5.7) with 1 M HCl prior to leaching through the soils to prevent any major changes in original pH of soils. After leaching, the soils were washed free of excess chloride and air dried prior to the glass house experiment. Exchangeable K in the leached soils was measured on air dry samples to determine if the artificial leaching procedure had removed all of the native  $K_{ex}$ .

#### 4.2.3 Glasshouse experiment

The K supplying power of the unleached (UL) soils and the artificially leached (L) soils was determined in a pot experiment using a modified Stanford and DeMent (1957) procedure. This technique was designed to be highly exploitive for the nutrient under study. A 250 ml plastic container with the bottom removed was placed in a second intact plastic container and filled with 400 g of water-washed silica sand. Perennial ryegrass (*Lolium perenne* L; Grasslands "Nui") was used as a test crop and 30 seeds were sown and later thinned to 20 seedlings per pot. On the basis of preliminary work one mg K as KCl in solution was added initially to all the pots to assist germination. A K-free nutrient solution (modified Middleton and Toxopeaus, 1973) was then applied regularly and moisture was maintained at field capacity daily.

After 45 days, the roots of the ryegrass had grown throughout the sand medium and had formed a dense mat at the base of the pot. The plants were then cut to a level 20-30

mm above the sand surface. The inner pot (with roots) was then transferred into another intact pot containing 20 g of soil which had previously been moistened to field capacity. As a control treatment, the inner container was transferred onto 20 g of water-washed silica sand. The addition of K-free nutrient solution was continued until the completion of the experiment and the pots were watered daily with distilled water based on weight loss.

As well as the 19 unleached soils used in the study additional pots of 8 soils were duplicated and received complete (including K) nutrient solution for monitoring K deficiency symptoms in treated pots. The experiment thus involved two treatments viz, unleached (UL) and leached (L), with four replicates giving a total of 156 pots including the four control pots and an additional 32 (8x4) pots that received nutrient solution containing K. The pots were completely randomised and repositioned twice a week in the glasshouse to minimise any effects of uneven environmental factors, such as light, temperature and air movement. The plants were harvested four times. After each harvest, the plant material was dried at 60<sup>o</sup> C for 48 h, weighed, and analyzed for K by nitric acid digestion. After the final harvest, the soil was separated from the sand, and roots separated from the soil. The soils were air dried and analyzed for exchangeable K. The total K uptake of shoots from unleached and leached soils was obtained from the sum of the uptakes of the four individual harvests and expressed as mg K 100 g<sup>-1</sup> air dry soil.

Potassium taken up by plants from non-exchangeable sources ( $K_{\text{dex}}$ ) i.e., the  $K_{\text{dex}}$  supplying power was calculated as described in section 2.7.1.

$K_{\text{dex}}$  supply = Total K uptake -  $d K_{\text{ex}}$ , where

Total K uptake = Total amount of K removed by ryegrass from soils over the four harvests

$d K_{\text{ex}}$  = Change in  $K_{\text{ex}}$  releasing power ( $K_{\text{ex}}$  method using  $\text{NH}_4\text{OAc}$  as an extractant) of the soil over the experiment

i.e.,  $K_{ex}$  before cropping -  $K_{ex}$  after cropping

#### 4.2.4 Statistical analyses

Differences among the soils for each treatment were tested for significance using analysis of variance test (SAS, 1985).

### 4.3 RESULTS AND DISCUSSION

#### 4.3.1 Exchangeable K release before cropping in the unleached and in the leached soils

The 19 unleached soils can be grouped into low (9 soils), medium (5 soils) and high (5 soils) categories of  $K_{ex}$  release. This is based on the  $K_{ex}$  rating procedure of Metson (1980) given in Table 4.1. The  $K_{ex}$  of low K category soils ranged from 6.5 to 18.2 mg 100 g<sup>-1</sup>, for medium soils from 20.9 to 25.8, and for high soils from 31.7 to 71.4 (Fig. 4.1).

After leaching with 0.05 M chloride solution of Ca and Mg the commensurate  $K_{ex}$  levels were 3.0 to 9.9, 9.2 to 11.6, and 8.6 to 12.7 (Fig. 4.2). The average proportion of  $K_{ex}$  removed by leaching was 33 % (0 to 54 % range), 55 % (48 to 65 % range), and 75 % (68 to 82 % range), respectively. Thus those soils with highest initial  $K_{ex}$  levels lost the highest proportion of  $K_{ex}$  by leaching. All the leached soils therefore released  $K_{ex}$  to very low levels, despite the artificial leaching technique. The dynamics of the  $K_{neq} \leftrightarrow K_{ex}$  equilibrium are such that  $K_{ex}$  is always present.

#### 4.3.2 Dry matter yield

The dry matter yields of each harvest for each soil and treatment are given in Appendix 4.1.

#### 4.3.2.1 Total dry matter yields from unleached soils

The undeveloped Opuha (S18) and Timaru (S14) soils recorded significantly higher dry matter yields than all other soils and the lowest dry matter was recorded in Marton soils (S5 and S6).

There were large differences in total dry matter yields (average of four replicates) among unleached soils of different regions (Fig. 4.3). Raumai (S9) and Tokorangi (S1) recorded significantly higher dry matter than the remaining soils of the Manawatu and Rangitikei regions. The higher dry matter yield recorded by Milson was expected because of the initial high  $K_{ex}$  but that of Raumai (S9) was unexpected given the low  $K_{ex}$  content.

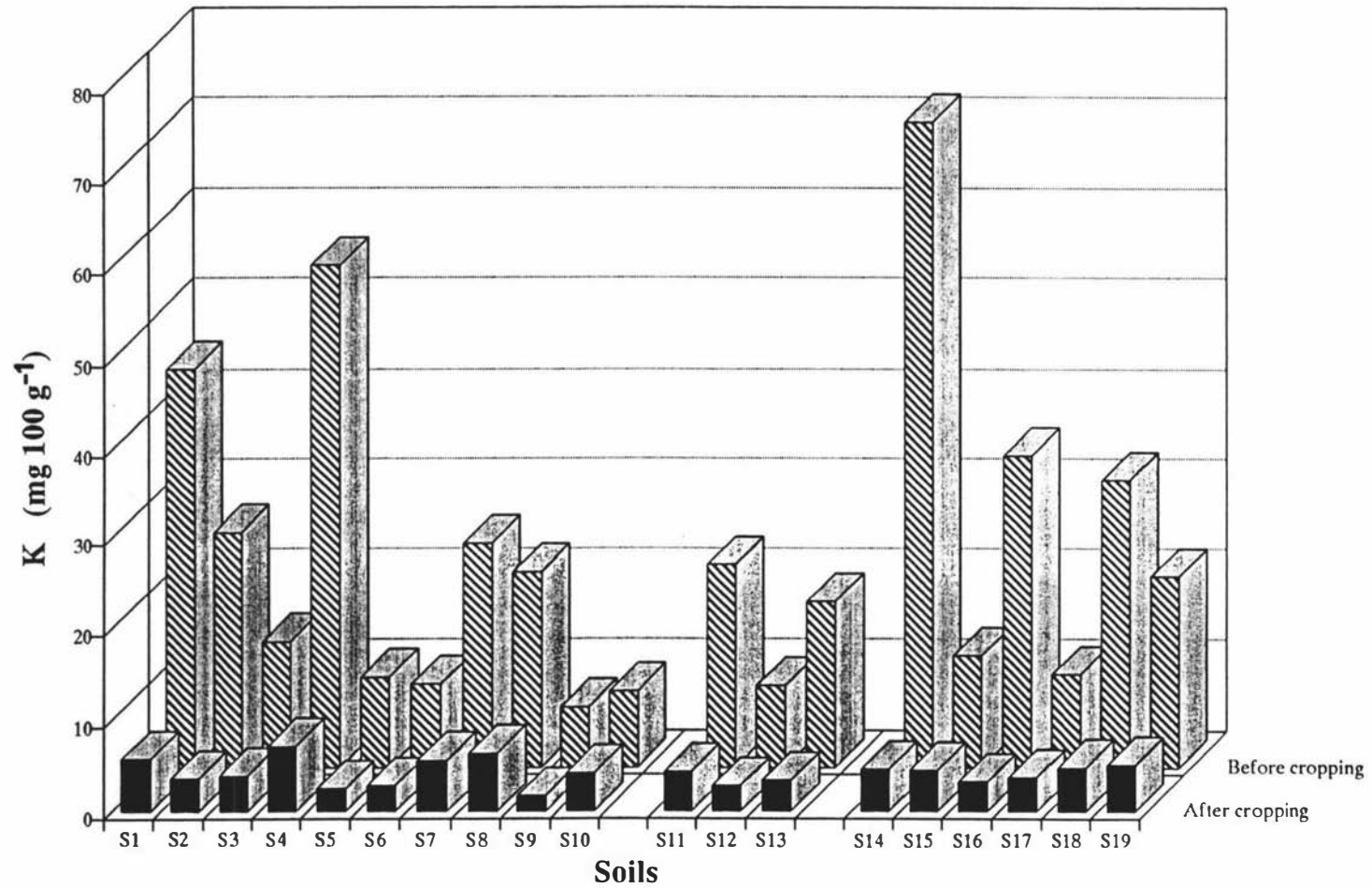
In the Hawke's Bay and Wairarapa regions, the Pirinoa (S13) soil recorded significantly higher dry matter yield than Matapiro (S11) and Wharekaka (S12) soils.

The undeveloped Claremont soil (S16) of the South Canterbury region recorded a significantly lower dry matter yield than the undeveloped Timaru (S14) and Opuha (S18) soils. In their developed counterparts, however, Timaru (S15) and Claremont (S17) soils recorded lower dry matter yields than did the Opuha soil (S19).

There were marked differences in dry matter yields of developed and undeveloped sites on the same soil (Fig. 4.3) the exception being the Marton soil sites (S5 and S6), due to the initial low exchangeable K of S5 and S6. The higher dry matter recorded for undeveloped sites as compared to developed sites on the same soil is largely due to a higher initial  $K_{ex}$  of the undeveloped sites (Fig. 4.1).

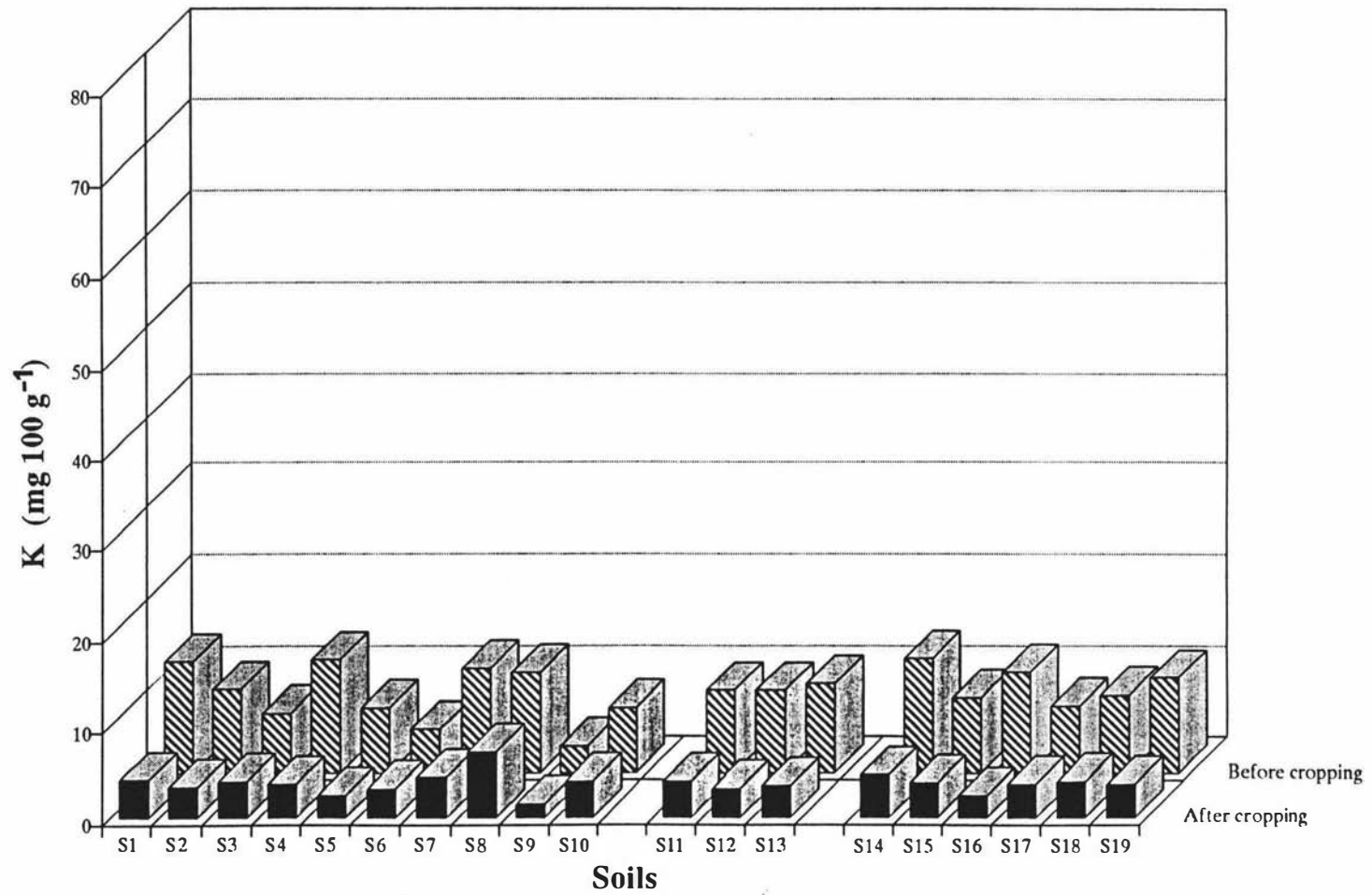
From the above comparisons it can be concluded that differences in dry matter yields amongst the soils resulted not only from  $K_{ex}$  release but also from  $K_{nex}$  release assessed by the  $K_c$  status (Table 4.2). For example, the higher dry matter yield recorded by the Raumai (S9) soil as compared to the Milson (S4) soil (Fig. 4.3) despite higher  $K_{ex}$  release of the latter (Fig. 4.1) may be due to the higher  $K_c$  value of the former soil (Table 4.2). Similarly the Pirinoa soil (S13) that recorded significantly higher dry

**Fig. 4.1  $K_{ex}$  of unleached soils before and after cropping**





**Fig. 4.2  $K_{ex}$  of leached soils before and after cropping**



matter yield than Matapiro soil (S11) had a higher  $K_c$  value despite varying  $K_{ex}$  values.

Dry matter yields in the additional pots of 8 soils that received complete (including K) nutrient solution (section 4.2.3) increased considerably (data not presented).

#### 4.3.2.2 *Total dry matter yields from leached soils*

As expected, the dry matter yields from the leached soils (Fig. 4.3) were considerably lower compared with their unleached counterparts. The exceptions to this trend, however, are the Marton (S5 and S6), Raumai (S9), Te Arakura (S10), Wharekaka (S12), and developed Timaru (S15) soils which showed no significant reduction in dry matter yields due to leaching. The trend in the leached soils may be explained due to their initial low  $K_{ex}$  levels.

Interestingly, the Raumai (S9) soil, which registered a lower dry matter yield than that of the undeveloped Canterbury soils (S18 and S14) in the unleached treatment, recorded highest for the leached treatment.

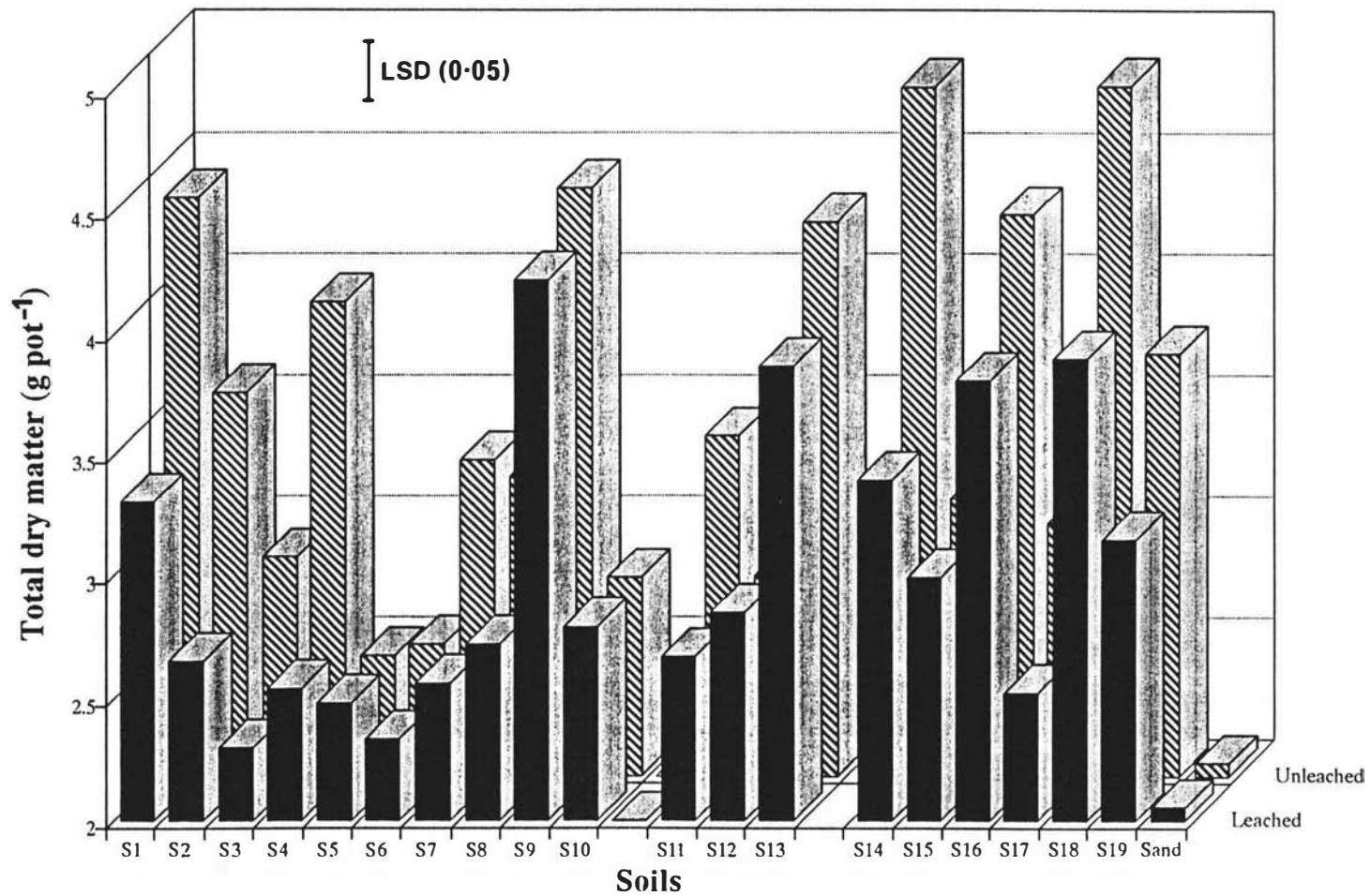
Although there were differences in the dry matter yields among the leached soils, they appeared to be of a lesser extent when compared to that observed in dry matter yield from unleached soils. The differences result mostly from  $K_{nec}$  release rather than  $K_{ex}$ .

As for unleached soils, differences in dry matter yields between undeveloped and developed sites on the same soil also occurred in leached soils (Fig. 4.3), but to a lesser extent (except in the Claremont and Marton soils) which is because of little difference in  $K_{ex}$  of these leached soils (Fig. 4.2). For example, the differences in dry matter yield between undeveloped (virgin) and developed (pasture) sites of Tokomaru (S2 and S3), Timaru (S14 and S15), and Opuha (S18 and S19) soils were 0.68, 1.69, and 1.10 g pot<sup>-1</sup> in unleached soils and 0.35, 0.41, and 0.74 in leached soils, respectively.

#### 4.3.3 Potassium content of herbage

The herbage K contents of each harvest for each soil and each treatment (expressed in

**Fig. 4.3 Total dry matter of ryegrass grown on unleached and leached soils**



percent) are given in Appendix 4.2. The K concentration in the herbage for all soils was highest at the first harvest and then declined to very low values by the fourth harvest.

There were significant differences in herbage K concentration among various soils for both treatments. Furthermore, wider differences that occurred in the first harvest reduced to a narrow range in the final harvest, which suggests that the plants gradually depleted plant available K from the soils. For example, K contents of tops from undeveloped Timaru soil (S14) were at least 6 and 1.6 times that of herbage from the Marton soil (S5) in the first and fourth harvest, respectively.

Over the four harvests, the mean K concentration in the tops for the unleached soils ranged from 0.19 % in Marton soils (S5 and S6) to 0.59 % for the undeveloped Timaru soil (S14). Even at the first harvest herbage K levels were well below the accepted level considered sufficient for optimum growth of ryegrass (2-2.5 % by Cornforth and Sinclair, 1984). The low values could be due to the small quantity of soil (20 g) used in the Stanford and DeMent method compared to the large volume of soil tapped by plant roots in the field.

Low values for herbage K were also observed by Jackson (1985) for the Marton (0.46 %) and Timaru (1.01 %) soils, while growing 12 ryegrass plants in a pot containing 100 g soil with a harvesting interval of 6-8 weeks. By comparison, herbage K after the first harvest (3 weeks growth) in this study for the undeveloped Marton (S5) and Timaru (S14) soils was 0.19 and 1.19 % and for their developed counterparts (S6 and S15) was 0.21 and 0.32, respectively. Similarly, in an exhaustive pot experiment, Portela (1993) found that for 6 out of 20 soils, the K concentration in ryegrass plants at the first harvest was lower than the optimal level.

The mean K concentration in the tops over the four harvests for all the leached soils ranged from 0.17 % to 0.41 %. Despite these values being similar to those for the unleached soils, the visual plant symptoms of K deficiency were more marked.

As with the trends for the dry matter yields from unleached and leached soils described in section 4.3.2, significant variation existed in the herbage K concentration between

developed and undeveloped soils e.g., Tokomaru (comparing S2 and S3), Timaru (S14 and S15), Claremont (S16 and S17), and Opuha (S18 and S19). Thus pastoral development can markedly affect the cation composition of herbage as a result of soil exploitation.

The mean K concentrations in the tops over the four harvests from the 8 unleached soils that received additional K, ranged from 1.06 to 1.21 % and gave large increases in both K uptake and dry matter yield when compared with the minus K treatment. These herbage K values are low, but the plants did not show K deficiency symptoms. This indicates that field values for herbage K optimum concentrations may not necessarily relate to glasshouse conditions. These results confirm K deficiency as the major limiting factor for dry matter yields in the pots that did not receive additional K.

#### 4.3.4 Potassium uptake

Potassium data of each harvest for each soil and treatment are given in Appendix 4.3.

##### 4.3.4.1 *Potassium uptake from control pots*

The ryegrass plants that were grown in control pots (sand only) extracted 3.83 mg K pot<sup>-1</sup> (400 g sand) over the four harvests (Appendix 4.3). This is attributed to K in the sand. For the purpose of undertaking valid statistical analysis, this background value has not been subtracted from the K uptake results for the treatments (Fig. 4.4 and Appendix 3) but has been subtracted to obtain the actual total K uptake i.e., the actual K supplying power of the soils (Fig. 4.5 and Fig. 4.6). This is used to calculate comparative contributions of  $K_{cx}$  and  $K_{ncx}$  i.e.,  $K_{cx}$  supply and  $K_{ncx}$  supply in section 4.3.6.

##### 4.3.4.2 *Potassium uptake from unleached soils*

Considerable differences in total K uptake were observed for the 19 soils. The range was from 22.3 mg K 100 g<sup>-1</sup> for the Marton soil (S5) to 112.5 mg for the undeveloped Timaru (S14) soil (Fig. 4.4). Most of the variation could be explained by the  $K_{cx}$  levels

**Fig. 4.4 Total K uptake by ryegrass grown on unleached and leached soils**

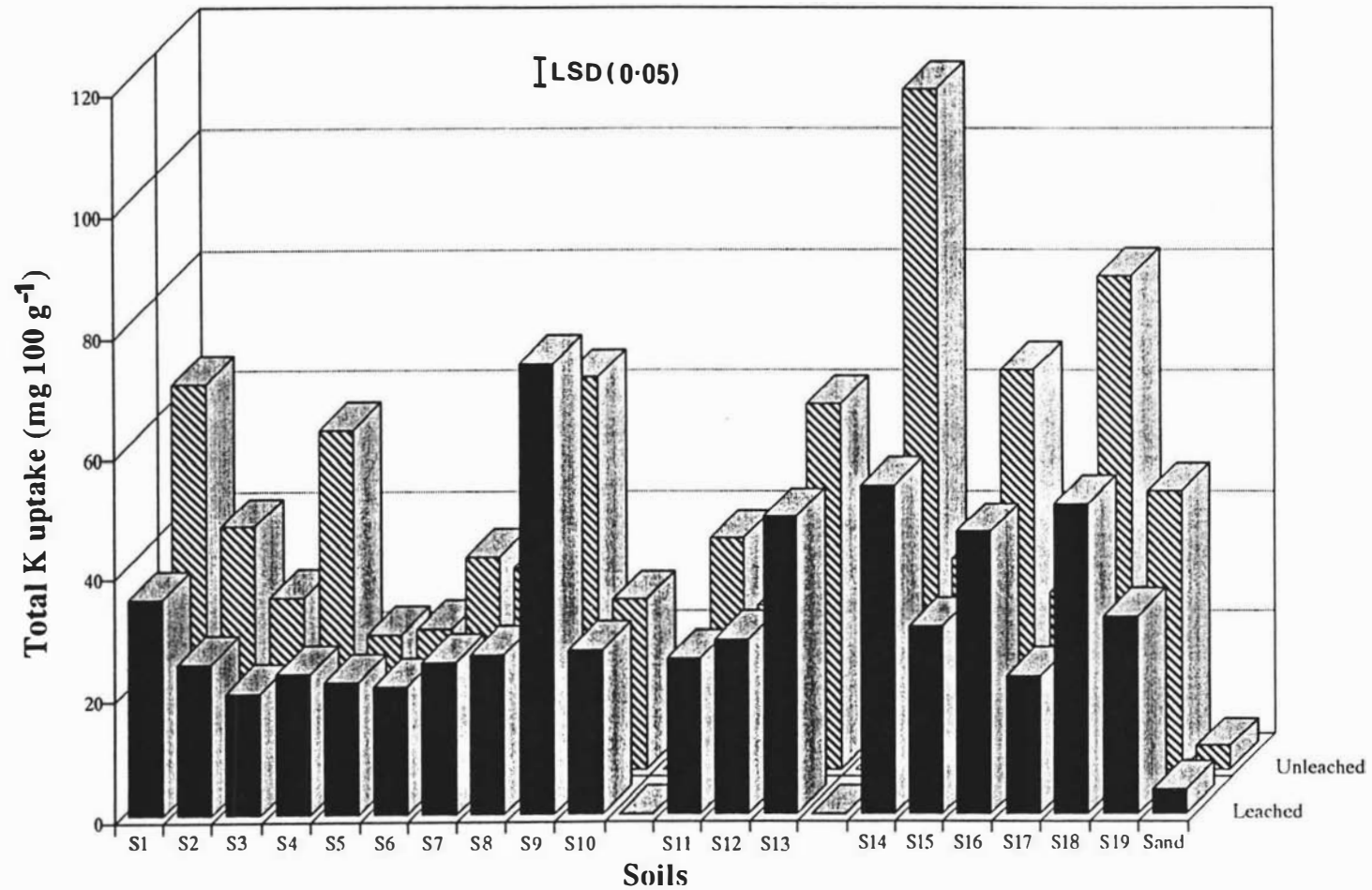


Fig. 4.5 Actual  $K_{ex}$  and  $K_{nex}$  contribution from the unleached soils

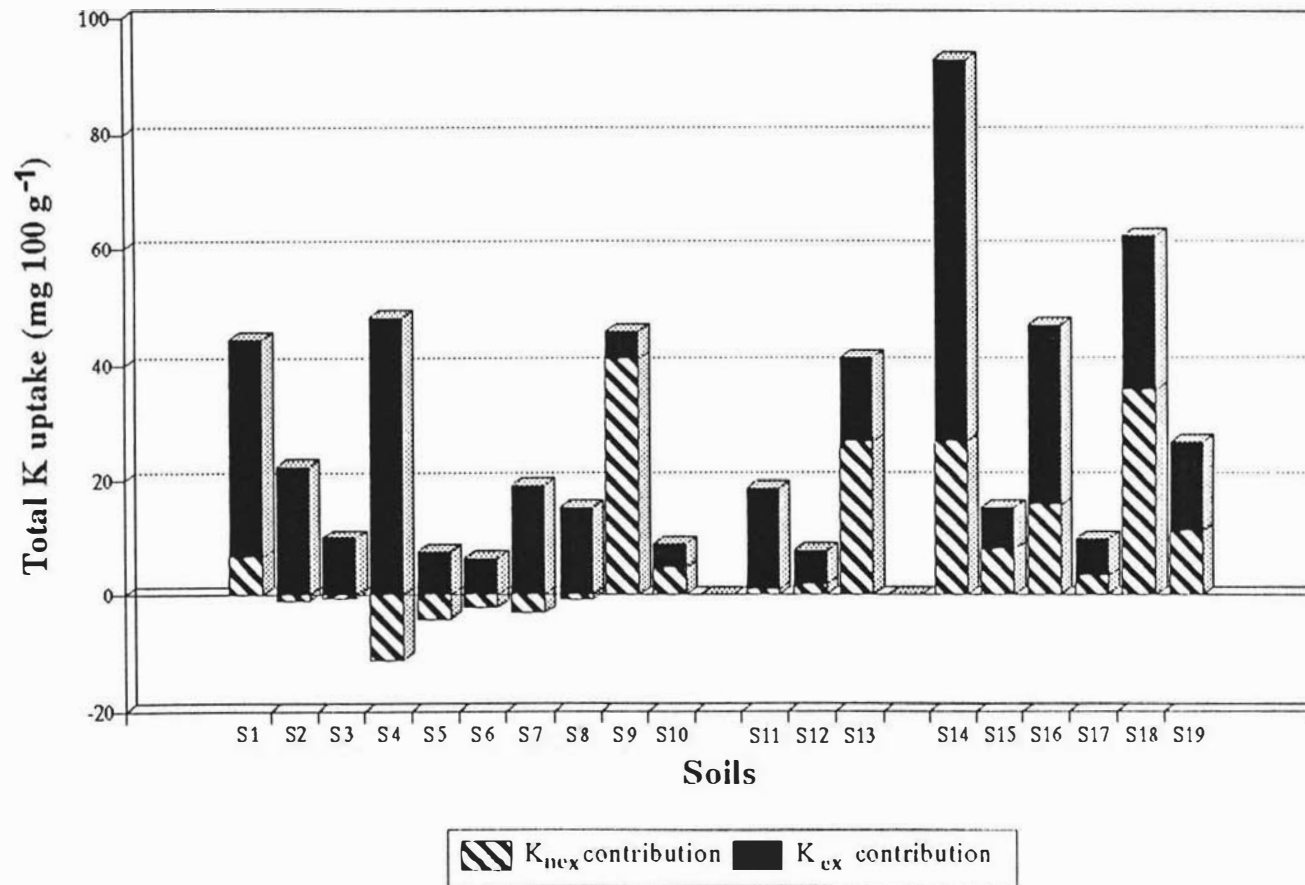
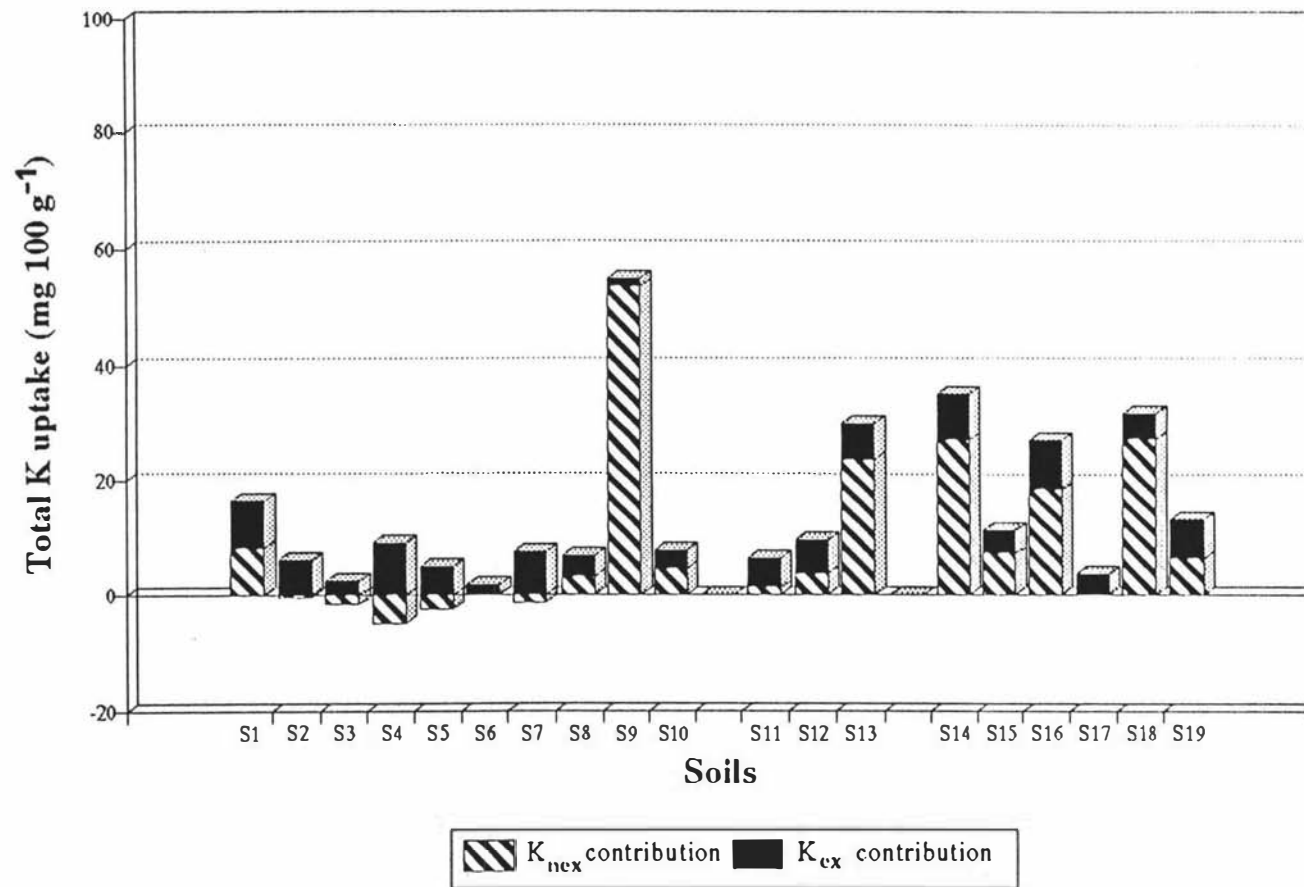


Fig. 4.6 Actual  $K_{ex}$  and  $K_{nex}$  contribution from the leached soils





of the unleached soils.

For the soils of the North Island the range of total K uptake for the undeveloped soils was 22.3 to 64.9 and for the developed analogues it was 23.1 to 63.9 mg 100 g<sup>-1</sup>. The range for the undeveloped soils was presumed to reflect different mineralogies and for the developed soils it probably reflects the extent of cropping and grazing systems involved over a period of many years.

There were also large differences in the amount of K extracted by ryegrass from soils which had similar initial  $K_{ex}$  status. For example,  $K_{ex}$  levels before cropping were similar for undeveloped sites of Timaru (S15) and Tokomaru (S3), but K supply over four harvests was significantly higher for the former soil. Similarly, the undeveloped site of Claremont soil (S16) had a K supply level significantly lower than the undeveloped site of Opuha (S18), despite similar  $K_{ex}$  levels. The pot trial results of Wood and Schroeder (1992) also indicated that the K used by a sorghum crop grown on a range of soils with similar  $K_{ex}$  values was not constant.

The contrast between undeveloped and developed soils of the same type is especially evident for the South Island YGE soils e.g., S14 and S15, S16 and S17, S18 and S19. The undeveloped sites supplied more K to ryegrass than did their developed counterparts. The drop in K uptake from the developed site was 69 % in Timaru (S14 and S15), 56 % in Claremont (S16 and S17), and 44 % in Opuha (S18 and S19) soils. The reduced total K uptake from developed sites reflects exploitation of K reserves over many years.

#### **4.3.4.3 Potassium uptake from leached soils**

As expected, the total K uptake by herbage harvested from leached soils was less than that from unleached soils (Fig. 4.4). The one exception was Raumai soil (S9) for which there was a statistically significant increase despite the removal of  $K_{ex}$  by leaching. It appears that for reasons not fully understood, leaching with Ca and Mg increased the rate of supply of K from  $K_{nex}$  sources.

The exception to the above trend was observed in Marton (S5 and S6), Te Arakura (S10), Wharekaka (S12), and developed Timaru (S15) soils for which leaching treatment did not markedly change K uptake. This is likely to be related to low  $K_{ex}$  status of these soils.

As is the case with unleached soils considerable differences in K uptake by ryegrass were also observed in the leached soils, the range being from 20.1 mg 100 g<sup>-1</sup> for the developed Tokomaru silt loam (S3) to 74.6 mg 100 g<sup>-1</sup> for the Raumai sandy loam (S9). Compared with the unleached treatment, most of these differences cannot be accounted for by  $K_{ex}$  because of very little difference in  $K_{ex}$  levels (low) of the leached soils (Fig. 4.2). Within the North Island soils Raumai (S9), Pirinoa (S13), and Tokorangi (S1) showed significantly higher K uptake.

There were marked differences in the K uptake of the leached group of soils between the developed and undeveloped sites (Fig. 4.4). For example, K uptake over four harvests for the Claremont undeveloped site (S16) was 46.5 mg 100 g<sup>-1</sup> and for the developed site (S17) it was 22.7. For the Opuha soil the values were 51.2 (S18) and 32.5 (S19), respectively.

#### 4.3.5 Exchangeable K release after cropping the unleached and the leached soils

On completion of the pot trial the  $K_{ex}$  of the unleached and the leached soils ranged from 1.63 mg 100 g<sup>-1</sup> in the Raumai soil (S9) to 7.20 in the Milson soil (S4) and from 1.36 in the Raumai (S9) to 7.10 in the Ohakea (S8), respectively (Fig. 4.1 and Fig. 4.2). Thus for all soils, unleached and leached,  $K_{ex}$  decreased to a more or less constant level below 7.20 mg 100 g<sup>-1</sup>, irrespective of large differences in the initial  $K_{ex}$  contents. This may be due either to the soils tending to maintain a minimal levels of  $K_{ex}$  regardless of  $K_{ex}$  removed by artificial leaching and/or cropping or to an artefact of the displacement of  $K_{ex}$  by  $NH_4^+$  ions when  $K_{ex}$  is determined by  $NH_4OAc$  leaching. The latter option is more likely, combined with the tendency of micaceous materials to leak  $K^+$  into the bathing (leaching) solution along a  $K^+$  concentration gradient. Such possible leakage is likely always to confound interpretation of extractable K values.

#### 4.3.6 Comparative contribution of $K_{ex}$ and $K_{nex}$ to total K uptake from unleached and leached soils

Of the total K removed by ryegrass after four harvests, the  $K_{ex}$  contribution to uptake from unleached soils i.e., the  $K_{ex}$  supply, ranged from 4.08 mg for Te Arakura (S10) to 66.67 mg 100 g<sup>-1</sup> for undeveloped Timaru (S14) soil (Fig. 4.5). For the leached soils (Fig. 4.6) the range was 1.59 for Raumai (S9) to 8.92 for Milson (S4). The uptake over and above  $K_{ex}$  supply is assumed to have come from the non-exchangeable K pool.

The  $K_{nex}$  supply varied greatly between soils, the range being from 0 to 40.93 mg 100 g<sup>-1</sup> for unleached soils and from 0 to 53.81 for the leached soils.

There were consistent differences between developed and undeveloped sites on South Island YGE soils in the amounts of  $K_{nex}$  taken up by plants from both unleached (Fig. 4.5) and leached (Fig. 4.6) soils.

##### 4.3.6.1 *Unleached soils*

Figure 4.5 shows that of the 13 soils in the North Island, 7 YGE soils contributed no  $K_{nex}$  to plant uptake because the difference between the  $K_{ex}$  release before and after cropping is higher than the actual total K uptake value. This indicates an efficient mechanism for fixation (retention) of  $NH_4OAc$  extractable K by partially expanded 2:1 layered clays i.e., there was a shift in the K fixation/release equilibrium towards stronger K retention. The results of During (1973) showed that K retention was related to the type of clay mineral present. The mineralogy of the above 7 soils in comparison with the soils that supplied  $K_{nex}$  to plant uptake is addressed in Chapter 8.

The Raumai soil (S9) had the lowest  $K_{ex}$  (6.45 mg 100 g<sup>-1</sup>) and the highest  $K_{nex}$  contribution whereas the Milson soil (S4) had the highest  $K_{ex}$  (55.40 mg 100 g<sup>-1</sup>) and zero  $K_{nex}$  contribution. The  $K_{ex}$  content of the 7 soils that contributed no  $K_{nex}$  to plants ranged from 8.95 to 55.40 mg 100 g<sup>-1</sup>. Thus the level of  $K_{ex}$  appears not to influence the uptake of  $K_{nex}$ .

There were also large differences in the  $K_{nex}$  supply from soils which had similar initial  $K_{ex}$  release. For example, ryegrass grown on developed Tokomaru (S3) soil did not supply non-exchangeable K, whereas 7.84 mg 100 g<sup>-1</sup> were taken from Timaru (S15) soil. Similarly, the undeveloped Opuha (S18) soil contributed twice as much as its Claremont counterpart (S16) to  $K_{nex}$ . These results support the findings of Richard *et al.* (1988) who explained the differences in total K uptake by alfalfa, from southern Ontario soils with similar initial  $K_{ex}$ , entirely in terms of the greater uptake of non-exchangeable K.

All the South Island YGE soils, developed and undeveloped (S14 to S19), contributed  $K_{nex}$ . The range of contributions was 3.38 to 35.39 mg 100 g<sup>-1</sup>. Again, the extent of  $K_{nex}$  uptake was independent of soil  $K_{ex}$  (cf. S2 to S8).

#### 4.3.6.2 *Leached soils*

As observed above, artificial leaching greatly reduced (to very low levels)  $K_{ex}$  of all soils (section 4.3.1), and the total K taken up by ryegrass (section 4.3.4.3). Artificial leaching did not result in considerable change of  $K_{nex}$  supply. It is interesting to note that of the 7 unleached YGE soils that did not supply  $K_{nex}$ , 2 (S6 and S8) supplied  $K_{nex}$  after leaching. Variability in the  $K_{nex}$  supply of the 19 leached was as wide as for the unleached treatment.

#### 4.3.6.3 *$K_{nex}$ supply versus $K_{ex}$ release*

In this section  $K_c$  values of the leached soils were assumed to be similar to those measured for the unleached soils.

While the  $K_{nex}$  supplied by the soils of the South Island (mean of 6 soils) was 16.6 mg 100 g<sup>-1</sup> and 14.4 mg in the unleached and leached treatment respectively, that of the North Island soils (mean of 13 soils) was 6.0 and 7.5 mg K. This difference between the North Island and South Island YGE soils is to be expected considering the  $K_c$  status of the two groups as recognised by AgResearch; the South Island soils fall in the high category (high K reserve soils) and the North Island soils in the medium category

(AgResearch grouping in Table 4.2).

What is unexpected is the wide range of  $K_{nex}$  supply and release within the soils of both the Islands. For example, even though the North Island YGE soils are considered to have medium K reserves (Table 4.2), the measured  $K_{nex}$  supply and the measured  $K_c$  values varied widely. The actual  $K_c$  values ranged from 7.8 to 18.6 mg 100 g<sup>-1</sup> (Table 4.2). This indicates a potential problem in determining K fertilizer requirements because in the CFAS model a constant value of  $K_c$  i.e., 11.7 mg 100 g<sup>-1</sup> is used to assess  $K_{nex}$  supply of these soils (section 2.9). A change in  $K_c$  of 3.9 mg 100 g<sup>-1</sup> is moreover equivalent to a change in annual soil K supply of 10 kg ha<sup>-1</sup> using the CFAS model (section 2.9).

The  $K_c$  values of the YGE soils in the South Island on the other hand ranged from 12.3 to 16.8 mg 100 g<sup>-1</sup> and overlapped with the range of their northern counterparts (Table 4.2).

In general, only those soils with a  $K_c$  value greater than 10 mg 100 g<sup>-1</sup> contributed  $K_{nex}$  to total K uptake by ryegrass. Thus the YGE and related soils in the present study can be broadly grouped into two categories (i) soils with a  $K_c$  range of 8-10 and (ii) with a  $K_c$  range of 12-19 mg 100 g<sup>-1</sup>.

The existing measure of  $K_{nex}$  release in New Zealand i.e., the  $K_c$  method, could not differentiate developed from undeveloped counterparts on the same soil as did the measure of  $K_{nex}$  supply. This has implications to the use of the soil group concept to estimate reserve K, because even though the measured  $K_c$  was more or less the same for both developed and undeveloped sites, the actual  $K_{nex}$  taken up by plants that were grown to K exhaustion in the glasshouse varied markedly between developed and undeveloped sites.

The  $K_{nex}$  supplies are generally more consistent with the classification (ranking) of the soils using the Metson criteria rather than using Campkin criteria both of which are based on measured  $K_c$  values (Tables 4.1 and 4.2). Thus those soils ranked high according to the Metson scale (S9, S10, S12, S14, S15, S18) contributed variable

amounts of  $K_{nec}$  to total K uptake by ryegrass. These soils, however, are all ranked medium according to the Campkin (AgResearch) scale. Thus calculations of K fertilizer requirements based on the CFAS model would result in over-estimates.

Similarly, over-estimates would occur for S4 and S5 which are ranked low by Campkin and medium by Metson (Table 4.2). The difficulty is compounded by AgResearch use, for convenience, of mean  $K_c$  values (3.9, 11.7, 27.3, Table 4.1) for low, medium, and high rankings, respectively.

This study confirms the recommendation of Campkin (1985) that when possible the actual  $K_c$  value (Metson, 1968a), if available for the site, should be used if the  $K_c$  method continues to be basis for the  $K_{nec}$  supply parameter in the CFAS model.

Since  $K_c$  is only a chemical index of  $K_{nec}$  release in the long run, the actual  $K_{nec}$  taken up by growing plants in this pot trial might be a more reliable index for placing these soils into different K fertility groups and also for reflecting the changes in K supplying power that result from continuous cropping and grazing.

#### 4.4 GENERAL DISCUSSION ON ARTIFICIAL LEACHING TECHNIQUE

The artificial leaching technique (section 4.2.2) was intended to saturate all the exchange sites with  $Ca^{++}$  and  $Mg^{++}$  so that K uptake by ryegrass plants could be equated solely to  $K_{nec}$  supply. This seemed to be a reasonable assumption because plants were forced to grow on the  $K_{ex}$  exhausted soils.

Artificially leaching, however, not only incompletely removed the  $NH_4OAc$ -extractable  $K_{ex}$  but also enabled those soils with high initial  $K_{ex}$  levels to loose K in high proportions (section 4.3.1). If it is assumed that all the K on exchange sites was displaced by  $Ca^{++}$  or  $Mg^{++}$  ions during the artificial leaching process the presence of  $K_{ex}$  after subsequent extraction with  $NH_4OAc$  may be due to  $K_{nec}$  moving into the  $K_{ex}$  pool along a potential gradient created by the low level of  $K_{ex}$  and/or to the removal of non-exchangeable  $NH_4OAc$  extractable K. Thus to some degree the appearance of  $K_{ex}$  after presumed replacement by  $Ca^{++}$  or  $Mg^{++}$  may be an artefact of the  $NH_4OAc$

extraction procedure. This is a possible explanation of the anomalous result for soil S12 (comparing Fig. 4.1 and Fig. 4.2)

On the other hand, even if  $\text{NH}_4\text{OAc}$  were used as a leaching solution zero levels of  $K_{\text{ex}}$  after leaching would not be expected because during the later subsequent measurement for  $K_{\text{ex}}$  on air dried soils, even by the same extractant, a new equilibrium is established based on the release of  $K_{\text{ex}}$  from  $K_{\text{nex}}$  sources. Moreover, a preliminary study on leaching the soils and their separates continuously, with either the leaching solution or the  $\text{NH}_4\text{OAc}$  solution, resulted in near total depletion of  $K_{\text{ex}}$  release after the second successive leaching (data not presented). Nash (1971) showed that 90 % of the  $K_{\text{ex}}$  was extracted by the first 25 ml of 0.01 M  $\text{NH}_4\text{OAc}$ .

Furthermore, removal of  $K_{\text{ex}}$  by leaching is extractant-specific in quantitative terms and any  $K_{\text{ex}}$  remaining after artificial leaching is a reflection of  $K_{\text{ex}}$  measured by a different extractant other than that used for  $K_{\text{ex}}$  removal.

Potassium uptake from the leached soils thus cannot be equated solely to  $K_{\text{nex}}$  supply. In addition,  $K_{\text{nex}}$  supply of the 'leached' soils was not of much higher magnitude than the  $K_{\text{nex}}$  supply of the original (unleached) soils which was contrary to expectations. Thus the artificial leaching technique was not as helpful as intended. The variations of  $K_{\text{nex}}$  supply observed in the unleached treatment, however, were test verified in the leached treatment.

#### 4.5 CONCLUSIONS

1. There was considerable variation in the availability of K to ryegrass from  $K_{\text{nex}}$  sources for the 19 soils examined. This is illustrated by the extent of  $K_{\text{nex}}$  supply that ranged from 0 to 41 and from 0 to 54 mg 100 g<sup>-1</sup> for unleached and leached soils, respectively.
2. According to the AgResearch categorisation (Cornforth and Sinclair, 1984) all the North Island YGE soils occur in the medium  $K_c$  group and the South Island soils in the high  $K_c$  group. This study delineates the selected soils of both these

Islands on the basis of actual  $K_c$  values and also on the K taken up by ryegrass plants from  $K_{nex}$  pool.

The results therefore imply that  $K_{nex}$  supply in the CFAS model could be better assessed if actual  $K_c$  for the site is determined. This is more so for the North Island soils where four out of 13 soils studied appeared to have abundant reserves of K as reflected in high  $K_{nex}$  release ( $K_c$ , Metson scale) and high  $K_{nex}$  supply ( $K_{nex}$  uptake), contrary to the AgResearch categorisation. Moreover, the variation in  $K_{nex}$  contribution to plant uptake is considerably greater in soils of the North Island compared to the South Island soils.

3. The lower levels of  $K_{nex}$  uptake by ryegrass from developed sites in the South Island as compared to their undeveloped counterparts have implications for the use of the soil group concept to estimate reserves of K ( $K_c$ ) in determining K fertilizer requirements by the CFAS method. For example, undeveloped unleached sites contributed 3 to 5 times more  $K_{nex}$  to total uptake of K by ryegrass than their developed counterparts.

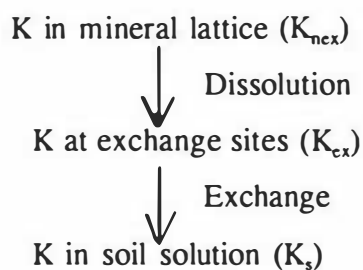


## CHAPTER 5

### POTASSIUM THRESHOLD LEVELS OF YGE SOILS IN RELATION TO K RELEASING POWER, SUPPLYING POWER, AND SPECIFICITY

#### 5.1 BACKGROUND

Release of  $K_{nex}$  from clay interlayers and from K bearing primary minerals occurs when  $K_{ex}$  and  $K_s$  levels are depleted by plant uptake (Doll and Lucas, 1973; McLean and Watson, 1985). The main sources of this  $K_{nex}$  are the interlayer spaces of micas, illites, and interstratified 2:1 layer silicates (Sparks and Huang, 1985; Quemener, 1986; Goulding, 1987). The release of K from  $K_{nex}$  in soil systems can be represented by the following combination of processes (Wiklander, 1954; Arnold, 1962):



According to Tucker (1964), however, there is no reason to suppose that K must pass through exchange sites before it is released into the soil solution. The  $K_{nex}$  can therefore be in direct equilibrium with  $K^+$  ions in the soil solution as suggested by Mortland (1958).

If crop removal is assumed to be a single large sink for K depletion (cf. the exhaustive cropping trial, Chapter 4) the plant availability of  $K_{nex}$  to ryegrass could be influenced by the rate of K release together with the K concentration (activity) in the soil solution. The rate of release is not only dependent on the degree of utilization of K by continuous crop uptake acting as a sink, but also on the nature of K bearing minerals in soils. In

addition to the K content of the minerals, the type of bonding within crystals, the extent of fracture surfaces and dislocations, the proportion of vacant sites, and the partial opening of interlayer space and the warping of the silicate layers will determine the rate of K release (Rich, 1968).

Working with "pure" clay minerals, Bassett (1959) and Scott and Smith (1966) showed that K release began below a particular  $K_s$  concentration termed the critical K concentration. This was in agreement with Rausell-Colom *et al.* (1965) who reported that  $K_s$  concentration influences the release of K from  $K_{ncx}$ . Furthermore, these authors demonstrated that for biotites and phlogopites suspended in a strong salt solution e.g., 1 M  $CaCl_2$ , the critical K concentration ranged from 8 to 66  $mg\ l^{-1}$  below which K was continuously released. Newman (1969) suspended a range of micas in 1 M NaCl and showed that the solution concentration ratio,  $C_K/C_{Na}$ , at equilibrium ranged from  $1 \times 10^{-5}$  for muscovite to  $1.2 \times 10^{-3}$  for a very reactive biotite, thus confirming the higher critical K concentration of biotite compared to muscovite.

Recent work of Datta and Sastry (1991) using Indian soils led to the introduction of the term "threshold K level" to denote the critical K concentration as distinguished from the critical K level of Mengel and Busch (1982), which is associated with the level of K in soil solution below which a yield increase is obtained when fertilizer K is applied. The theory behind the threshold K level (Datta and Sastry, 1991) is relatively simple.

The soil is equilibrated with weak  $CaCl_2$  solution at a series of soil:solution ratios followed by filtration and further extraction of the residual  $K_{cx}$  with  $NH_4OAc$ . As the soil:solution ratio is widened the total amount of K extracted i.e., K desorbed in  $CaCl_2$  solution plus K extracted with  $NH_4OAc$  (termed  $K_T$ ) remains more or less constant until a critical value of K concentration (a measure of intensity of K release) is reached. This critical value of K concentration in the equilibrated solution is termed the threshold K level because lowering the K concentration below this value will initiate K release from  $K_{ncx}$  sources resulting in sharp increase in  $K_T$ .

The following seems to be the mechanism of  $K_{ncx}$  release. Datta and Sastry (1991)

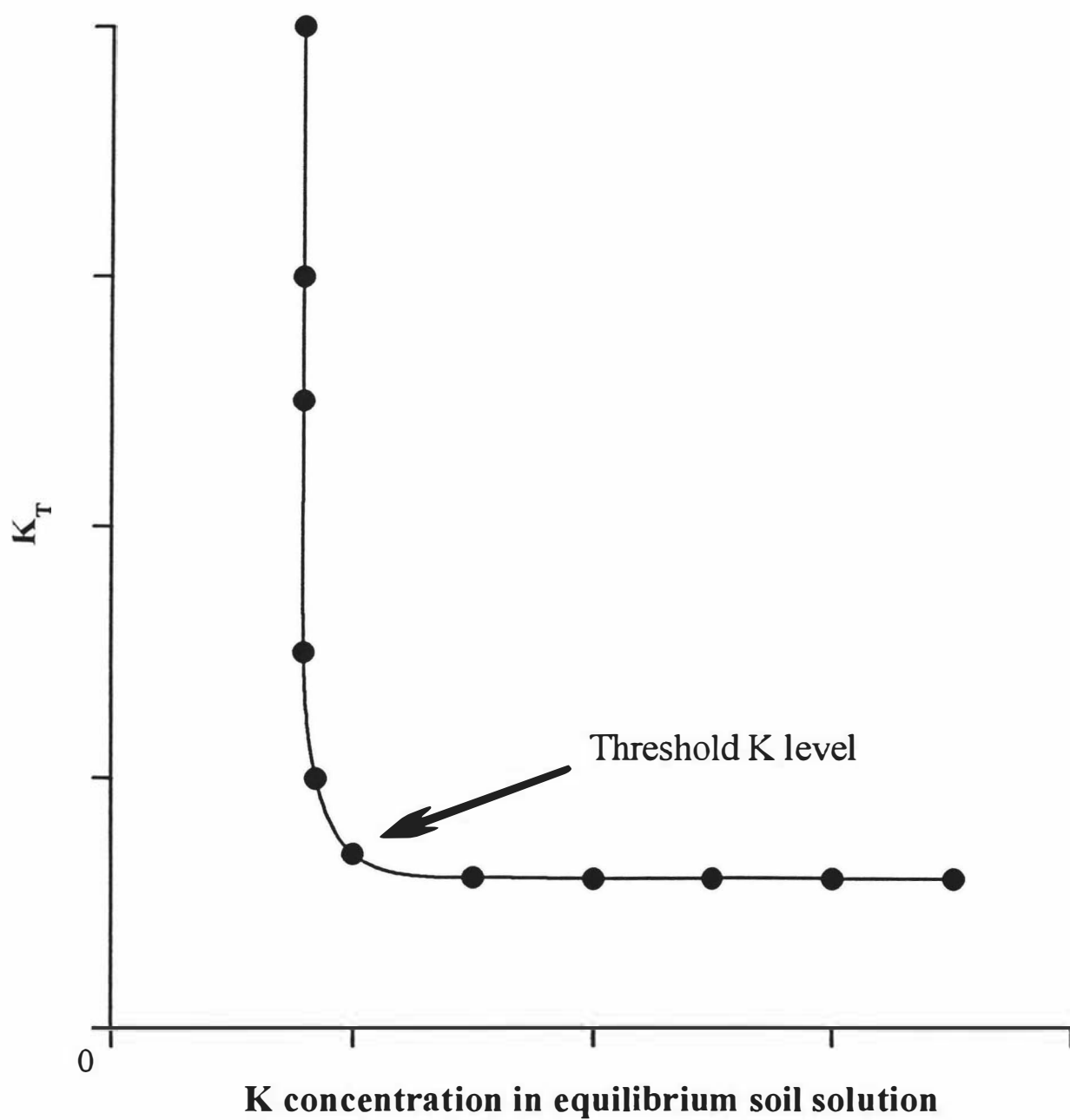
suggested that during initial extraction of the soil by  $\text{CaCl}_2$ ,  $\text{Ca}^{++}$  replaces  $\text{K}^+$  at planar sites (p- positions). In the subsequent extraction with  $\text{NH}_4\text{OAc}$ ,  $\text{NH}_4^+$  (ionic diameter 0.29 nm) replaces  $\text{K}^+$  (ionic diameter 0.27 nm) in the wedge zones of layered clay minerals. Eventually, at reduced K concentrations in the equilibrating solution that is achieved by wider soil:solution ratios, K moves from the wedge sites and the layers are then forced further apart due to net negative charges. The larger hydrated  $\text{Ca}^{++}$  ions then enter the wedge zone thus allowing release of more interlayer K into the equilibrated soil solution and therefore resulting in increased  $K_T$ . The value of the threshold K level was believed to be dependent on the ease with which  $K_{\text{ex}}$  is released. Thus higher threshold K values should indicate weaker binding of K in the wedge zones of micaceous minerals and further indicate higher levels of  $K_{\text{ex}}$  available to plants.

Thus when  $K_T$  at different soil:solution ratios is plotted against K concentrations corresponding to the respective ratios, the line runs parallel to the x-axis with decreasing K concentrations (or increasing soil:solution ratios) up to the threshold K level and thereafter tends to become parallel to the y-axis (Fig. 5.1). The point on the x-axis at which  $K_T$  begins to rise steeply is identified as the threshold K level.

Alternatively,  $K_T$  is plotted against (i) K-Ca activity ratio ( $\text{AR}^{\text{K}}$ ) in the equilibrated solution (another measure of K intensity) that is determined by Q/I relationship, and (ii) exchangeable K (a measure of quantity that is extractable with  $\text{NH}_4\text{OAc}$  after K removal by  $\text{CaCl}_2$  equilibration) to obtain threshold K levels expressed in terms of these indices of K releasing power. Thus threshold K level can be obtained in terms of (i) K concentration in the equilibrated soil solution, (ii)  $\text{AR}^{\text{K}}$ , and (iii)  $K_{\text{ex}}$ .

Higher threshold K levels in terms of  $K_{\text{ex}}$  also indicate higher amounts of specifically held K (Datta and Sastry, 1991). As discussed in Chapter 2 (section 2.2.2) a number of exchange sites are present on the planar surfaces, and around the edges and wedges of the silicate layers. The planar exchange sites may be called non-selective (non-specific) sites and those around edges and wedges selective (specific) sites. The Gapon constant ( $K_G$ ) gives a measure of the relative tightness of binding of  $\text{K}^+$  in relation to

**Fig. 5.1 Theoretical relationship between K concentration in the equilibrium soil solution and  $K_T$**



other cations (Mengel and Kirkby, 1987). The higher the  $K_G$  the greater is the specificity of the binding site for  $K^+$ . For example, the  $K_G$  values for the three different  $K^+$  binding sites of illite as reported by Schuffelen (1972) were 2.21 (p-position), 102 (e-position), and infinite (i-position). The units for  $K_G$  were  $(Mm^{-3})^{-1/2}$ .

Thus when  $K_G$  values for different soil:solution ratios are plotted (y-axis) against the  $K_{ex}$  values at the respective ratios (x-axis), a graph similar to Fig. 5.1 is obtained. The point on the x-axis at which the curve begins to rise is the amount of specifically held K in wedge zones because at this point most of the  $K_{ex}$  is strongly held. The corresponding point on the y-axis gives a measure of  $K_G$  for the planar sites. Thus a higher value of specifically held K means more specific sites in the clay minerals that can release K when K concentration (or activity) in the equilibrated solution is reduced.

In Chapter 4 it was evident that there is considerable variation in the availability of K to ryegrass in the 19 soils examined and that  $K_{dex}$ , which is not ordinarily extractable with  $NH_4OAc$  is an important, but variable, source of K for ryegrass. For example, while the  $K_{dex}$  contribution to plant uptake ( $K_{dex}$  supplying power) for the unleached Raumai soil (S9) was 40.9 mg 100 g<sup>-1</sup> (Table 5.1), 7 YGE soils in the North Island contributed no  $K_{dex}$  (in fact negative  $K_{dex}$  uptake suggesting K fixation) to plant K uptake (Fig. 4.5). Similarly, the Timaru soil (S14) which is undeveloped and unexploited had a  $K_{dex}$  contribution to plant uptake 3 to 4 times greater than its developed counterpart (S15).

Since  $K_{dex}$  uptake by plants is dependent on the K release from  $K_{dex}$  sources, the threshold K level in terms of the above indices (K concentration, K-Ca activity ratio, and  $K_{ex}$ ), and the amount of specifically held K would be expected to be higher for the soils that have contributed maximum  $K_{dex}$  to plant uptake. This K release from  $K_{dex}$  sources may be analogous to a saturated solution in equilibrium with its solid phase. It is hypothesised therefore, that the Raumai soil (S9) has a higher threshold K level and also higher amounts of specifically held K than all other soils in the North Island. Similarly, the undeveloped Timaru soil (S14) should theoretically have a higher value of threshold K level than the developed Timaru soil (S15). The differences in the

threshold K levels and the amounts of specifically held K among the soils should therefore ideally be in the same ranking order as that obtained by  $K_{\text{nex}}$  uptake by ryegrass (Chapter 4) and K extracted by  $\text{HNO}_3$  (step K, and  $K_c$ ).

The objective of the study reported in this chapter is to establish the threshold K levels in terms of the K concentration and the activity ratio in the equilibrated soil solution,  $K_{\text{ex}}$ , and the amount of specifically held K, and hence provide an explanation for the variations in the  $K_{\text{nex}}$  uptake by ryegrass. The concept of threshold K levels is also important because it potentially facilitates differentiation of soils based on their  $K_{\text{nex}}$  supplying power to growing plants.

## 5.2 MATERIALS AND METHODS

### 5.2.1 Soils - S3, S6, S9, S12, S14 and S15.

These six soils were selected from the 19 soils, as they have differing levels of plant  $K_{\text{nex}}$  uptake (Chapter 4). A detailed description of these soils is given in Chapter 3. Table 5.1 shows the features used for selecting soils for this study.

### 5.2.2 Determination of the threshold K level

The method of Datta and Sastry (1991) was modified as follows for determining the threshold K levels. The K concentrations (or K-Ca activity ratios in the soil solution) were lowered to different levels by shaking duplicate soil samples with 0.01 M  $\text{CaCl}_2$  at different soil:solution ratios (Table 5.2) for 1 h in a 200 ml centrifuge bottle and then allowing them to equilibrate for 24 h. The bottles were then centrifuged at 2000 rpm for 2 min and the concentrations of K, Ca, and Mg in the filtrate for each soil:solution ratio measured. K, Ca, and Mg present in the exchangeable phase in the soil after the equilibration were determined for each soil:solution ratio, by shaking the residual soil in the centrifuge bottle with neutral 1 M  $\text{NH}_4\text{OAc}$  (soil:solution ratio of 1:10) for 30 min, followed by centrifuging and filtering. Since a portion of the  $\text{CaCl}_2$  solution was entrapped in the soil after filtering, the amount of exchangeable cations extracted by

Table 5.1 Some features used for selecting soils to determine threshold K levels

Soil No.	Soil name	Region	* Ranking of		Step K** (Chapter 6)	K <sub>nex</sub> uptake (Chapter 4 data)	
			K <sub>ex</sub>	K <sub>c</sub>		Unleached soils	Leached soils
mg 100 g <sup>-1</sup>							
S6	Marton	Rangitikei	L (8.95)	M (8.18)	31	-2.21	0.11
S3	Tokomaru	Manawatu	L (13.65)	M (9.42)	30	-0.72	-1.73
S12	Wharekaka	Wairarapa	L (8.80)	H (14.71)	49	1.88	3.52
S15	Timaru (b)	South Canterbury	L (12.10)	H (14.50)	62	7.84	6.98
S14	Timaru (a)	South Canterbury	H (71.35)	H (16.79)	75	26.63	27.04
S9	Raumai	Pohangina	L (6.45)	H (17.33)	106	40.90	53.81

(a) Undeveloped site

(b) Developed site

Values in brackets are the measured values (Table 3.3, Table 4.2)

\* Refer Table 4.2

\*\* Step K = a method to assess K<sub>nex</sub> releasing power (Chapter 6)

**Table 5.2** Soil:solution ratios used for determining threshold K levels

<b>Serial No.</b>	<b>Soil:solution ratio</b>	<b>Soil weight (g)</b>	<b>Volume of 0.01 M CaCl<sub>2</sub> (ml)</b>	<b>Volume of 1 M NH<sub>4</sub>OAc (ml)</b>
1	1:2	10	20	100
2	1:4	5	20	50
3	1:5	5	25	50
4	1:10	2	20	20
5	1:15	2	30	20
6	1:25	2	50	20
7	1:50	2	100	20
8	1:100	2	200	20
9	1:150	1	150	10
10	1:200	1	200	10
11	1:400	0.5	200	5



$\text{NH}_4\text{OAc}$  was corrected by subtracting the amount present in the entrapped solution. The quantity of entrapped solution was calculated from the difference between the weight of the wet soil that contained entrapped solution and the weight of the air dry soil.

The K-Ca activity ratio ( $\text{AR}^{\text{K}}$ ) for each soil:solution ratio was calculated using the following formula (Ganeshamurthy and Biswas, 1984).

$$\text{AR}^{\text{K}} = \frac{a_{\text{K}}}{a_{(\text{Ca}+\text{Mg})}^{1/2}} \quad (5.1)$$

The activity of K is given by

$$a_{\text{K}} = C_{\text{K}} f^+ \quad (5.2)$$

Where  $C_{\text{K}}$  is the concentration of K expressed in mole  $\text{l}^{-1}$  and

$f^+$  is the activity coefficient for K.

The activity of Ca+Mg is given by

$$a_{(\text{Ca}+\text{Mg})}^{1/2} = C_{(\text{Ca}+\text{Mg})}^{1/2} f^{2+} \quad (5.3)$$

Where,

$C_{(\text{Ca}+\text{Mg})}^{1/2}$  is the square root of concentration of Ca+Mg expressed in mole  $\text{l}^{-1}$ .

$f^{2+}$  is the activity coefficient for Ca+Mg where  $f^+$  and  $f^{2+}$  are given by

$$-\log f = \frac{0.509 Z^2 \mu^{1/2}}{1 + 1.5 \mu^{1/2}} \quad (5.4)$$

giving

$$f = 10^{-\frac{0.509 Z^2 \mu^{1/2}}{1+1.5\mu^{1/2}}} \quad (5.4)$$

$Z$  is the valency of the ion and

$\mu$  is the ionic strength given by

$$\mu = \frac{1}{2} \left( \sum M Z^2 \right) \quad (5.5)$$

Where  $M$  is the Molar concentration of cations (K, Ca and Mg) and anion (Cl).

The units for  $AR^K$  are  $(\text{mole l}^{-1})^{1/2}$ .

The Gapon constant,  $K_G$ , for each soil:solution ratio, was calculated using the following equation:

$$K_G = \left( \frac{K_{ex}}{\text{Exchangeable Ca+Mg}} \right) \left( \frac{a^{1/2} (Ca+Mg)}{a_K} \right) \quad (5.6)$$

$$= \left( \frac{K_{ex}}{\text{Exchangeable Ca+Mg}} \right) \left( \frac{1}{AR^K} \right)$$

The units for  $K_G$  are  $(\text{mole l}^{-1})^{-1/2}$ .

$K_T$  (total extractable K = solution K +  $K_{ex}$ ) was plotted against the K concentration in  $\text{CaCl}_2$  soil solution,  $AR^K$ , and  $K_{ex}$  corresponding to each soil:solution ratio and the curves were drawn free-hand. The threshold K levels for K release in terms of K

concentration in the soil solution,  $AR^k$ , and  $K_{ex}$  were determined from these curves as mentioned earlier.

Specifically held  $K$  and  $K_G$  for the soils can be obtained from a graph that shows the values of Gapon constant of K-Ca exchange (y-axis) as a function of  $K_{ex}$  (x-axis) at each soil:solution ratio.

### 5.3 RESULTS AND DISCUSSION

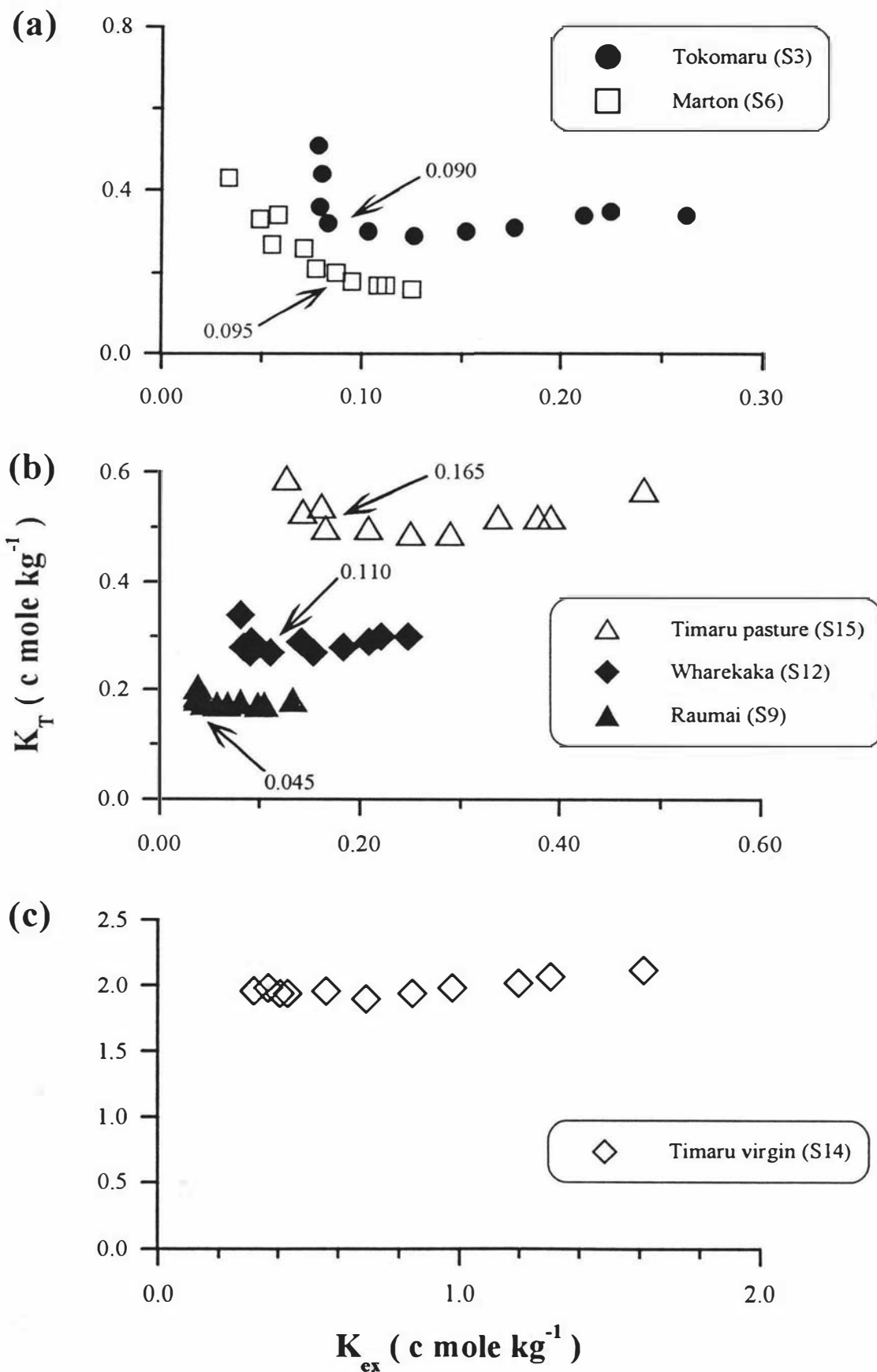
#### 5.3.1 Threshold K levels expressed in terms of K concentration in the equilibrating soil solution

Figures 5.2, 5.3, and 5.4 show the curves of  $K_T$  versus the K concentration in equilibrium  $CaCl_2$  solution,  $AR^k$ , and  $K_{ex}$ , respectively. Each of these expressions of threshold K level describe the K releasing power of soils and are related to each other. Threshold K levels in terms of K concentration ( $mM\ l^{-1}$ ) in the equilibrated soil solution were mainly used to characterize soils in the present study with respect to  $K_{nex}$  availability to plants. This was because studies of Datta and Sastry (1988) indicated that threshold K levels in the equilibrated solution in terms of K concentration remained unchanged whereas that in terms of  $K_{ex}$  and  $AR^k$  changed with decrease in the  $CaCl_2$  concentration (from 0.01 to 0.002 M).

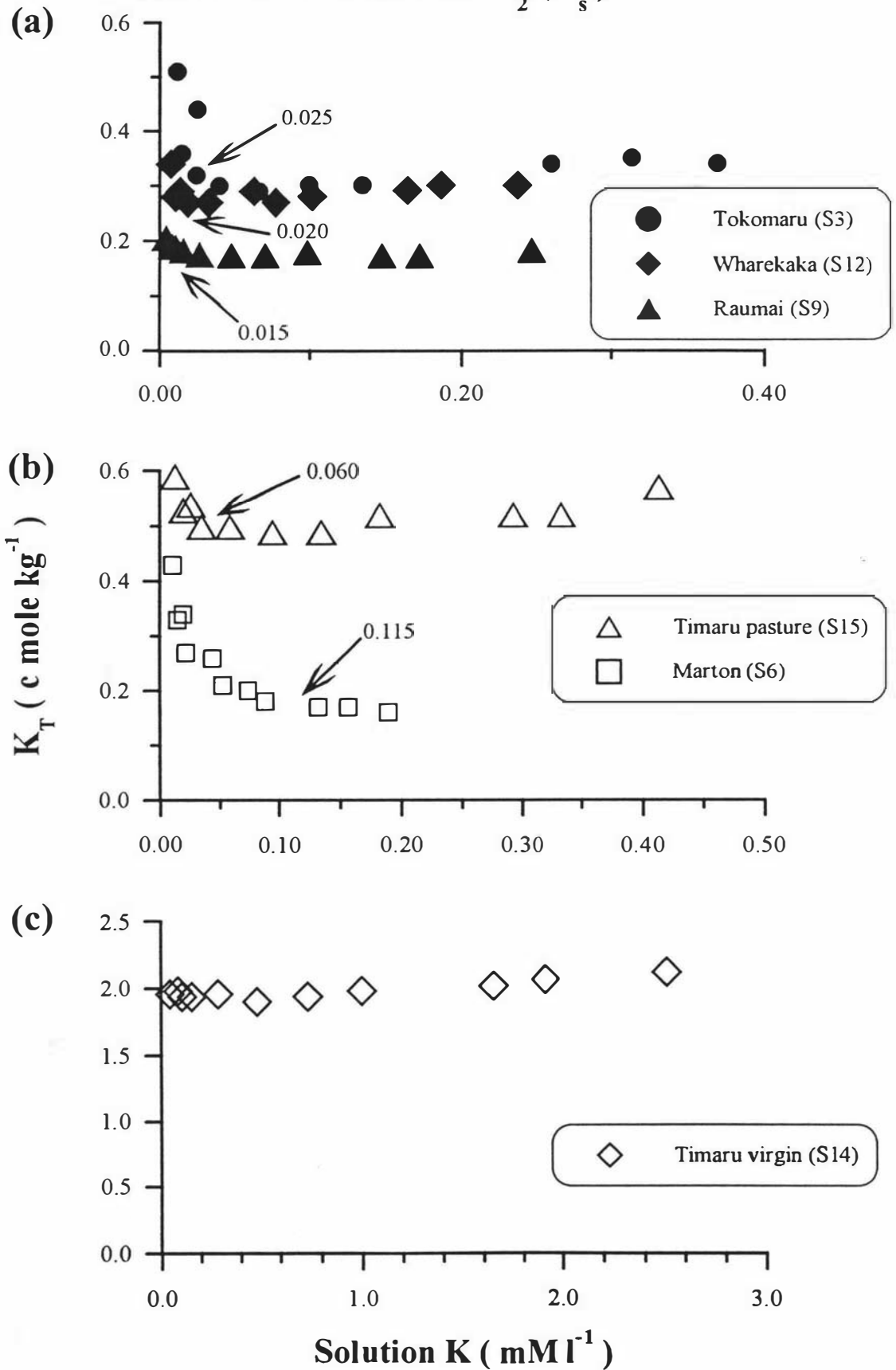
The curves for all the soils except the undeveloped Timaru soil (S14) are more or less similar, i.e., the line running almost parallel to the x-axis with decreasing solution K concentration (or with increasing soil:solution ratio) up to a certain value where  $K_T$  increases more or less sharply and then the line tending to become more or less parallel to y-axis indicating release from  $K_{nex}$ . The value of equilibrium K concentration in the soil solution where the  $K_T$  begins to increase sharply is termed the threshold K level (Datta and Sastry, 1991) because lowering the K concentration below this level initiated K release from  $K_{nex}$  sources.

The threshold K level in terms of K concentration in the equilibrating soil solution,

**Fig. 5.2 Relationship between total K extracted ( $K_T$ )<sup>88</sup> and exchangeable K of soils**

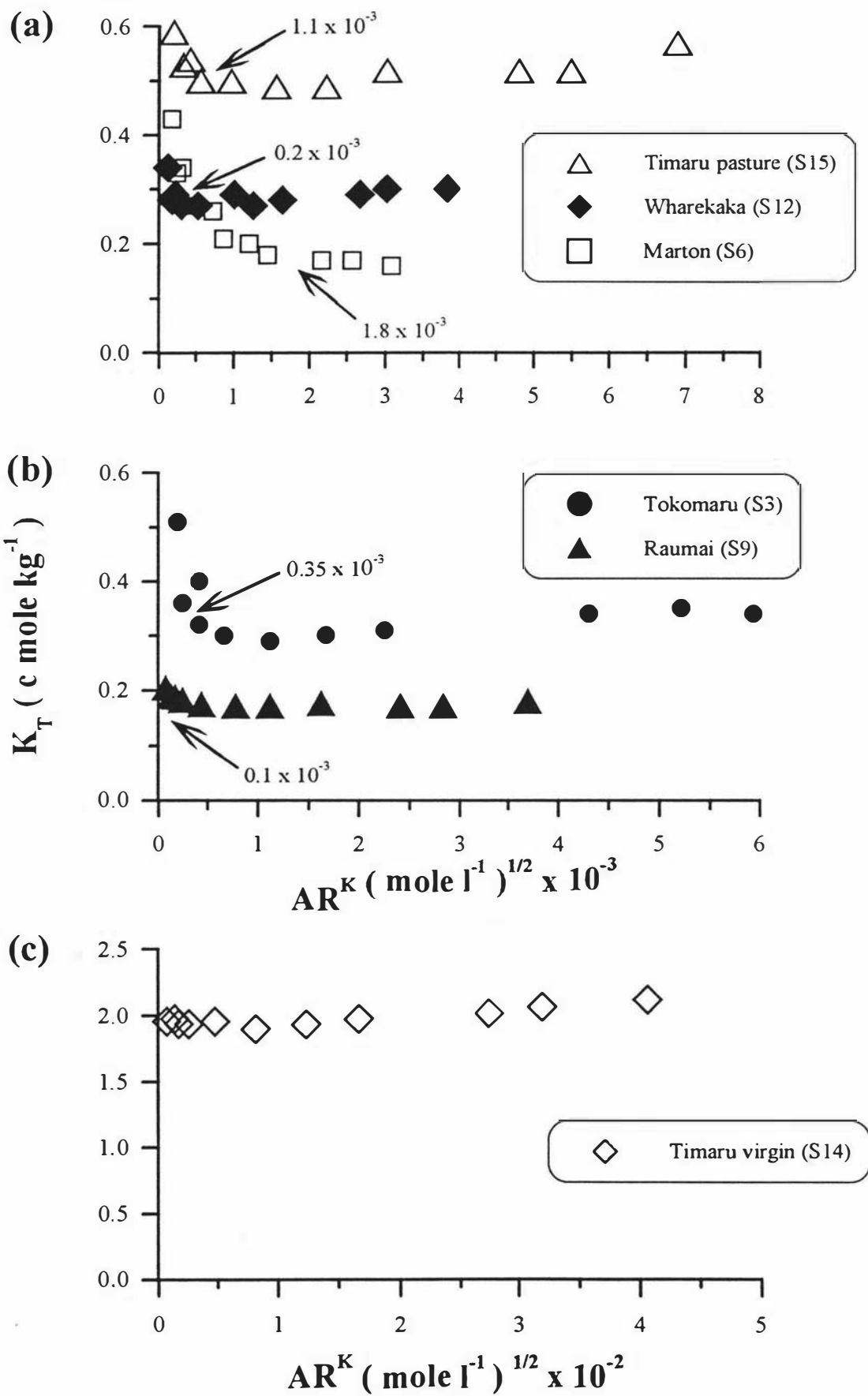


**Fig. 5.3 Relationship between total K extracted ( $K_T$ )<sub>89</sub> with K concentration in an equilibrated solution of 0.01 M CaCl<sub>2</sub> ( $K_s$ )**



**Fig. 5.4 Relationship between total K extracted ( $K_T$ )<sub>90</sub>**

**and K-Ca activity ratio ( $AR^K$ ) of soils**



$AR^K$ , and  $K_{ex}$  could not be determined for the undeveloped Timaru soil (S14) from the curves (Fig. 5.2, 5.3, and 5.4) despite its high K releasing/supplying power (Table 5.1). This indicated that a concentration of  $0.041 \text{ mM l}^{-1}$  in the equilibrated soil solution even at the widest soil:solution ratio (1:400) was insufficient to initiate release of  $K_{ex}$  to soil solution.

Attempts to reduce the K concentration to minimum levels in the undeveloped Timaru soil (S14) by widening the soil:solution ratios (1:800, 1:1000, and 1:2000) still further only lowered the K concentrations to  $0.022$ ,  $0.018$ , and  $0.009 \text{ mM l}^{-1}$ , respectively, with no appreciable increase in  $K_T$ . This indicated that the K concentration in the equilibrating soil solution was still too high to allow release of K from  $K_{ex}$  sources. This was peculiar because the remainder of the soils had threshold K levels more or less in the range of the above levels of K concentration in the equilibrating solution.

The threshold K levels in terms of equilibrium K concentration in  $\text{CaCl}_2$  solution for the 6 soils are presented in Table 5.3. These values are in the lower range of the threshold K levels of some Indian soils ( $0.025$  to  $0.300 \text{ mM l}^{-1}$ ) reported by Datta and Sastry (1988 and 1991). For the 6 soils in this chapter which contain variable reserves of micaceous minerals, however, the threshold K levels varied widely from soil to soil. Of interest is that, this variation is not in accordance with the variation of  $K_{ex}$  availability to ryegrass grown to K exhaustion in the glasshouse (Chapter 4) or with the variation of measures of  $K_{ex}$  releasing power (Chapters 4 and 6), as was hypothesised. For example, the Raunaki soil (S9) which had contributed the maximum  $K_{ex}$  to plant uptake (Table 5.1) has a threshold K level 7.7 times less than the Marton soil (S6) which did not contribute any  $K_{ex}$  to plant uptake. Similarly, there is an unexpected trend for the threshold K levels of other soils. The threshold K level of Wharekaka soil (S12) is lower than that of Marton (S6), and developed Timaru soil (S15).

The threshold K levels in terms of equilibrium K concentration in  $\text{CaCl}_2$  solution seemed to be analogous to the  $C_0$  measurement (the concentration of K in the soil solution at the point of zero change of non-exchangeable K) of Jackson and During (1979). Across a range of New Zealand soils  $C_0$  values, however, were not related to

**Table 5.3** Threshold K levels (mean of duplicates) in terms of K concentration in equilibrium soil solution,  $K_{ex}$ , and  $AR^K$ , and the amount of specifically held K

Soil No.	Soil name	Solution K concentration (mM l <sup>-1</sup> )	$K_{ex}$ (c mole kg <sup>-1</sup> )	$AR^K$ (mole l <sup>-1</sup> ) <sup>1/2</sup>	Specifically held K (c mole kg <sup>-1</sup> )	$K_G$ (mole l <sup>-1</sup> ) <sup>-1/4</sup>
S6	Marton	0.115	0.095	0.0018	0.135	4
S3	Tokomaru	0.025	0.090	0.00035	0.220	4
S12	Wharekaka	0.020	0.110	0.0002	0.220	6
S15	Timaru (b)	0.060	0.165	0.0011	0.390	6
S14	Timaru (a)	-	-	-	1.245	4
S9	Raumai	0.015	0.045	0.0001	0.105	3

- Note:**
1. Threshold K levels are expressed in terms of equilibrium K concentration,  $K_{ex}$ ,  $AR^K$ , or specifically held K
  2.  $K_G$  value corresponds to the point where the curve of  $K_G$  versus  $K_{ex}$  rises in Fig. 5.5



the  $K_{nex}$  fraction of the uptake by ryegrass. No explanation was given to this effect.

From Table 5.3 it can be seen that threshold K levels in terms of  $AR^k$  and  $K_{ex}$  also did not follow the expected trend.

### 5.3.2 Relationship between Gapon constant ( $K_G$ ) and $K_{ex}$

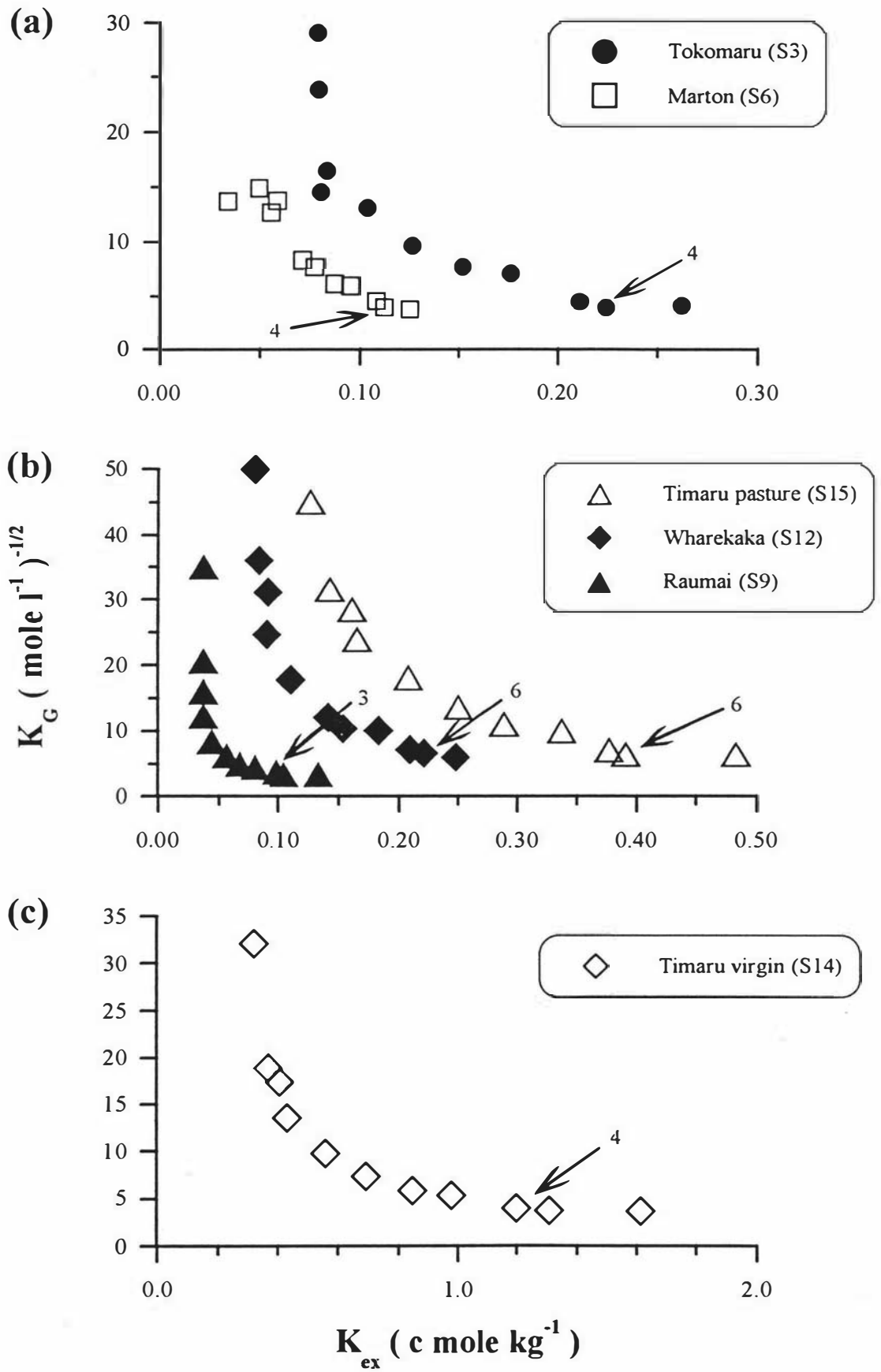
The curves of  $K_G$  versus  $K_{ex}$  (Fig. 5.5) for most of the soils seemed to have a continuous gentle curve unlike the curves in Fig. 5.2, 5.3, and 5.4. Below a certain level of  $K_{ex}$ ,  $K_G$  rises. The level of  $K_{ex}$  at this increase in  $K_G$  value corresponds to the amount of specifically held K in the wedge zones. The corresponding values of  $K_G$  on the y-axis gives a measure of the strength of binding of  $K^+$  relative to  $Ca^{++}$  on the planar (p-) positions of the clay surface.

From Fig. 5.5 and Table 5.3 it can be seen that the levels of  $K_{ex}$  below which the value of  $K_G$  increases are 0.135, 0.220, 0.220, 0.390, 1.245, and 0.105 c mole  $kg^{-1}$  for S6, S3, S12, S15, S14, and S9, respectively. These amounts of  $K_{ex}$  are specifically held and are present in the wedge zones. As expected, the sequence for specifically held K followed more or less the same order as threshold K levels in terms of  $K_{ex}$  (Table 5.3). This is because of the mechanism for  $K_{nex}$  release described in section 5.1. As was the case for solution K concentration, the amount of specifically held K did not predict differences in  $K_{nex}$  uptake by ryegrass.

### 5.3.3 Variation of threshold K levels

As suggested by Datta and Sastry (1991) the variation of threshold K levels may be attributed to a number of factors. These include the type of K bearing minerals, the predominance of tri- or di- octahedral components, structural irregularities, specific sites (development of wedge zones and the amount of specifically held K), cleavage planes and the amount of  $K_{nex}$  (reserve K) as measured by chemical methods. The amount of specifically held K in relation to threshold K level (in terms of  $K_{ex}$ ) is discussed in the earlier section.

**Fig. 5.5 Relationship between Gapon constant ( $K_G$ )<sup>94</sup> and exchangeable K ( $K_{ex}$ ) of soils**



An attempt to relate measures for  $K_{\text{dex}}$  releasing power viz, step K and  $K_c$  with the threshold K levels indicated that the Raumai soil (S9), had the lowest threshold K level (Table 5.3), but had relatively high amounts of  $K_{\text{dex}}$  measured by step K (106 mg 100 g<sup>-1</sup>) and  $K_c$  (17.33 mg 100 g<sup>-1</sup>) methods, when compared with the Tokomaru (S3) and Marton (S6) soils (Table 5.1). Similarly, the developed Timaru soil (S15) has twice the amount of soil  $K_{\text{dex}}$  as the Marton (S6), but had a threshold K level (in terms of K concentration) only half that of the latter. Nevertheless, one would expect that both the threshold K level and the amount of the plant available  $K_{\text{dex}}$  (measure of K supplying power), would be dependent on the clay structure and the degree of expansion and hence follow a similar trend.

It can be argued that rather than the threshold K level which is the concentration of the equilibrating soil solution below which  $K_{\text{dex}}$  release into the soil solution occurs, the increase in  $K_T$  beyond the threshold K level i.e.,  $K_T$  at the widest soil:solution ratio minus  $K_T$  at threshold K level may be a better parameter than the threshold K concentration itself, for comparing plant  $K_{\text{dex}}$  uptake in the pot trial. This is because both the total plant  $K_{\text{dex}}$  uptake and the increase in  $K_T$  beyond threshold K level are quantity factors that can be related to each other. The higher plant  $K_{\text{dex}}$  uptake of the Raumai soil (S9) than, for example, the Marton soil (S6), may not necessarily result in a higher threshold K level (in terms of equilibrium K concentration in soil solution) because over a period of time this level ( $K_s$ ) may be constantly replenished resulting in greater release of  $K_{\text{dex}}$ . The equilibrium K concentration at the threshold K level for S6, on the other hand, may have been only maintained for a short period of time, which indicates these soils are highly selective for K at wedge sites at very low K saturation. Inspection of Table 5.4, however, indicated that there was no relationship between  $K_{\text{dex}}$  uptake and any increase in  $K_T$  beyond the threshold K level. For example, the increase in  $K_T$  beyond the threshold K level is much higher for the Marton soil (S6) than for the Raumai soil (S9).

It appears therefore that there was a different trend of threshold K level in this experiment compared to that expected from the  $K_{\text{dex}}$  availability to plants in the pot trial (Chapter 4). This is in addition to the difficulty in determining the threshold K level

**Table 5.4 Increase in  $K_T$  beyond threshold K level in relation to  $K_{dex}$  uptake**

Soil No.	Soil name	$K_T$ at widest soil:solution ratio (1:400)	$K_T$ at threshold K level *	Increase in $K_T$ beyond threshold level	$K_{dex}$ uptake from unleached soils (Table 5.1)
		c mole $kg^{-1}$			
S6	Marton	0.43	0.17	9.47	-
S3	Tokomaru	0.51	0.31	0.20	-
S12	Wharekaka	0.34	0.27	0.07	0.05
S15	Timaru (b)	0.59	0.50	0.09	0.20
S14	Timaru (a)	1.96	-	-	0.68
S9	Raumai	0.21	0.18	0.02	1.05

\* Identified from solution K versus  $K_T$  graphs (Fig. 5.3)

for S14 (undeveloped Timaru soil). These inconsistencies may be attributed to the differences in the mechanism of  $K_{\text{nex}}$  release in the method of determining the threshold K level in the laboratory, and in growing plants to K exhaustion in the glasshouse. Both involved reduction of K concentration in the soil solution which is a prerequisite for  $K_{\text{nex}}$  release. But there were two important differences.

In the pot experiment, the lowering of K concentration in the soil solution was achieved by continuous uptake of K by roots, but in the threshold K level experiment, it was effected by increasing the soil:solution ratio. The constant uptake of K by plants may place greater drain on the soil. This, however, may not be a major criticism because in the present experiment K concentrations were sufficiently lowered to induce  $K_{\text{nex}}$  release. Given this the rhizosphere effects are a major possibility.

While the pH of 0.01 M  $\text{CaCl}_2$  varied over the period of the threshold K level experiment (6.7 to 8.3) that of the rhizosphere pH is expected to be lower due to  $\text{NH}_4^+$  used in the pot experiment (in the minus K nutrient solution) and also due to net proton extrusion by roots. Net proton extrusion by plant roots was regarded as a strategy by which  $K_{\text{nex}}$  is released to soil solution (Jungk and Classen, 1986; Tributh *et al.*, 1987).  $\text{NH}_4$  is not only likely to replace interlayer K at the edges of the particles, but it may also cause the layers to collapse at the edges, entrapping K at sites in the interlayer position (van Diest, 1978).

It was thought therefore that the shaking time (1 h) used by Datta and Sastry (1991) may be too short to bring about the expected trend in the threshold K levels. The study on the changes in solution and exchangeable K with increasing shaking times (1, 24, 72, and 144 h) at 1:400 soil:solution ratio, however, indicates (Table 5.5) that shaking time is not a limiting factor for obtaining the expected trend of threshold K levels. Interestingly, K concentration of the Marton soil (S6) dropped to about 50% after 144 h of shaking time which indicates possible fixation of K at reduced K concentrations.

**Table 5.5 Changes in Solution and Exchangeable K (mean of duplicates) with increasing shaking time (h) at 1:400 Soil:CaCl<sub>2</sub> solution ratio**

Soil No.	Soil name	K concentration in equilibrium soil solution K (mg l <sup>-1</sup> )				Exchangeable K (c mole kg <sup>-1</sup> )			
		1 h	24 h	72 h	144 h	1 h	24 h	72 h	144 h
S5	Marton	0.29	0.23	0.24	0.13	0.05	0.06	0.06	0.04
S3	Tokomaru	0.30	0.29	0.33	0.29	0.07	0.08	0.08	0.09
S12	Wharekaka	0.29	0.30	0.30	0.25	0.08	0.08	0.08	0.08
S15	Timaru (b)	0.45	0.42	0.45	0.46	0.12	0.11	0.13	0.11
S14	Timaru (a)	1.70	1.75	1.85	1.80	0.24	0.24	0.27	0.26
S9	Raumai	0.44	0.29	0.28	0.27	0.03	0.04	0.04	0.04

## 5.4 CONCLUSIONS

1. The threshold K level method of Datta and Sastry (1991) is not suitable for characterising the soils in this study on the basis of  $K_{\text{nex}}$  supply/release. It is concluded that the threshold K levels (in terms of equilibrium K concentration,  $K_{\text{ex}}$ , and  $AR^K$ ) and the amount of specifically held K determined in this experiment do not concur with  $K_{\text{nex}}$  uptake.
2. Measurement of the equilibrium K concentration in the  $\text{CaCl}_2$  soil solution below which  $K_{\text{nex}}$  release is initiated may not be representative of the situation in the rhizosphere. The discord between the threshold K levels and crop performance possibly results from and underscores the role of  $\text{H}^+$  and  $\text{NH}_4^+$  in the release of K in the rhizosphere during crop growth.

## CHAPTER 6

# ASSESSMENT OF THE K RELEASING POWER OF YGE SOILS IN RELATION TO PLANT AVAILABLE K USING SELECTIVE SOIL TESTING PROCEDURES

### 6.1 BACKGROUND

There is an increasing awareness of the need to apply K fertilizers at rates which are adequate to maintain high pasture production levels. Soil testing procedures (methods of assessing K releasing power that give an index of soil K supply, section 2.8) therefore must provide reliable data to ensure that plant K demand is matched by optimum application rates. The usefulness of a soil test depends on the reliability of the measurement and other criteria relevant to a particular crop. The soil test should require a minimum of calibration, and once calibrated, it should reliably predict the extent of the response of plants to added K.

It has long been recognised that for some New Zealand soils the current soil test (quick test K measurement using  $\text{NH}_4\text{OAc}$  i.e, QTK) level does not necessarily represent the true plant available K status (Williams *et al.*, 1986). A low QTK level may not always indicate a lack of plant available K in the soil. This problem is apparent for the YGE soil group (P.E.H. Gregg, pers. comm.) where accurate prediction of K responsiveness using QTK has long been difficult because of the variable amounts of micaceous minerals which seem to be a major source of available non-exchangeable K. For example, the less leached and less weathered YGE soils (e.g., Timaru silt loam) in the South Island appear to contain high  $K_{\text{nex}}$ /reserve K (as assessed by  $K_c$ ), whereas the more leached and more weathered YGE soils (e.g., Marton silt loam) in the North Island appear to have low  $K_{\text{nex}}$  (section 2.7.2.3). Metson *et al.* (1956) pointed out that exchangeable K ( $\text{NH}_4\text{OAc}$  extractable) is often quite low in the YGE soils, although their K supplying power remains high.



As pointed out in Chapter 2 (section 2.7.2.3)  $K_c$  is considered as the long term rate of  $K_{nex}$  releasing power. Although it may be giving an indication of K releasing power, the fact that it does not measure  $K_{cx}$  and short term  $K_{nex}$  release makes it unsuitable as a soil test by itself.

The failure of these soil tests (QTK, and  $K_c$ ) to serve as a good predictor for K supplying power (plant available K) in the K fertilizer recommendation model led to the development of sodium tetraphenyl boron (NaTPB) extractable K (Jackson, 1985). In a pot trial that covered a wide range of soil types in New Zealand including some YGE soils, Jackson (1985) found that NaTPB K was highly correlated with K uptake by ryegrass. But for routine determination of plant available K status, the NaTPB reagent is not suitable owing to its high cost and lengthy procedure. Furthermore, R.G. Smith (pers. comm.) pointed out that there is little justification for using the NaTPB test on YGE soils in the Manawatu region because these soils contained a reasonably constant ratio of exchangeable K to NaTPB K.

It seems reasonable to conclude that there is no method to assess K releasing power, which gives an extensive understanding of the plant available K status of New Zealand soils. The present study seeks to identify a method to assess K releasing power for predicting plant available K so as to enable accurate fertilizer K requirements. In this chapter a range of soil testing procedures is described with a view to assessing the plant available K status of YGE and related soils using the dry matter yield and the K uptake data from Chapter 4. The soil testing procedures chosen are QTK,  $K_{cx}$ , resin K,  $K_c$ , NaTPB K, and an acid extraction procedure.

There are indications that sand and silt fractions of some New Zealand soils can account for appreciable proportions of non-exchangeable K (Metson *et al.*, 1956; Lee and Gibson, 1974). This study also aims to assist in understanding the K releasing power of the soil separates (sand, silt, and clay) and thus the contribution of K bearing primary minerals to the plant available K pool. The primary objectives of this study are therefore:

1. To assess the effectiveness of several soil testing procedures to predict dry matter yield and K uptake by ryegrass in the pot trial.
2. To assess the acid-extractable K levels in the soil separates.

## 6.2 MATERIALS AND METHODS

### 6.2.1 Soils

The 19 soils used in this study have been described in Chapter 3. The artificially leached soils (Chapter 4) were also used in this study.

### 6.2.2 Plant growth studies

The dry matter yields and the K uptake data from the unleached and leached soils in Chapter 4 were used in this study.

### 6.2.3 Chemical extraction methods for assessing K releasing power

#### 6.2.3.1 *Conventional methods*

Quick test K, resin K,  $K_c$ , and NaTPB K for the unleached soils were determined using the methods of Mountier *et al.* (1966), Saggar *et al.* (1990), Blakemore *et al.* (1987), and Jackson (1985), respectively. The  $K_{ex}$  data for unleached and leached soils were obtained from Chapter 4. Acid-extractable K of unleached and leached soils was determined using the method described in section 6.2.3.3.

Since  $K_c$  is expected to be unaffected by short term cropping (Haylock, 1956a; Lee and Gibson, 1974; Metson, 1980) no attempt was made to measure  $K_c$  in the unleached soils after cropping and in the leached soils. QTK, resin K,  $K_c$ , and NaTPB K were not determined for the leached soils.

### 6.2.3.2 *Standardisation of an acid extraction procedure*

The first extract of the  $K_c$  method, obtained by treating the soil with boiling 1 M  $HNO_3$  at a wide soil:solution ratio includes  $K_{ex}$ , plus the more soluble portion of  $K_{dex}$  (Metson, 1980). This is referred to as the acid extraction procedure (acid-extractable K) in this study.

To standardise the methodology of the acid extraction procedure the soils were treated with boiling 1 M  $HNO_3$  at a wide soil:solution ratio (1:100) over two time periods and the K extracted was compared with the K uptake by ryegrass from the unleached soils. The correlation coefficient ( $r$ ) of the acid-extractable K with plant K uptake by ryegrass from the unleached soils decreased from 0.96 to 0.88 as the boiling time was increased from 20 min to 200 min using a reflux condenser. Nevertheless, the longer boiling time extracted greater amounts of K, the range after 200 min being 74-219 mg 100 g<sup>-1</sup> compared with 34-147 mg 100 g<sup>-1</sup> extracted by 20 min boiling from the Marton (S5) and the undeveloped Timaru (S14) soils, respectively. The 20 min boiling time was therefore preferred because of its higher predictive value ( $R^2 = 92\%$ ) and was chosen as a practical extraction time. The "step K" computed from the 200 min boiling acid-extractable K and the  $K_{ex}$  ( $NH_4OAc$  extractable) of the unleached soils were also well correlated with  $K_{dex}$  uptake by ryegrass from the unleached soils ( $R^2 = 82\%$ ).

### 6.2.3.3 *Acid extraction procedure*

To 2 g soil in a 400 ml wide-mouthed conical flask were added 200 ml 1 M  $HNO_3$ . The suspension was boiled for 20 min with a small conical flask inverted in the neck to act as a reflux condenser. The water lost by boiling was measured by the difference in the weight of the flask before and after boiling. This amount of distilled water was used for transferring the contents of the flask into a 250 ml centrifuge bottle, which was centrifuged for 5 min at 2000 rpm. An aliquot was taken and diluted with distilled water by a factor of two. Potassium in the diluted aliquot was measured against K standards in 0.5 M  $HNO_3$  matrix.

The use of a small conical flask as a reflux condenser, the inconsistency in the weight differences of the  $\text{HNO}_3$  solution before and after boiling for different extractions, and the use of distilled water to make up the weight loss due to boiling presumably altered the concentration of the acid. Nevertheless, when the final aliquot was measured against the background concentration of 0.3, 0.4, and 0.6 M  $\text{HNO}_3$ , the differences in the acid-extractable K were negligible (data not presented). This indicated that the concentration of the acid in the boiled solution did not affect the extractable K levels at the levels of matrix solution concentrations examined.

#### **6.2.3.4 Step K**

Since the acid-extractable K includes  $K_{\text{ex}}$  and a portion of  $K_{\text{nex}}$ , a single measurement of  $K_{\text{nex}}$  releasing power was obtained by subtracting  $K_{\text{ex}}$  ( $\text{NH}_4\text{OAc}$ -extractable) from the acid-extractable K. This was called "step K" (section 2.7.2.3).

Alternatively, step K was computed using the QTK method of assessing  $K_{\text{ex}}$  releasing power. This was entitled as "quick step K" (QSK).

#### **6.2.4 Sand and silt separation**

On completion of the particle size analysis (Chapter 3), the silt fraction (2-63  $\mu\text{m}$ ) was separated from the silt plus clay suspension by repeated centrifugations (1000 rpm for the appropriate period of time based on the temperature of the suspension) and washings until the suspension was clear (Kirkman and Pullar, 1978). The sand fraction was separated by wet sieving using a 63  $\mu\text{m}$  sieve. No attempt was made in this study to obtain a clay separate from the clay suspension.

#### **6.2.5 Relative contribution of the soil separates to whole soil acid-extractable K**

The acid-extractable K in the peroxidised soil, sand, and silt was determined by the method described in section 6.2.3.3. Any acid-extractable K lost due to the peroxidation treatment was obtained by the difference between the acid-extractable K

before and after peroxidation. The percent contributions of the acid-extractable K from sand, and silt, on a whole soil basis were calculated using the following formula.

$$Y = \left( \frac{A}{C} \frac{B}{C} \right)$$

Where,

Y = Percent contribution of the acid-extractable K from sand or silt calculated on a whole soil basis

A = Percent sand, or silt in the soil (Table 3.2)

B = Acid-extractable K of the soil separate (mg 100 g<sup>-1</sup>)

C = Acid-extractable K of the peroxidised soil (mg 100 g<sup>-1</sup>)

Since no attempt was made in this study to separate the clay fraction for determination of acid-extractable K, the percent contribution of acid-extractable K from the clay fraction (Z) was calculated indirectly by difference as suggested by Lee and Gibson (1974), and Lee and Widdowson (1977). The acid-extractable K of the clay was then computed using the following equation.

$$\text{Acid-extractable K of clay} = \left( \frac{Z}{A} \frac{C}{A} \right)$$

Where,

C = Acid-extractable K of the peroxidised soil (mg 100 g<sup>-1</sup>)

A = Percent clay in the soil (Table 3.2)

## 6.3 RESULTS AND DISCUSSION

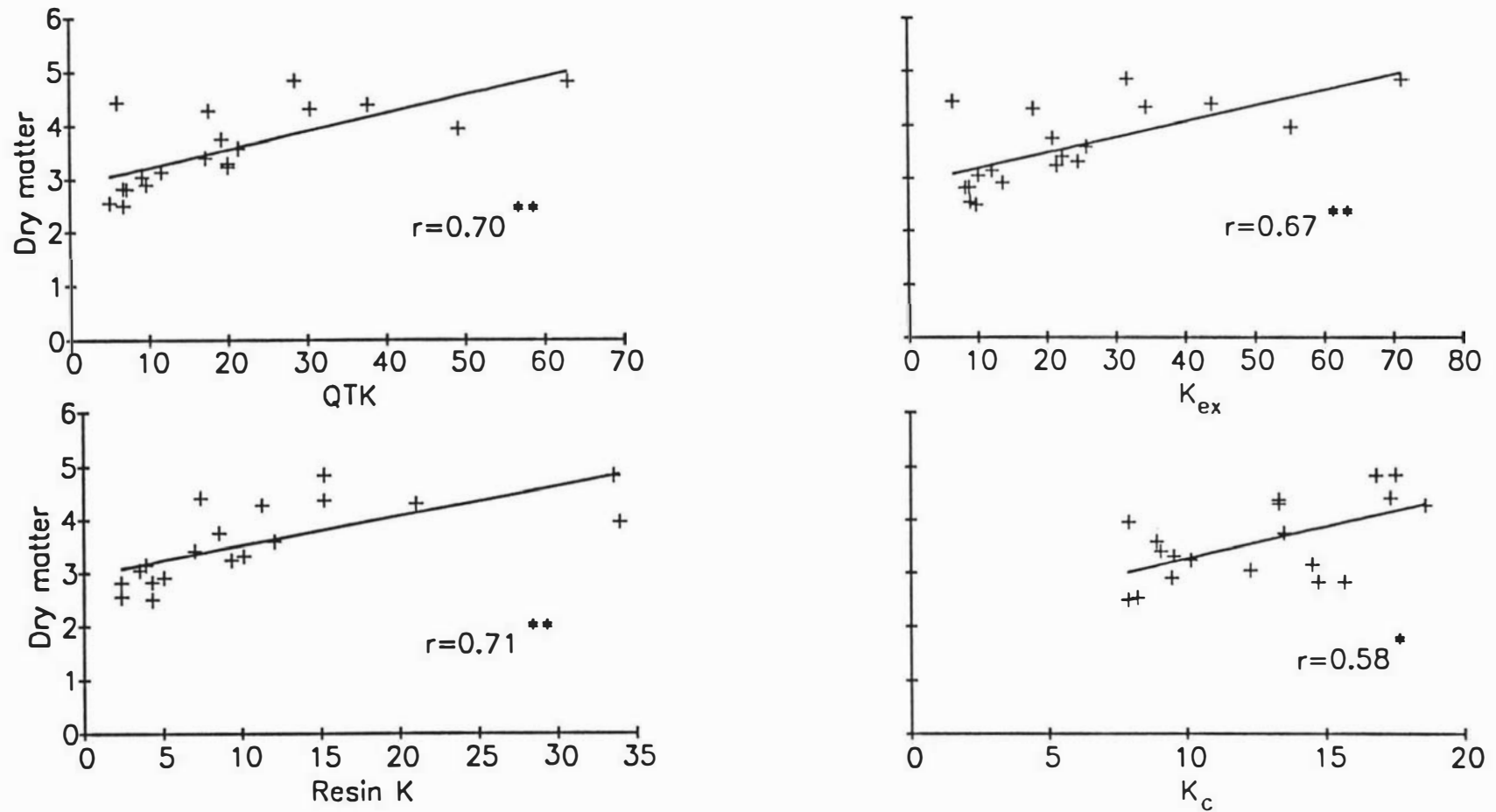
### 6.3.1 Relationship between soil tests and dry matter yield of ryegrass grown on the unleached and the leached soils

Correlation and regression analyses between the six soil tests and the total dry matter of ryegrass tops (shoots) grown on the unleached soils are shown in Fig. 6.1 and in Table 6.1. Except for  $K_c$ , which was correlated at the 5 % level, all other K extraction procedures were correlated at the 1 % level. The acid extraction method and the NaTPB K gave the highest  $r$  values reported (Fig. 6.1), signifying their superiority over the other procedures.

While the exchangeable fraction of the unleached soils measured partly or wholly by QTK, resin K, and  $K_{ex}$  explained 50 %, 50 %, and 45 % of the variation in dry matter yield of ryegrass, respectively, the acid extraction method and the NaTPB K accounted for 80 and 87 % of the variation, respectively (Table 6.1). Similar research in a pot experiment (Jackson, 1985) revealed K extracted by the NaTPB method to be more highly correlated to dry matter yield of ryegrass grown than QTK,  $K_{ex}$ , and  $K_c$  in a range of New Zealand soils. The results contradict the field research of Williams *et al.* (1986), who reported that  $K_{ex}$  levels of Recent South Island soils were better correlated with relative yield of pasture than NaTPB K.

When  $K_{ex}$  and step K measurements were included in the step-wise regression analysis, an increase in  $R^2$  value was observed for the unleached soils (Table 6.1). The increase in prediction was similar to that of the acid-extractable K as expected. A similar answer was obtained with a combination of QTK and step K as well as with QTK and "quick step K".

The findings conform to those reported by Barber and Matthews (1962) who found that the prediction of yield variation of wheat, oats, corn, and potatoes grown in the field was improved when both  $K_{ex}$  and "moderately available  $K_{mod}$ " were taken into account. The "moderately available  $K_{mod}$ " of Barber and Matthews is speculated to be analogous



**Fig. 6.1** Relationship between soil tests ( $\text{mg K } 100 \text{ g}^{-1}$ ) and dry matter yield ( $\text{g pot}^{-1}$ ) of ryegrass grown on the unleached soils

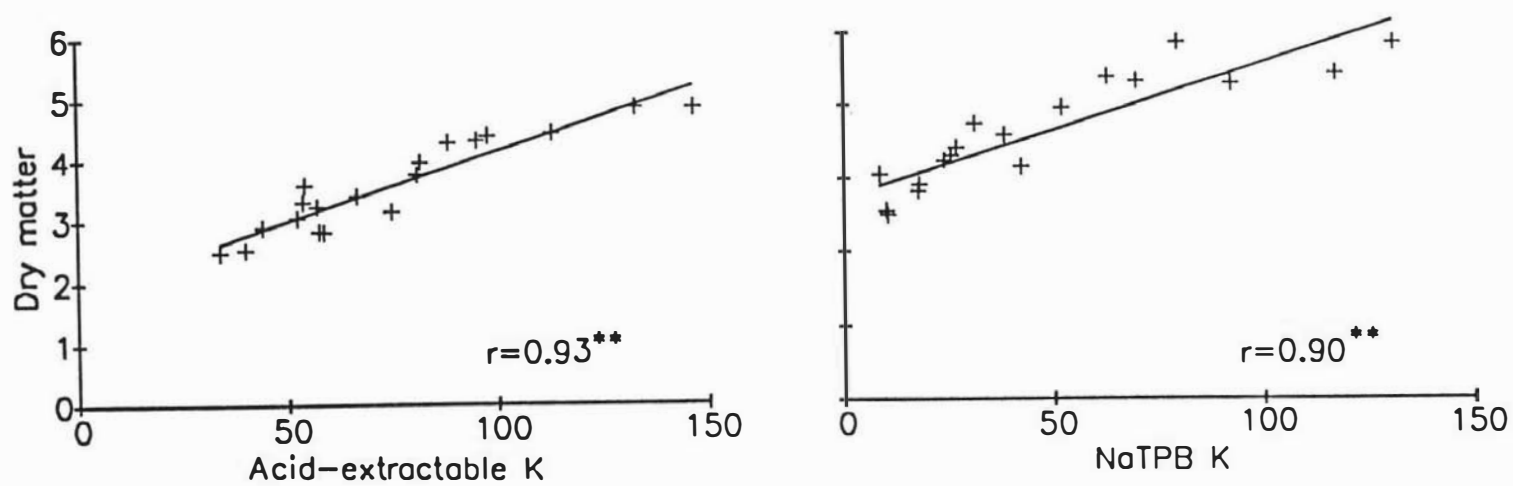


Fig. 6.1 (contd.)

Relationship between soil tests (mg K 100 g<sup>-1</sup>) and dry matter yield (g pot<sup>-1</sup>) of ryegrass grown on the unleached soils



**Table 6.1** Regression analyses between dry matter (g pot<sup>-1</sup>) and K releasing power (mg 100 g<sup>-1</sup>)

	Regression equation	R <sup>2</sup> (%)
Unleached soils	Y = 2.89 + 0.034 QTK	50
	Y = 2.95 + 0.057 Resin K	50
	Y = 2.89 + 0.029 K <sub>ex</sub>	45
	Y = 2.73 + 0.018 NaTPB K	80
	Y = 1.88 + 0.023 Acid-extractable K	87
	Y = 1.96 + 0.030 QTK + 0.020 Step K	88
	Y = 1.90 + 0.026 K <sub>ex</sub> + 0.021 Step K	88
	Y = 1.91 + 0.027 K <sub>ex</sub> + 0.020 QSK	88
Leached soils	Y = 2.96 + 0.005 <sup>NS</sup> K <sub>ex</sub>	1
	Y = 1.73 + 0.027 Step K	80
	Y = 1.42 + 0.028 Acid-extractable K	84
	Y = 1.26 + 0.045 <sup>NS</sup> K <sub>ex</sub> + 0.028 Step K	84

Y = Dry matter (g pot<sup>-1</sup>)

NS = Non significant

to the "step K" in the present study.

There was no relationship between the  $K_{ex}$  and the total dry matter yield of ryegrass for the leached soil treatment (Fig. 6.2). The new acid extraction procedure, however, was highly correlated with the dry matter yield, thus mirroring the results for the unleached soils.

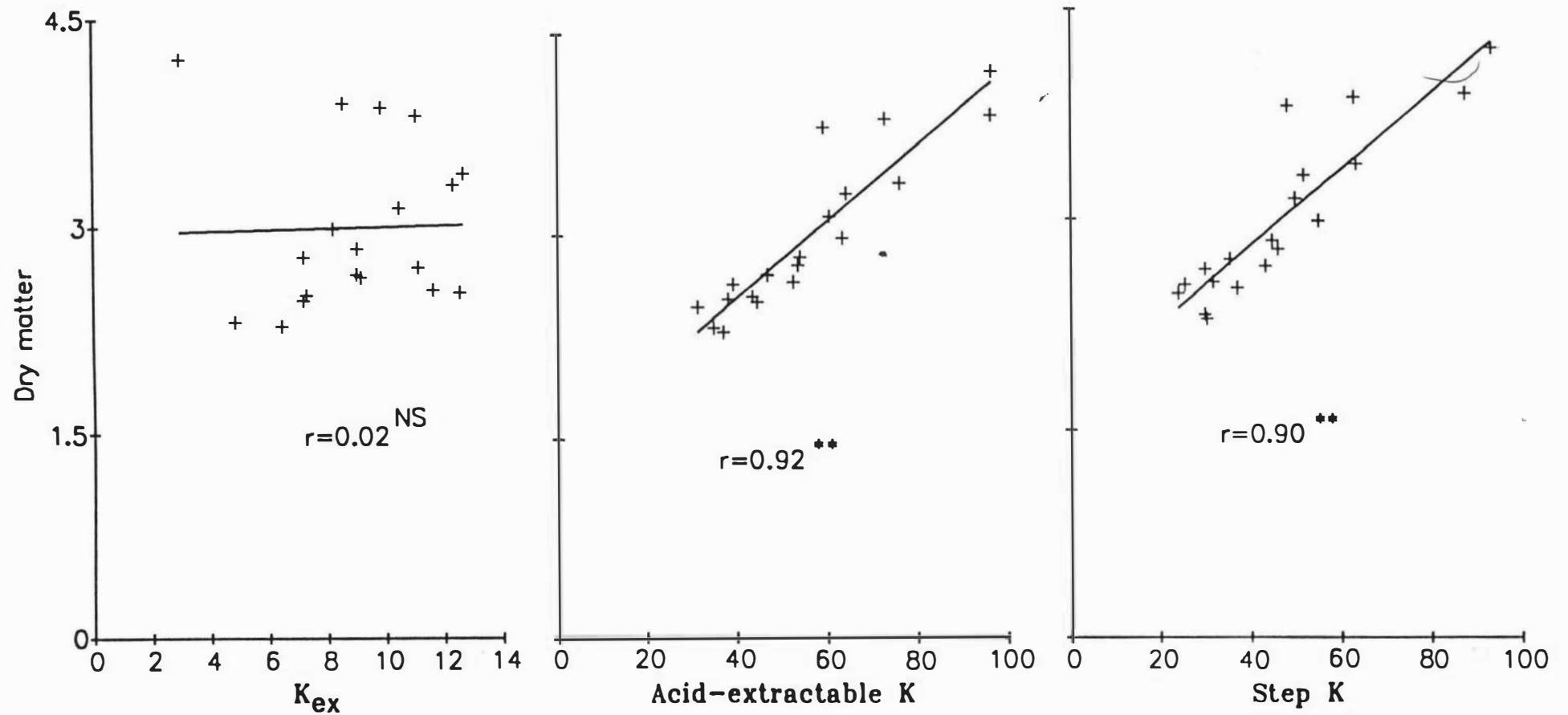
### 6.3.2 Relationship between soil tests and K uptake from the unleached and the leached soils

Figure 6.3 shows the correlation between soil tests for K, and K uptake by ryegrass from the unleached soils. All the K soil tests were significantly correlated with the K uptake. The highest  $r$  value of 0.96 was obtained with the acid-extractable K followed by NaTPB K (0.92).

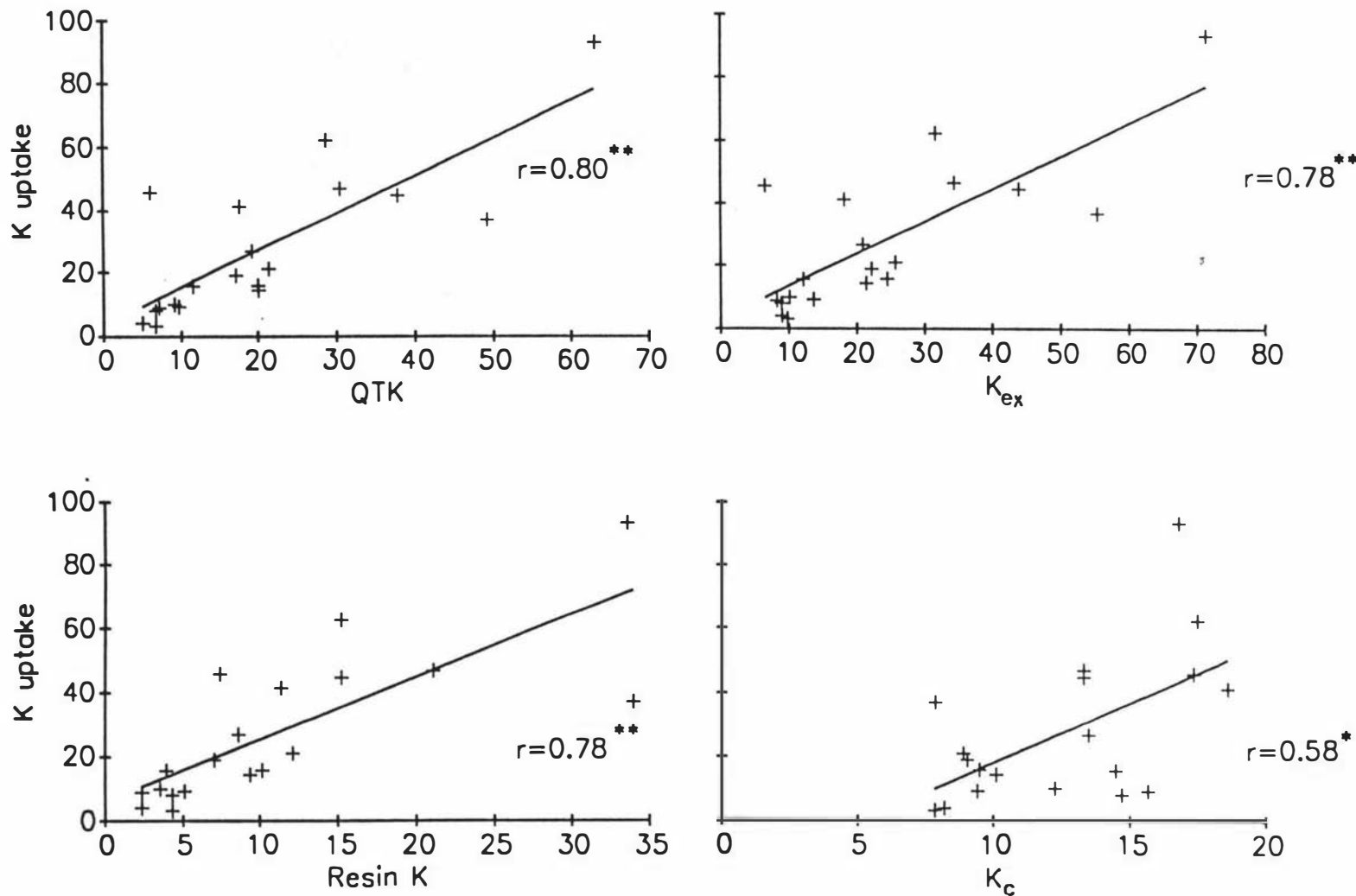
The regression analysis (Table 6.2) also revealed that about 92 % of the variation in the K uptake can be explained by the acid-extractable K while 85 % was explained by NaTPB K and about 60 % by the soil tests measuring only exchangeable K. Of the 19 YGE soils tested, 12 contributed  $K_{ncx}$  to plant uptake (Chapter 4). This was revealed by acid extraction procedure but not by the  $K_{ex}$  measurements. Similarly a poor prediction of K uptake by ryegrass with  $K_{ex}$ , and a good prediction with NaTPB K was observed by Jackson (1985) in a pot trial covering a wide range of New Zealand soils.

The results of Liu and Bates (1990), Wood and Schroeder (1992), and Grzebisz and Oertli (1993) showed that 1 M boiling  $HNO_3$  is the best predictor of plant available K. Furthermore, the results of Richards and Bates (1989) showed that K extracted by 0.1 M  $HNO_3$  explained more variation in total K uptake by eight crops of alfalfa grown in glasshouse than did 1 M  $NH_4OAc$ .

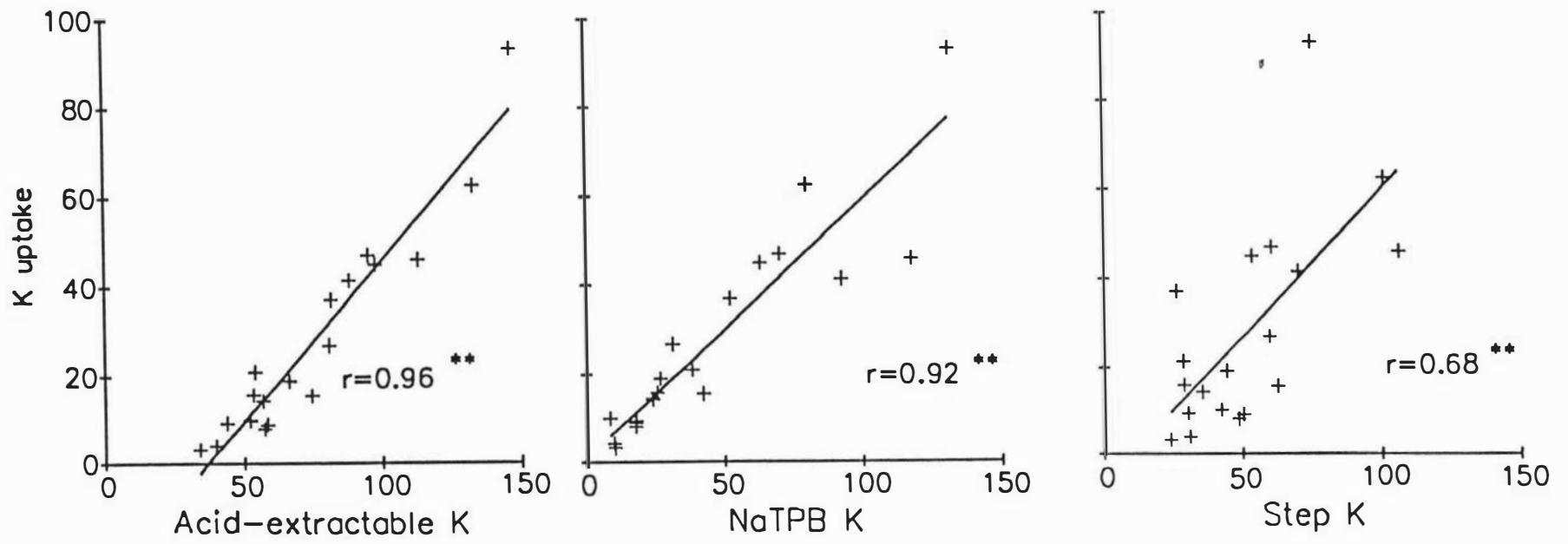
The  $K_c$  values on the other hand were poorly correlated ( $r = 0.58$ ) with K uptake from the unleached soils. This was because the readily exchangeable source (measured by the  $K_{ex}$  method) and the more soluble  $K_{ncx}$  (measured by the step K method) were not



**Fig. 6.2** Relationship between soil tests ( $\text{mg K } 100 \text{ g}^{-1}$ ) and dry matter yield ( $\text{g pot}^{-1}$ ) of ryegrass grown on the leached soils



**Fig. 6.3** Relationship between soil tests (mg K 100 g<sup>-1</sup>) and K uptake by ryegrass (mg 100 g<sup>-1</sup>) from the unleached soils



**Fig. 6.3 (contd.)** Relationship between soil tests (mg K 100 g<sup>-1</sup>) and K uptake by ryegrass (mg 100 g<sup>-1</sup>) from the unleached soils

**Table 6.2** Regression analyses between K uptake and K releasing power<sup>r</sup>(mg 100 g<sup>-1</sup>)

	Regression equation	R <sup>2</sup> (%)
Unleached soils	Y = 3.49 + 1.19 QTK	64
	Y = 5.46 + 1.95 Resin K	61
	Y = 3.14 + 1.04 K <sub>ex</sub>	60
	Y = -19.3 + 3.75 K <sub>c</sub>	33
	Y = -6.28 + 0.66 Step K	46
	Y = 0.68 + 0.59 NaTPB K	84
	Y = -26.7 + 0.73 Acid-extractable K	92
	Y = -35.1 + 1.11 QTK + 3.21 K <sub>c</sub>	88
	Y = -39.7 + 1.00 K <sub>ex</sub> + 3.48 K <sub>c</sub>	89
	Y = -22.8 + 1.07 QTK + 0.56 Step K	96
	Y = -24.5 + 0.98 QTK + 0.60 QSK	96
	Y = -25.5 + 0.10 K <sub>ex</sub> + 0.59 Step K	97
	Y = -26.5 + 0.10 K <sub>ex</sub> + 0.57 Step K + 0.18 <sup>NS</sup> K <sub>c</sub>	97
Leached soils	Y = 19.7 - 0.57 <sup>NS</sup> K <sub>ex</sub>	1
	Y = -17.7 + 0.69 Step K	83
	Y = -24.6 + 0.70 Acid-extractable K	83
	Y = -22.0 + 0.42 <sup>NS</sup> K <sub>ex</sub> + 0.70 Step K	83

Y = K uptake (mg 100 g<sup>-1</sup>)

NS = Non significant

included in the  $K_c$  measurement (Metson, 1980) and it is therefore unlikely to relate well to short term plant uptake (Jackson, 1985).

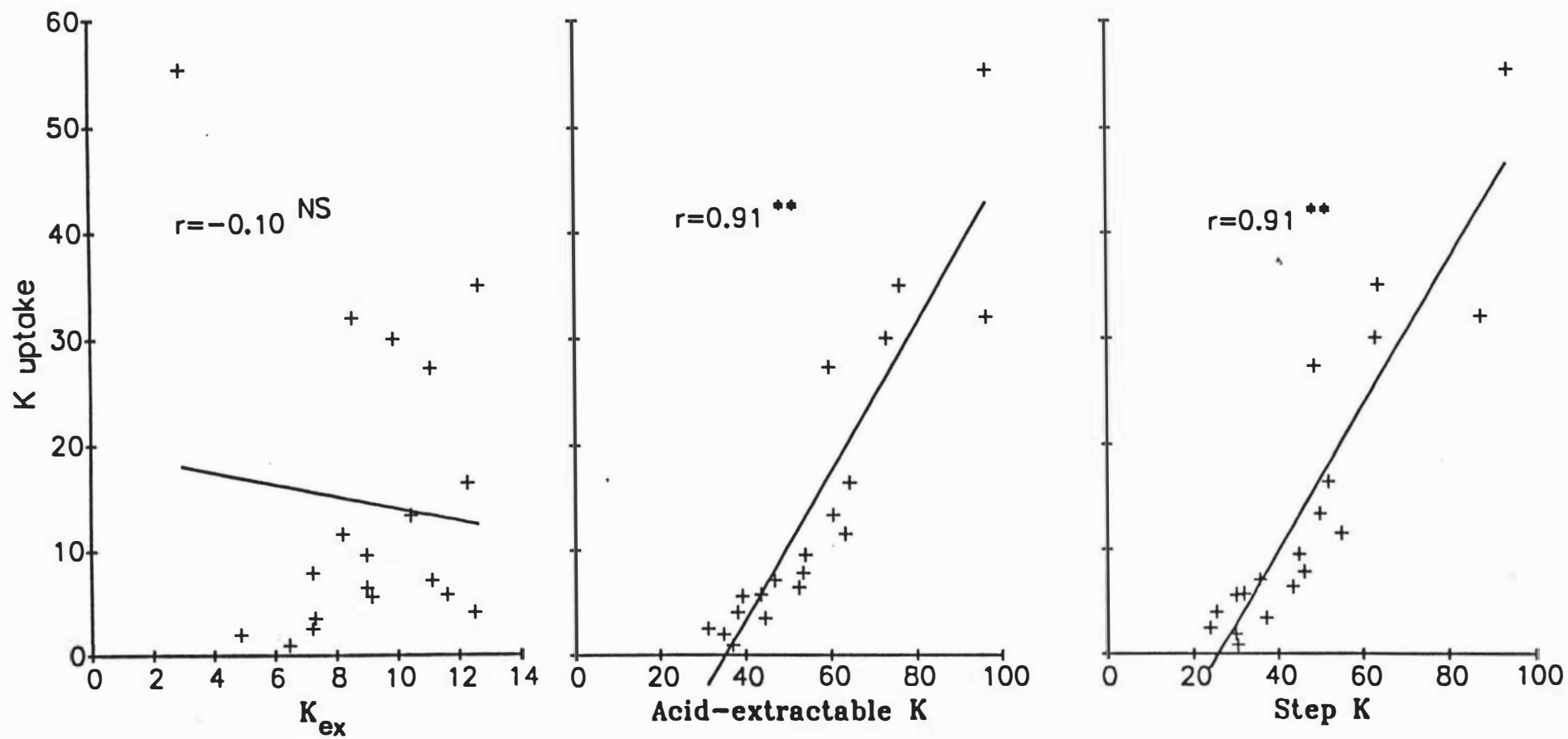
Step-wise regression analysis between the total K uptake and the soil tests (Table 6.2) showed a similar trend to that for the dry matter. It can be seen that a combination of the method used to assess  $K_{ex}$  release (QTK, or  $K_{ex}$ ) and the method used to assess  $K_{nec}$  release (step K, or quick step K) predicted K uptake better than the acid-extractable K alone. This might not be a satisfactory outcome considering the additional measurement (QTK, or  $K_{ex}$ ) required for the former soil tests.

Furthermore, a combination of step K and either of the methods of assessing  $K_{ex}$  releasing power ( $K_{ex}$ , or QTK) proved to better predict the variations of K uptake among the soils than a combination of  $K_c$  and the methods of  $K_{ex}$  release. When  $K_c$  was included in the regression model along with  $K_{ex}$  and step K there was no further improvement of  $R^2$ . The combination thus might have potential in replacing the current soil tests (QTK, and  $K_c$ ) used in New Zealand to predict soil K supply (gains). Liu and Bates (1990) also concluded that a combination of the  $NH_4OAc$ -extractable K and a measure of  $K_{nec}$  best predicts the availability of K in Ontario soils.

The correlations of  $K_{ex}$ , the acid extraction procedure, and step K with K uptake from the leached soils (Fig. 6.4) clearly indicates that the variations in the K uptake among the leached soils cannot be accounted for by  $K_{ex}$ . As these soils have low levels of  $K_{ex}$ , the acid-extractable K might well give a measure of  $K_{nec}$  releasing power.

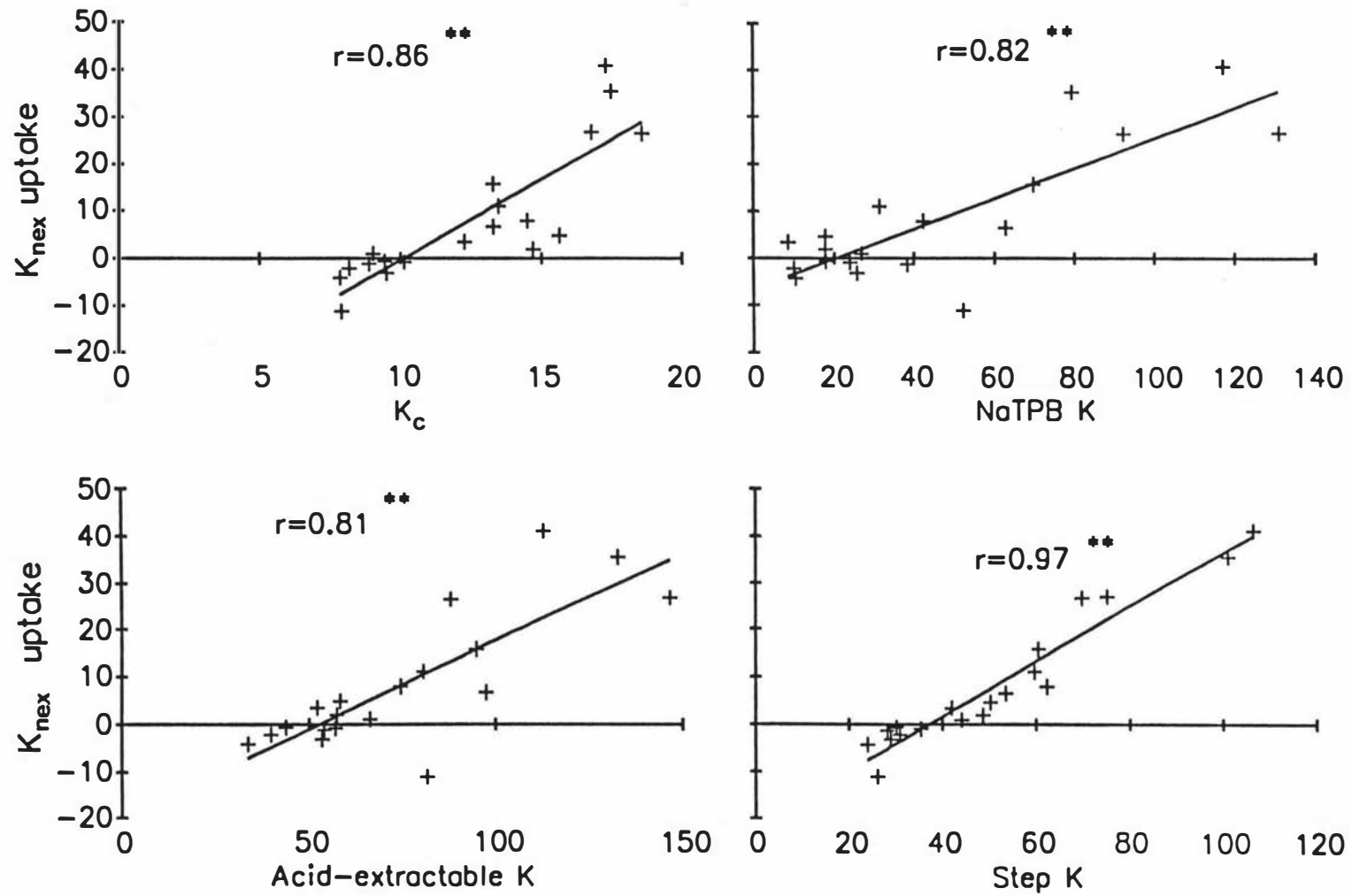
### 6.3.3 Relationship between soil tests and $K_{nec}$ uptake

Of all the methods for determining K releasing power in this study the step K method was significantly correlated with the  $K_{nec}$  uptake (a measure of  $K_{nec}$  supplying power), the highest  $r$  value being 0.97 for the unleached soils (Fig. 6.5) and 0.92 for the leached soils (Fig.6.6).

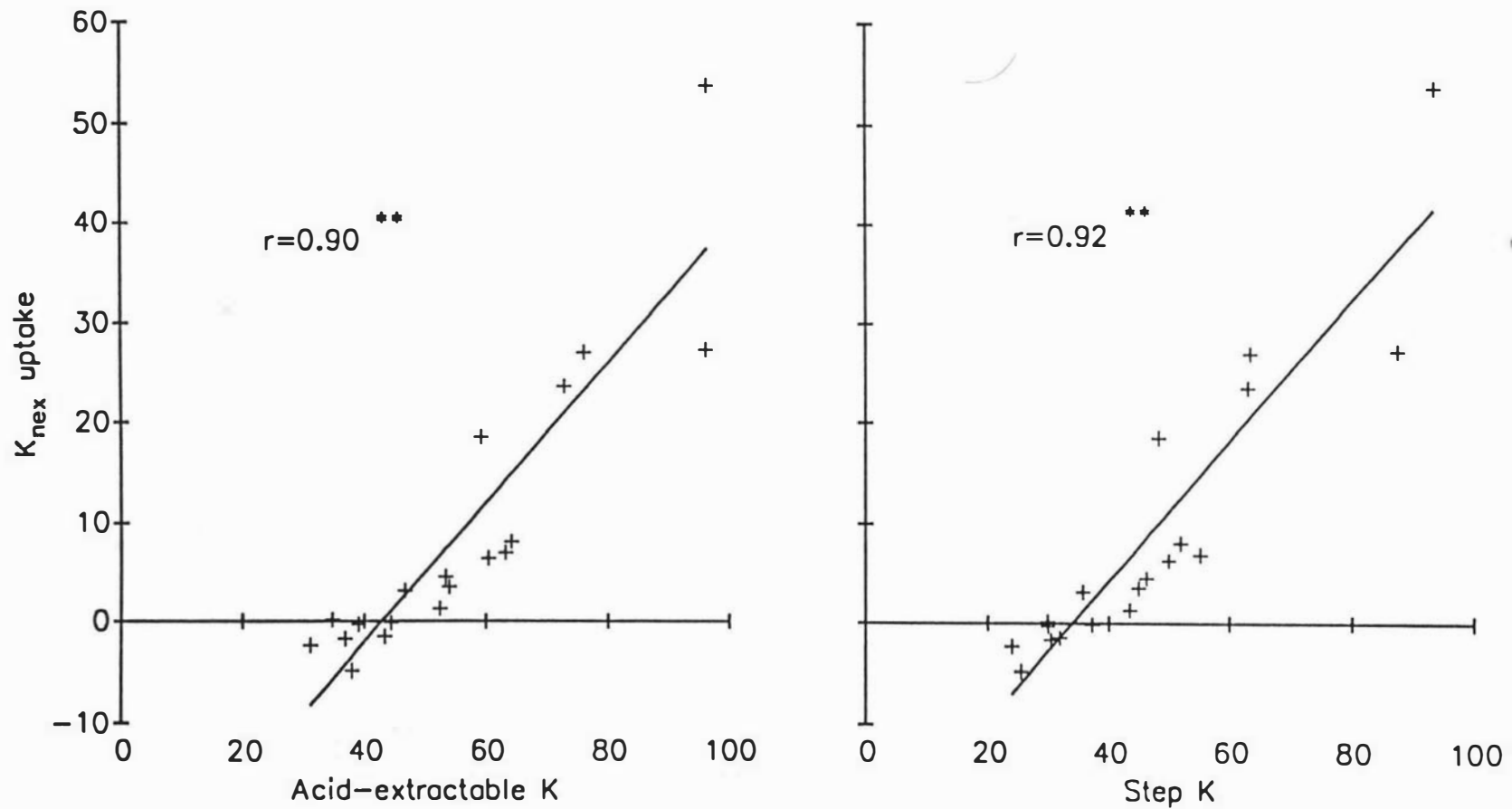


**Fig. 6.4** Correlation of soil tests (mg K 100 g<sup>-1</sup>) with K uptake (mg 100 g<sup>-1</sup>) from the leached soils





**Fig. 6.5** Correlation of  $K_c$ , NaTPB K, acid-extractable K, and step K with  $K_{nex}$  uptake from the unleached soils ( $\text{mg } 100 \text{ g}^{-1}$ )



**Fig. 6.6** Correlation of soil tests (acid-extractable K, and step K) with  $K_{n\text{ex}}$  uptake from the leached soils ( $\text{mg K } 100 \text{ g}^{-1}$ )

The closer relationship of  $K_{nec}$  uptake with step K than with the acid-extractable K and  $K_c$  confirms the finding of Hay (1971) who reported that the "step K" ( $K_{int}$ , section 2.7.2.3) values of A horizons of Canterbury loessial soils were well correlated with  $K_{nec}$  release to ryegrass plants grown to K exhaustion in the glasshouse.

The results of the present study are also in agreement with those reported by McLean (1961), and Richards and Bates (1988) who found that the "step K" of Canadian soils (whose clay mineralogy is dominated by illites with lesser amounts of vermiculites and chlorites) was more closely related to  $K_{nec}$  uptake by alfalfa than "constant rate K" (a measure of  $K_{nec}$  releasing power that is analogous to  $K_c$ ).

The "step K" in all the previous studies (Chapter 2 e.g., Haylock, 1956a; Metson *et al*, 1956; Hay, 1971; Richards and Bates, 1988) was also a calculated value, as for the present study. But the important difference is that this study provides the simplest method of measuring step K. For example, Richards and Bates (1988) obtained "step K" by the difference between "Mactotal K" (which is the total amount of  $K_{nec}$  extracted in seven sequential extractions with boiling 1 M  $HNO_3$ ) and the "constant rate K". This led them to conclude that if a simple method of measuring the more soluble fraction of  $K_{nec}$  i.e., "step K" can be found, soil tests for plant available K in Ontario soils may be greatly improved.

When  $K_c$  was included in the regression model along with step K (Table 6.3) there was no further increase in the percent prediction.

The step K in this study therefore seems to be a potential method for assessing plant available  $K_{nec}$ , which was not only an important but also a variable source of K to ryegrass grown to K exhaustion (Chapter 4).

**Table 6.3** Regression analyses between  $K_{\text{nex}}$  uptake and  $K_{\text{nex}}$  releasing power for unleached soils ( $\text{mg } 100 \text{ g}^{-1}$ )

Regression equation	$R^2$ (%)
$Y = -34.4 + 3.40 K_c$	74
$Y = -21.3 + 0.58 \text{ Step K}$	93
$Y = -22.5 + 0.55 \text{ Step K} + 0.20^{\text{NS}} K_c$	93

$Y = K_{\text{nex}}$  uptake ( $\text{mg } 100 \text{ g}^{-1}$ )

NS = Non significant

#### 6.3.4 Characterization of YGE soils based on acid-extractable K and step K methods of assessing K releasing power

Since characterization of soils using  $K_c$  was inadequate for at least some of the YGE soils under examination (Chapter 4), this section aims to categorise the soils based on the acid extraction procedure and step K, which had better correlations with total plant uptake and  $K_{\text{nex}}$  uptake, respectively. The amount of acid-extractable K in the unleached soils ranged from 34  $\text{mg } 100 \text{ g}^{-1}$  in the Marton soil (S5) to 147  $\text{mg } 100 \text{ g}^{-1}$  in the undeveloped Timaru soil (S14). After leaching, the corresponding acid-extractable K levels were 31 and 76  $\text{mg } 100 \text{ g}^{-1}$ , respectively.

The average proportion of acid-extractable K removed by leaching was 23 % (the range being 0 to 82 %) as compared with 50 % (6 to 53 % range) for  $K_{\text{ex}}$  ( $\text{NH}_4\text{OAc}$ -extractable). As expected, artificial leaching had less effect on step K than on acid-extractable K. The average proportional drop of step K of the 19 soils due to artificial leaching was therefore only 7 % (0 to 16 % range).

Step K, which measures the more soluble fraction of soil  $K_{\text{nex}}$ , varied widely, the range being 24 to 106  $\text{mg } 100 \text{ g}^{-1}$  in the unleached Marton (S5) and Raumai (S9) soils and 24 to 93  $\text{mg } 100 \text{ g}^{-1}$ , in the respective leached soils. Furthermore, the step K of Tokomaru (S2 and S3), Milson (S4), Marton (S5 and S6), Halcombe (S7),

Ohakea (S8), and Matapiro (S11) soils did not change due to leaching (Fig. 6.7). This indicates the relative tightness with which K is held in the wedge zones of these soils.

Step K differentiated the undeveloped YGE soils of the South Island from their developed counterparts better than  $K_c$ . For example, the undeveloped and developed Claremont soils (S16 and S17) had similar  $K_c$  values (13.3 and 12.3 mg 100 g<sup>-1</sup>, respectively) but varied widely in step K (60.4 and 42.0 mg 100 g<sup>-1</sup>) and  $K_{nex}$  uptake (15.6 and 3.4 mg 100 g<sup>-1</sup>) values.

The results in this study, together with those of McLean (1961), Barber and Matthews (1962), and Richards and Bates (1988) show that soil  $K_{nex}$  assessed by the step K method is an important source of  $K_{nex}$  uptake of plants grown to K exhaustion in pot trials for the majority of the soils. For the 7 YGE soils of the North Island (S2 to S8), the contribution to uptake from  $K_{nex}$  sources i.e., the  $K_{nex}$  supplying power in both the unleached and the leached soils is nil. This is reflected by the constancy of the step K after cropping (Fig. 6.7). Presumably a heavy load was imposed on the K supplying power of these soils and the replenishment rate of solution K from  $K_{nex}$  sources was insufficient.

As mentioned in Chapter 2 (section 2.7.1), the  $K_{nex}$  supplying power of soils varies with the pot trial technique used. There is evidence to show that the K uptake by ryegrass from the Marton soil in earlier studies was 8 (Campkin, 1972) and 5 (Jackson, 1985) times greater than in the present study. Interestingly, while the K releasing power (assessed by  $K_{ex}$ , acid-extractable K, step K, and  $K_c$ ) of the Marton (S3) soil in this study and that of the pot trial study of Campkin (1972) was more or less the same, the  $K_{nex}$  supplying power varied widely (Table 6.4). Moreover, the soil to plant ratio used by the above workers was 66 (Campkin, 1972) and 8 (Jackson, 1985), respectively compared to 1 in this study (Chapter 4).

Thus S2, S3, S4, S5, S6, S7, and S8 can be designated as soils with low  $K_{nex}$  supplying capacities in comparison with all other soils in the study. The  $K_{nex}$

### North Island YGE and related soils

### South Island YGE soils

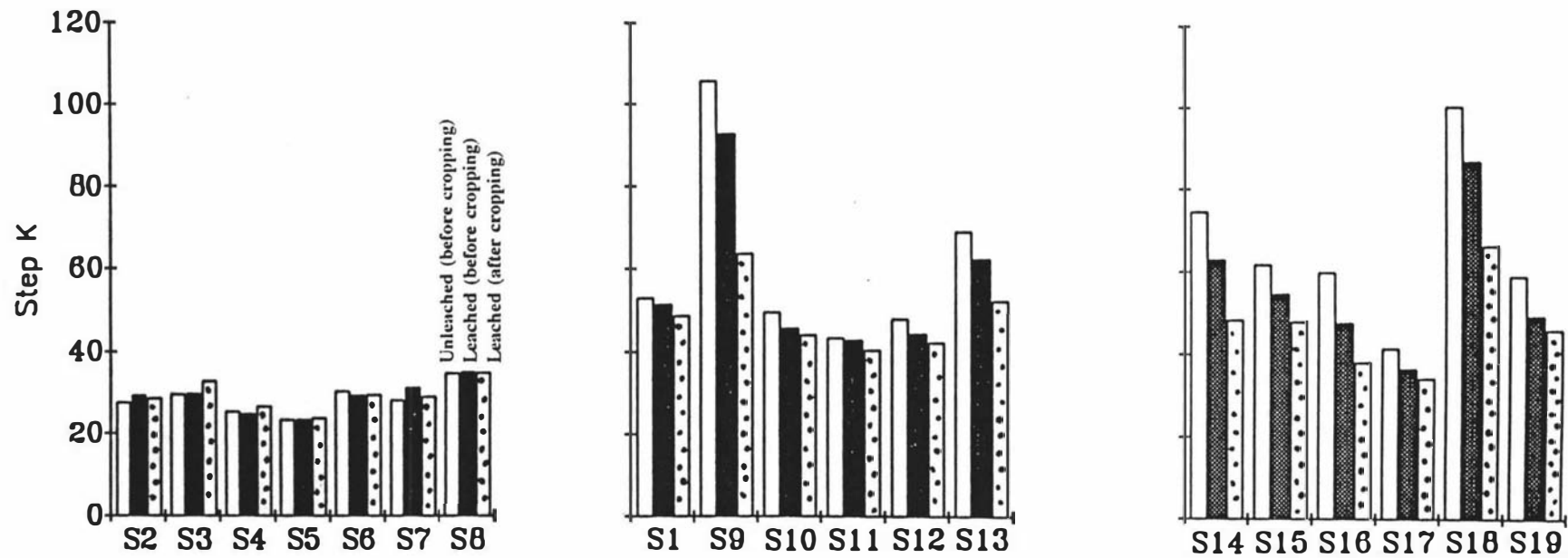


Fig. 6.7 Changes in step K (mg 100 g<sup>-1</sup>) of soils due to leaching and cropping

**Table 6.4** K releasing and supplying power ( $\text{mg } 100 \text{ g}^{-1}$ ) of Marton soil used in this study compared to the pot trial of Campkin (1972)

	Campkin (1972)	Chapter 4 & 6 data for S3
$K_{\text{ex}}$	12.09	9.75
Acid-extractable K	33.93	33.70
Step K	21.84	23.95
$K_{\text{c}}$	8.19	7.80
Dry matter ( $\text{g pot}^{-1}$ )	6.03	2.49
Herbage K (%)	2.77 (cut 1) - 0.22 (cut 8)	0.23 (cut 1) - 0.16 (cut 4)
K uptake	24.57	3.10
$K_{\text{nex}}$ uptake	15.99	-4.21
Weight of soil per pot	400 g	20 g
No. of plants per pot	6	20
Duration of cropping	24 weeks	16 weeks

releasing power (assessed by step K) of these unleached soils is also lower, the range being 24 (S5) to 35 (S8) mg 100 g<sup>-1</sup>. All this might be due to an intrinsic property of the soils and could probably be explained by the K-bearing mineral phases (see Chapter 8).

Thus after the uptake of  $K_{ex}$ , plants exhaust the easily available  $K_{dex}$  fraction (that can be assessed by step K) and might finally depend on the not easily available  $K_{dex}$  (that can be assessed by  $K_c$ ) release. This pattern of  $K_{dex}$  release is in agreement with the work of Haylock (1956b), Arnold (1960), McLean (1961), Beckett (1970), and Hay (1971). Beckett (1970) stated that "by and large step K bears the brunt of the K demand by a years' cropping in the field or of exhaustive cropping in pot trials. Reserve K is usually too slow and where step K is exhausted the K uptake of test crops falls off sharply".

The results presented in this study indicate that soils with  $K_c$  values more than 10 mg 100 g<sup>-1</sup> (Chapter 4, section 4.3.6.3) and step K values more than 35 mg released  $K_{dex}$  to ryegrass plants grown to K exhaustion. This, however, does not mean that soils with  $K_c$  and step K lower than these values (some YGE soils in the North Island) do not release  $K_{dex}$  to plants in the field. This is because exploitation of  $K_{dex}$  in the field is higher due to the extension of the root system in an unlimited volume of soil when compared to the limited volume in a pot.

### 6.3.5 Contribution of acid-extractable K from soil separates

Even though clay is the single most important soil constituent that determines the plant availability of K (Tabatabai and Hanway, 1969; Bertsch and Thomas, 1985), there is evidence that primary minerals in the sand and silt separates might be quite an effective source for K release (Munn et al., 1976; Metson, 1980; Al-Kanani *et al.*, 1984). Information on the K releasing power from the soil separates of New Zealand soils is limited (Haylock, 1956b; Metson *et al.*, 1956; Lee and Gibson, 1974). This section reports on acid-extractable K levels in the different size fractions of the 19 soils.



### 6.3.5.1 *Potassium extracted from the peroxidised soil and soil separates by the acid extraction procedure*

Since treatment with  $\text{H}_2\text{O}_2$  is a prerequisite for soil particle separation, it is possible that some K may be lost during the peroxidation procedure. Despite this, the ranking of the soils in terms of acid-extractable K after peroxidation was similar to that before peroxidation. This was substantiated by the high correlation ( $r = 0.98^{**}$ ) between acid-extractable K before and after  $\text{H}_2\text{O}_2$  treatment. The values ranged from 22.9 mg 100 g<sup>-1</sup> for S5 to 108.3 mg 100 g<sup>-1</sup> for S14 (Table 6.5). On an average 26 % of acid-extractable K was lost due to peroxidation, the range being 17-43 %.

Generally, when expressed as mg K 100 g<sup>-1</sup> of separate the acid-extractable K of the clay fraction (< 2  $\mu\text{m}$ ) was the highest followed by the K in the coarser fractions (sand and silt). Lee and Gibson (1974) also found the clay fractions from selected New Zealand soils to have the highest  $K_{\text{dex}}$  as assessed by the resin K method. Lee and Widdowson (1977), however, reported higher  $K_{\text{dex}}$  values (step K) in the sands than in the clays (dominantly halloysite with no micaceous material) of some Tongan soils. It should be noted, however, that the K in the clay fraction in all the above studies was obtained by a simple calculation (section 6.2.5) not by chemical extraction.

Within a size fraction, there were differences among the soils in the amount of K extracted (Table 6.5). For example, of the soils of the North Island the Raumai soil (S13) clay fraction contained the highest amount of acid-extractable K (166 mg 100 g<sup>-1</sup>) and the clays of the Marton soils (S5 and S6) the lowest (30 and 35 mg K 100 g<sup>-1</sup>, respectively). The wide differences in the acid-extractable K of the North Island clays may be a reflection of variations in the mineralogy of the clays that dictate the release of K.

In the South Canterbury region the acid-extractable K of the clay of the undeveloped Timaru soil (S14) was the highest (335 mg 100 g<sup>-1</sup>). The lowest K (71 mg 100 g

**Table 6.5 Acid-extractable K of peroxidised soil and its separates (mg 100 g<sup>-1</sup>)**

Soil No.	Soil name	Soil	Sand	Silt	Clay*
S1	Tokorangi	70.2	32.2	48.7	134.8
S2	Tokomaru (a)	41.4	24.8	22.1	101.8
S3	Tokomaru (b)	32.4	29.8	20.8	65.1
S4	Milson	51.5	23.4	23.5	138.7
S5	Marton (a)	22.9	24.6	18.3	35.2
S6	Marton (b)	25.3	23.5	23.7	30.0
S7	Halcombe	44.4	25.4	20.8	129.6
S8	Ohakea	43.2	30.0	25.9	89.7
S9	Raumai	87.7	82.1	74.3	165.6
S10	Te Arakura	46.4	36.2	33.4	86.6
S11	Matapiro	48.3	36.6	46.6	67.8
S12	Wharekaka	46.6	35.8	26.8	91.3
S13	Pirinoa	68.3	62.9	44.8	106.8
S14	Timaru (a)	108.3	42.8	48.3	335.2
S15	Timaru (b)	61.7	39.6	36.4	152.7
S16	Claremont (a)	57.5	38.6	33.3	142.5
S17	Claremont (b)	38.4	31.8	22.6	70.6
S18	Opuha (a)	96.1	59.0	53.0	147.8
S19	Opuha (b)	57.5	38.6	33.3	134.2

\* Acid-extractable K in clay determined by computation (section 6.2.5)

(a) Undeveloped site

(b) Developed site

clay<sup>1</sup>) was found in the developed Claremont soil (S17). The differences in the amounts of K extracted by boiling 1 M HNO<sub>3</sub> in the sand (> 63 μm) and silt (2-63 μm) fractions of soils are not as great as for the clay fraction (Table 6.5).

The acid-extractable K values of the soil separates of the undeveloped soils were higher than those of the developed soils, though more markedly so for the South Canterbury soils. The calculated acid-extractable K in the clay fraction of the undeveloped Opuha soil (S18) did not differ much when compared to its developed (S19) counterpart (148 and 134 mg 100 g<sup>-1</sup>, respectively) because of a much higher clay content of the former (44 %) compared to the latter (24 %) soil (Table 3.2).

It is evident that variations exist among the YGE and related soils not only in the K uptake of ryegrass (Chapter 4), and step K (section 6.3.4), but also in the acid-extractable K within the soil separates.

Richards and Bates (1988) found that more "step K" was present in the clay fraction (coarse + fine clay) of the nine Ontario soils they investigated than in the silt fractions, the range being 57 to 177 and 4 to 65 mg 100 g<sup>-1</sup> in the clay and in the silt fractions, respectively. They did not extract the sands with boiling HNO<sub>3</sub>. When recalculated using the formulae in the present study, the step K of the sands ranged from 4 to 21 mg 100 g<sup>-1</sup>. These values are in the range of the acid-extractable K of the soil separates of the soils considered here, but it should be noted that the measurement of the "step K" of Ontario soil separates (Richards and Bates, 1988) is different to the acid extraction method used in this study.

The K uptake by ryegrass grown on the unleached soils in the glasshouse experiment (Chapter 4) was significantly correlated with the amount of acid-extractable K in the soil separates (sand, silt, and clay) before cropping and with the acid-extractable K lost due to peroxidation. The respective *r* values were 0.512\*, 0.652\*\*, 0.874\*\*, and 0.893\*\*. The prediction of K uptake improved ( $R^2 = 94\%$ ) when all the above were inserted into a multiple regression model (not presented). This indicates that acid-extractable K of all three soil separates might possibly be a source of K to

ryegrass plants grown in the glasshouse and their effect on K uptake by plants is complementary.

The quantity of acid-extractable K in the unleached whole soil was not correlated with the sand, silt, and clay content of the soils (data not presented). This indicates that the availability of K to plants cannot be deduced from the clay content of the soils and confirms the work of Richards and Bates (1988).

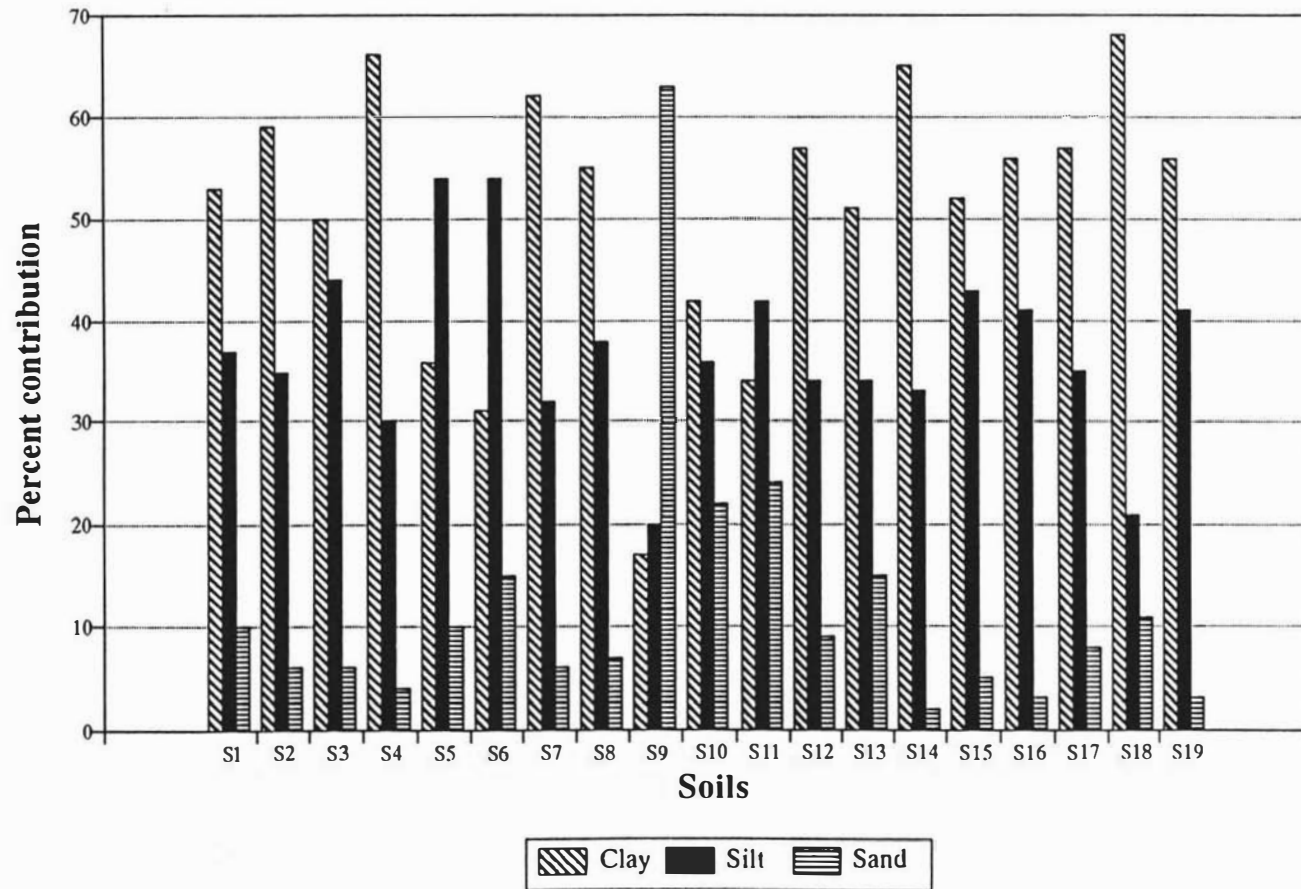
#### 6.3.5.2 *Relative contribution of the soil separates to whole soil acid-extractable potassium*

The contribution of the acid-extractable K from the soil separates to the whole soil can be evaluated best when recalculated on a whole soil basis. Thus the ranges are 2-63 %, 20-55 %, and 17-68 % for the sand, silt, and clay fractions, respectively (Fig. 6.8). On average the clay fraction accounted for only 50 % of the acid-extractable K, the remainder was attributed to the sand and silt fractions.

With the exception of the Marton (S5 and S6), Raumai (S9), and Matapiro (S11) soils, the percent contribution of acid-extractable K from the clay fraction was more than 40 %. Thus much of the K released by nitric acid came from the sand and silt separates of the Marton, Raumai, and Matapiro soils. In a separate study (Lee and Gibson, 1974) the sand and silt fractions of Marton silt loam contributed more to whole soil resin K than the clay fraction. The sand and silt fractions of most of the Tongan soils involved in the study of Lee and Widdowson (1977) also accounted for a large proportion of the  $K_{\text{ex}}$  release.

Within the sand fraction, the percent contribution of acid-extractable K was the highest for the Raumai (S9) soil followed by the Matapiro soil (S11). This may be due to K bearing primary minerals (possibly micas) in the sand fraction of the Raumai soil and the presence of K-bearing volcanic glass in the Matapiro sand fraction (see chapter 8).

**Fig. 6.8 Percent contribution of acid-extractable K from the soil separates**



## 6.4 CONCLUSIONS

1. Methods of assessing K releasing power by measuring soil  $K_{ex}$  plus  $K_{dex}$  viz, acid extraction and NaTPB, provide better indices of K availability than the methods used to assess either of them separately (the  $K_{ex}$  method for measuring soil  $K_{ex}$ , and the step K method for assessing soil  $K_{dex}$  releasing power). Even though the NaTPB method successfully predicted the amount of soil K available to ryegrass ( $R^2 = 85\%$ ) it may not be suitable for routine soil testing because of its cost and time requirements. Both acid-extractable K and NaTPB K tests were well correlated with each other ( $r = 0.91^{**}$ ). Thus, like the NaTPB method (Jackson, 1985), the acid extraction procedure could possibly be used as a promising soil test to predict both  $K_{ex}$  and  $K_{dex}$  fractions available to plants in the short-medium term.

Perhaps K supply from the 19 YGE and related soils in the present study can best be estimated by a single soil test i.e., acid extraction method, rather than by a combination of a test for QTK and a crude estimate of  $K_c$ , which is currently used by AgResearch to predict soil K gains in the fertilizer model.

2. Step K, which is the difference between the acid-extractable K and  $K_{ex}$  and which is the easily available fraction of soil  $K_{dex}$ , was highly correlated with  $K_{dex}$  uptake by ryegrass. Step K gave a more reliable estimate of the variations in the  $K_{dex}$  release than did  $K_c$ .
3. Among the three soil separates, the clay fraction released the most acid-extractable K. Variations exist among the soils in the acid-extractable K of the soil separates. When expressed on a whole soil basis, the sand and the silt fractions contributed substantially (about 50 %) to the acid-extractable K. The exceptionally high percent contributions observed for the sand plus silt fractions of the Marton (64 % for S5 and 69 % for S6), Raumai (83 %), and Matapiro (66 %) soils indicates a likely important contribution of these fractions to the K nutrition of plants.

## CHAPTER 7

### POTASSIUM RELEASING POWER AND SUPPLYING POWER OF SOIL TEXTURAL SEPARATES

#### 7.1 BACKGROUND

Several workers e.g., Merwin and Peech (1950), Pratt (1952), McLean and Brydon (1963), Smith *et al.* (1968), Talibudeen and Weir (1972), Lee and Gibson (1974), Lee and Widdowson (1977), Al-Kanani *et al.* (1984), Havlin *et al.* (1985), Comerford *et al.* (1990), and Simard *et al.* (1992) have demonstrated that the amounts of potassium that can be extracted from soils using a range of extractants such as resins, 1 M HNO<sub>3</sub>, strong salt solutions, and sodium tetraphenyl boron (NaTPB) increased with decreasing particle size. Thus for many soils the clay and fine silt fractions released most K on a unit of material basis whereas fine and coarse sand fractions released relatively little K.

On the other hand fewer workers recalculated the K released on a whole soil basis. For example, James and Weaver (1975) found that of the total K released after 12 extractions to a strong salt solution by the Shano silt loam 31 % was contributed by the sand, silt (63 %) and clay (6 %). Munn *et al.* (1976) found that for 4 Ohio soils extracted with 0.01 M CaCl<sub>2</sub> the clays contributed 30-74 %, the silts 24-50 %, and the sands 3-21 % of the total K released. Lee and Widdowson (1977) worked on 6 selected soils of the Kingdom of Tonga and found that "step K" for the sands ranged from 4-54 % (mean 34.5 %) on a whole soil basis, for silts 9-87 % (mean 31.3 %), and for clays 9-84 % (mean 34.2 %). Despite the wide range of values the sand and silt fractions clearly contributed substantially to plant available K defined as step K. Al-Kanani *et al.* (1984) showed that for 5 Quebec soils the clays contributed 47-70 % of K extracted by 1 M HNO<sub>3</sub>, the silts 12-26 %, and the fine to medium sands 9-28 %.

In Chapter 6 it was concluded that the acid extraction procedure was well correlated with the plant available K pool in soil. It was also found that for 19 YGE and associated soils the K released to 1 M HNO<sub>3</sub> increased with decreasing particle size on a unit basis, but that on a whole soil basis the contributions of the silt and sand fractions were appreciable for some soils. For example, it was shown (Chapter 6, section 6.3.5.2) that the silt fraction of the Marton soil (S6) and the sand fraction of the Raumai soil (S9) contributed most to whole soil acid-extractable K (Fig. 6.8 and Table 7.1). High percent contributions were observed for sand plus silt fractions of the Marton (64 %), Raumai (83 %), and Matapiro soils (66 %). Based on these results it was speculated that the sand and silt separates may be playing a role at least as important as that of the clay fractions in the K nutrition of plants.

It appears that despite many reports on the characterization of the K status of soils and textural fractions by chemical extraction procedures few attempts (e.g., Doll *et al.*, 1965) have been made to grow a crop on textural fractions and to relate crop yield and crop K content to chemical extraction criteria.

It also appears that despite many reports on the relative contribution of soil separates to whole soil K release, very few attempts (e.g., McLean and Brydon, 1963; Al-Kanani *et al.*, 1984) have been made to determine if the computed K release for the textural fractions on a whole soil basis (predicted) match the analytical K release value of the whole (peroxidised or unperoxidised) soil (actual). Obviously the assumption underlying the computation method of arriving at the relative contributions of the individual soil separates, is that they behaved in the whole soil in a manner similar to the behaviour exhibited, when they are investigated as discrete fractions. In this chapter an attempt to test the validity of this computation is described.

It should be noted that in Chapter 6, the acid-extractable K was measured on the peroxidised soil, and on the sand and the silt fractions. The contribution of the clay fraction was arrived at by difference. To check this the acid-extractable K analyses were repeated for 6 selected soils in this chapter, and measurements were made on peroxidised soil, sand, silt, and clay fractions.



The objectives of the study described in this chapter are:

1. To assess the relative contribution of sand, silt, and clay fractions to whole soil K releasing and supplying power using chemical extractions and an agar pot trial, respectively.
2. To evaluate the relationship between the contribution of acid-extractable K of the textural fractions and plant available K.

## 7.2 MATERIALS AND METHODS

### 7.2.1 Soils - S6, S9, S11, S12, S13 and S18

Six soils representing different regions (Chapter 3) and with varying levels of acid-extractable K contribution from soil separates (Chapter 6) were selected. Table 7.1 shows some characteristics of the soils selected for this study.

**Table 7.1** Some details of the soils selected for the study based on Chapter 6 data

Soil No.	Soil name	Total K of soils (%) (Table 3.3)	Acid-extractable K (mg 100 g separate <sup>-1</sup> )			Acid-extractable K as % contribution from		
			Sand	Silt	Clay	Sand	Silt	Clay
S6	Marton	1.00	24	24	30	15	54	31
S9	Raumai	1.49	82	74	166	63	20	17
S11	Matapiro	1.26	37	47	68	24	42	34
S12	Wharekaka	1.06	36	27	91	9	34	57
S13	Pirinoa	1.41	64	45	107	15	34	51
S18	Opuha	1.15	59	53	148	11	21	68

### 7.2.2 Separation of textural fractions (soil separates)

Separation of textural fractions (sand, silt, and clay) was performed by the sedimentation method (Chapter 3). After separating the silt from the silt plus clay suspension (section 6.2.4) a concentrated clay suspension was obtained by repeated centrifugation of diluted clay suspension at 5000 rpm for 10-15 min and by subsequent freeze drying. The freeze dried samples were subjected to light crushing to reduce them to a homogeneous, fluffy, powdered clay suitable for chemical extractions.

### 7.2.3 Chemical extractions

The total K and  $K_{ex}$  of the soil separates were determined by the methods described in Chapter 3. The acid-extractable K and step K were determined by the methods described in Chapter 6 (sections 6.2.3.3 and 6.2.3.4, respectively). Chemical extractions were also carried out for the peroxidised whole soils.

### 7.2.4 Removal of $K_{ex}$ from the soil separates

The objective of this treatment was similar to that in Chapter 4 (section 4.2.2) i.e., to remove soluble and exchangeable K from the calgon-treated soil separates so that plants could use K only from the non-exchangeable pool. In this study, however, a shaking technique (as compared to an artificial leaching technique in Chapter 4) was adopted, using a solution containing Ca and Mg at an equivalent ratio of 4:1 (Chapter 4). The soil:solution ratio used was 1:12. A 25 g soil sample in a 500 ml centrifuge bottle was shaken twice with 300 ml of the solution. After each shaking (1 h) the contents of the bottle were centrifuged at 5000 rpm for 10-15 min and the supernatant discarded. The residue was washed free of chloride and dried (sands and silts oven dried at 60°C overnight and clays freeze dried followed by oven drying at 60°C) prior to chemical extractions and the growth chamber experiment.

Unperoxidised whole soils and peroxidised whole soils were not treated to remove  $K_{ex}$ .

### 7.2.5 Percent contribution of K content (total K, $K_{ex}$ , acid-extractable K, and step K) of the soil separates on a whole soil basis

The percent contribution of K content (as measured by total K,  $K_{ex}$ , acid-extractable K, and step K) of the soil separates on a whole soil basis was calculated using the following formula.

$$Y = \left( \frac{A \cdot B}{D} \right)$$

Where,

Y = Percent contribution of K content from sand or silt or clay on a whole soil basis.

A = Percent sand or silt or clay in the soil (Table 3.2).

B = K content as measured by total K,  $K_{ex}$ , acid-extractable K or step K of the soil separate (sand or silt or clay) expressed in mg 100 g<sup>-1</sup> of separate.

D = Total K release for the soil separates on a whole soil basis (mg 100 g<sup>-1</sup> of soil), which is a product of K release per g of soil separate and the percent of each fraction in the whole soil (Havlin *et al.*, 1985).

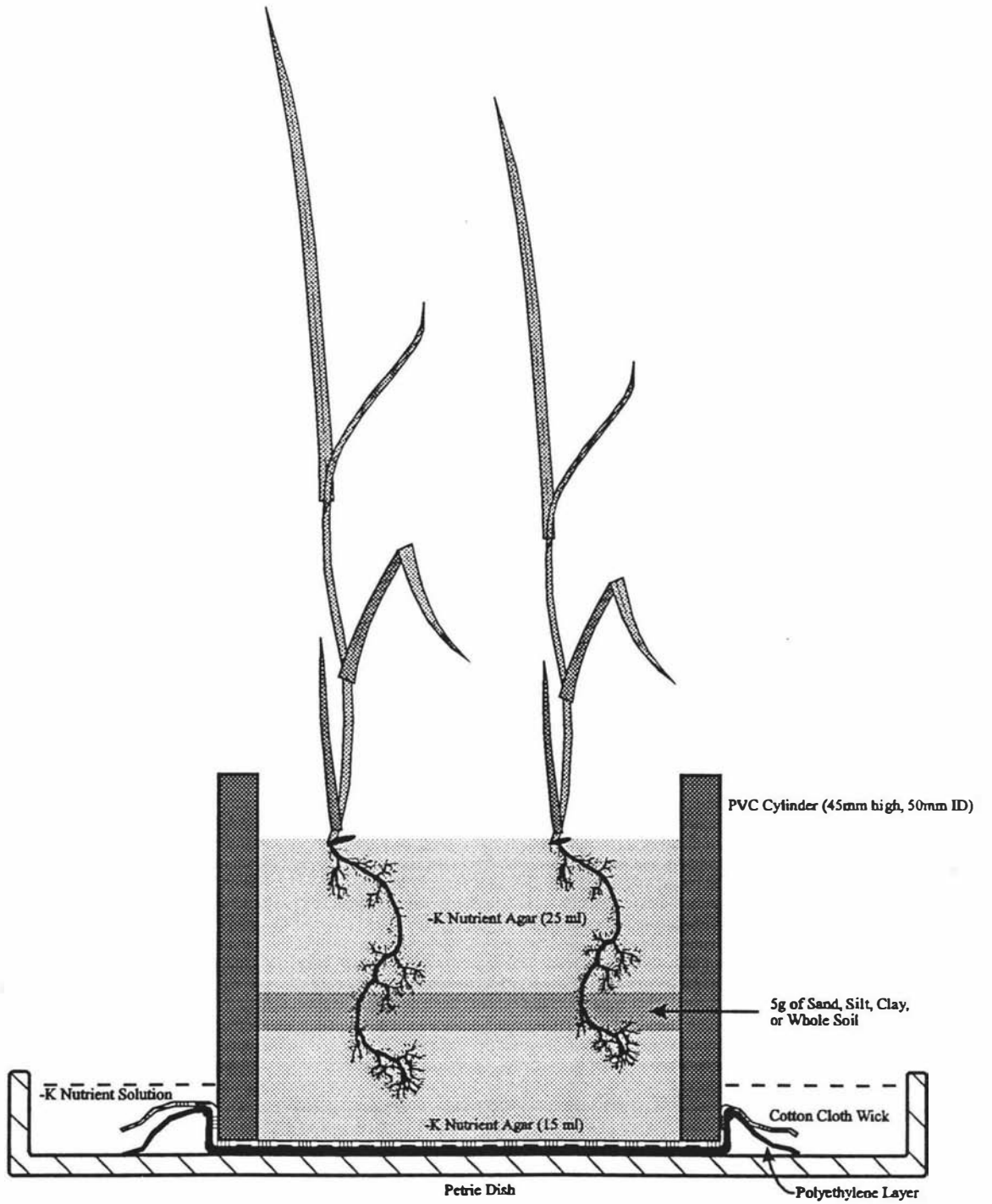
### 7.2.6 Growth chamber experiment

The plant availability of K in the soil separates that had been treated to remove  $K_{ex}$  was determined in a growth chamber experiment using an agar pot technique. Unperoxidised whole soils and peroxidised whole soils that have not been treated to remove  $K_{ex}$  were also included in the pot study.

#### 7.2.6.1 *Agar pot cylinder*

The agar pot is composed of a PVC cylinder of 45 mm height and 50 mm internal diameter, with a cotton cloth and a polythene sheet fastened to one end with a rubber band (Fig. 7.1). A 1 % nutrient agar gel was prepared by boiling a K-free nutrient

**Fig. 7.1 Agar Pot Cylinder**



solution (Hinsinger and Jaillard, 1990; Hinsinger *et al.*, 1992) with solid agar (Ionagar No. 2) at 90-95°C and allowing it to cool to a temperature just above gelification. A 15 ml portion was poured into the pot at a temperature as close as possible to its gelification point (39°C). The polythene sheet below the cloth prevented the loss of liquid agar through the cotton cloth. The nutrient agar gel was allowed to set and 5 g of either sand, silt, clay, or whole soil (unperoxidised, or unperoxidised) were spread on the surface of the gel. After 24 h another aliquot of K-free nutrient agar was prepared and a 25 ml portion was poured carefully down the sides of the cylinder and over the treatment material and then allowed to set as before. The treatment material was thus sandwiched between two layers of solidified nutrient agar. The pots were placed in petrie dishes containing the same nutrient solution to guard the agar against dehydration. The agar pot cylinder was then ready for use as a culture vessel to grow ryegrass plants.

#### 7.2.6.2 *Agar potting technique*

Perennial ryegrass (B1 P14 Yatsyn ryegrass) was chosen because of its enhanced K absorption ability and its efficiency in using non-exchangeable K (Hinsinger *et al.*, 1992). The seeds were sown on the surface of the agar gel at a rate of 50 seeds per pot to ensure rapid K uptake. The agar above and below the treatment material was kept moist with distilled water. While the cotton cloth functioned as a wick conducting water or K-free nutrient solution to the agar/root surface below the soil separate, the top portion of the agar was maintained moist by adding sufficient water uniformly to all pots with a pipette. After germination the K-free nutrient solution was applied regularly and the agar gel kept moist.

The experiment thus involved 6 soils with 5 treatments viz, sand, silt, clay, unperoxidised soil, and peroxidised soil and 4 replicates giving a total of 124 pots including 4 control pots in which plants were grown in the K-free nutrient agar with no treatment material. The pots were randomized in a growth chamber and 2 ml of Benlate (0.05 %) were added per pot at two week intervals to avoid fungal infection.

The plants (shoots) were harvested three times and at each harvest the shoots were cut to the level of the pot. After each harvest the plant material was dried, weighed, and analyzed for K as described in section 4.2.3. The dry matter of the four replicates was pooled for the three harvests to obtain sufficient material for the herbage K measurement. For the final cut (3 weeks growth) the cylinder was freed from the agar by removing the rubber band and the shoots were cut as close as possible to the root material. The dismantled agar pot was allowed to dry for 1-2 days and the top portion of the agar was peeled off by holding the cut portion of the roots and the cotton cloth. The exposed layer of treatment material was air dried and hence easily separated from the remainder of the pot. The bottom portion of the agar was also peeled off after removal of treatment material and wherever possible the bulk of the root material that had protruded through the cotton cloth obtained. The treatment material thus obtained was easily separated (by sieving) from the remnants of the root materials.

The total K content of the separated root material was measured after drying at 60°C. The total K uptake of shoots from the soil separates and from the whole soil was obtained from the sum of the uptake of the 3 individual harvests less the K uptake from the control pots and expressed as mg 100 g<sup>-1</sup>.  $K_{\text{ex}}$  uptake was calculated as described in section 4.2.3.

Since the dry matter of the replicates was pooled, statistical analyses could not be carried out for the total K uptake data but was carried for the total dry matter data using analysis of variance test (SAS, 1985).

#### **7.2.7 Relative contribution of the soil separates to whole soil plant K uptake**

The total K uptake and  $K_{\text{ex}}$  uptake were expressed as the percentage contribution from the soil separates on a whole soil basis by replacing the K content in the formula in section 7.2.5 with the plant K uptake and  $K_{\text{ex}}$  uptake, respectively.

## 7.3 RESULTS AND DISCUSSION

### 7.3.1 Potassium releasing power of soil separates

#### 7.3.1.1 *Total K in the soil separates*

With respect to the total K content of the separates, that of the sand fractions decreased in the order of S11 > S9 > S13 > S6 > S18 > S12, that of the silts S9 > S11 > S13 = S6 > S18 = S12 and that of the clays S13 > S18 > S12 > S9 > S6 > S11 (Table 7.2). While the differences among the sand and silt separates of the different soils were marginal (the range being 0.96-1.52 % for sands and 1.00-1.72 % for silts), for the clay fractions the differences were somewhat greater (0.94-3.01 %).

The clays of S12 (Wharekaka), S13 (Pirinoa), and S18 (Opuha) contained 2-3 times more K than the clays of S6 (Marton), S9 (Raumai), and S11 (Matapiro). This could be due to relatively weaker weathering of the former group of soils than the latter (A.S. Palmer, pers. comm). The latter soils contain more weathered clay minerals that contain less K viz, smectite, halloysite, and/or kaolinite (Pollok, 1975 and Chapter 8). The higher total K content of silt and sand of S9 (Raumai) and S11 (Matapiro) can be attributed to the predominance of K bearing minerals (mica and volcanic glass) in these soils (Chapter 8).

Of the 6 soils in this study Raumai soil (S9) recorded the highest total K for the whole (unperoxidised) soil (1.49 %, Table 7.1), despite having the lowest clay content (9 % as against more than 24 % clay for the other soils). This underscores the predominance of K-containing minerals in the sand and silt fractions of this soil.

The relative contribution of soil separates to the whole soil total K content (calculated using the formula in section 7.2.5) for the 6 soils ranged from 7-65 %, 20-58 %, and 8-70 % for sand, silt, and clay fractions, respectively. Using the total K content and the particle size distribution (3-19 % sand, 46-73 % silt, and 8-70 % clay) data of Munn *et al* (1976), the weighted contributions of the total K content of 4 Ohio soils was

**Table 7.2 Potassium contents of soil separates before artificial removal of  $K_{ex}$**

Soil separate	Soil No.	Total K (%)	$K_{ex}$	Acid-extractable K	Step K ( $K_{nex}$ )
Sand (T <sub>1</sub> )	S6	1.12	0.8	13.8	13.0
	S9	1.50	1.8	41.6	39.8
	S11	1.52	1.9	26.2	24.3
	S12	0.96	1.5	21.6	20.1
	S13	1.32	2.2	41.8	39.6
	S18	1.10	9.0	48.0	39.0
Silt (T <sub>2</sub> )	S6	1.12	0.3	21.0	20.7
	S9	1.72	5.3	103.9	98.6
	S11	1.33	3.3	42.4	39.1
	S12	1.00	0.9	25.4	24.5
	S13	1.12	1.5	36.1	34.6
	S18	1.00	2.8	52.3	49.5
Clay (T <sub>3</sub> )	S6	1.24	14.0	69.1	55.1
	S9	1.42	24.8	105.0	80.2
	S11	0.94	39.3	113.6	74.3
	S12	2.56	29.5	133.0	103.5
	S13	3.01	41.0	131.2	90.2
	S18	2.98	83.0	399.6	316.6



calculated to be 2-20 % for sands, 37-73 % for silts, and 15-61 % for clays.

### 7.3.1.2 *Exchangeable K of the soil separates*

When expressed as mg K 100 g separate<sup>-1</sup>, the NH<sub>4</sub>OAc-extractable K of the clay fractions was higher than the sand and silt in all the soils, that of the S18 (Opuha) being particularly high (Table 7.2).  $K_{ex}$  in the clays followed the order S6 < S9 < S12 < S11 < S13 < S18. Among the 6 soils, the Marton soil (S6) contained the lowest  $K_{ex}$  in all the separates.

When expressed as the percent contribution from the soil separate on a whole soil basis (calculated using the formula in section 7.2.5), more than 80 % of the NH<sub>4</sub>OAc-extractable K was extracted from the clay separate, the only exception being the Raumai clay which contributed only 47 % to  $K_{ex}$ . This is because of the sandy nature of the soil (67 % sand) and hence the 26 % and 27 % contribution from the sand and the silt separates to the  $K_{ex}$ , respectively.

After extracting the soil separates with an 0.05 M chloride solution of Ca and Mg to remove  $K_{ex}$  (section 7.2.4), the NH<sub>4</sub>OAc-extractable  $K_{ex}$  levels ranged from 0.84 mg 100 g<sup>-1</sup> (S9) to 3.24 (S18) for sands, 1.30 (S6) to 2.73 (S11) for silts, and 10.78 (S6) to 35.43 (S18) for clays (Table 7.3). Thus shaking did not completely remove all the NH<sub>4</sub>OAc-extractable  $K_{ex}$  from the soil separates. This is similar to the results given in Chapter 4 (section 4.3.1) where a leaching technique was used. The percentage of  $K_{ex}$  removed was generally higher in the clay fractions, although exceptions occurred (S9, Raumai and S18, Opuha). The percent  $K_{ex}$  removed from Raumai clay (41 %) was less than that from the sand (53 %) and silt (49 %), and that of Opuha clay (54 %) was less than that of the sand (64 %). Interestingly, for the sand and silt fractions, there was an increase in the  $K_{ex}$  after the extraction procedure for some soils. This increase could be due to leakage from K minerals in the sand (S6) and the silts (S6 and S12), which contained low levels of  $K_{ex}$  even before extraction.

**Table 7.3** Potassium contents (mg 100 g<sup>-1</sup>) of soil separates after extraction of K<sub>ex</sub> (before cropping)

Soil separate	Soil No.	K <sub>ex</sub>	Acid-extractable K	Step K
Sand	S6	1.04	21.6	20.56
	S9	0.84	42.2	41.36
	S11	1.40	26.8	25.40
	S12	1.63	23.0	21.37
	S13	1.26	48.2	46.94
	S18	3.24	55.8	52.56
Silt	S6	1.30	26.0	24.70
	S9	2.71	103.8	101.09
	S11	2.73	50.2	47.47
	S12	1.45	27.0	25.55
	S13	1.53	47.8	46.27
	S18	1.68	59.4	57.72
Clay	S6	10.78	67.6	56.82
	S9	14.65	115.9	101.25
	S11	21.26	114.2	92.94
	S12	18.66	113.9	95.24
	S13	21.80	132.5	110.70
	S18	35.43	346.0	310.57

### 7.3.1.3 *Potassium releasing power of soil separates as assessed by the acid-extraction procedure*

The results of extracting the peroxidised textural fractions with 1 M HNO<sub>3</sub> are shown in Table 7.2. As expected, the clays released more K (69-400 mg 100 g<sup>-1</sup>) than the silts (21-104 mg 100 g<sup>-1</sup>) and the sands (14-48 mg 100 g<sup>-1</sup>). The mean values (158, 47, and 32, respectively) indicate that the K released by the silt and sand fractions is by no means insignificant. In this regard, the high level of K released by the silt fraction of the Raumai (S9) soil is of interest. When recalculated on a whole soil basis the silt plus sand fractions contributed 15-85 % of the HNO<sub>3</sub> K (Table 7.4).

The acid-extractable K values for the peroxidised soil and its separates were different to those quoted in Chapter 6 (Table 6.5). Despite these differences the relative contribution of sand plus silt fraction to the whole soil acid-extractable K was substantial for S6 (45 %), S9 (85 %), and S11 (49 %) thus confirming the potential K releasing power of the coarser separates in these soils (Table 7.4). The differences, however, are presumed to be due mainly to (i) better control of the peroxidation procedure adopted in this chapter and imperfect separation (allowing interparticular mixing) of clay, silt, and sand particles during the sedimentation procedure, and (ii) variable K release by freeze drying of clays.

Thus the data in Table 7.4 might be expected to be the best possible estimate of relative contribution of textural fractions to whole soil acid-extractable K.

### 7.3.1.4 *Potassium releasing power of soil separates as assessed by step K*

The values for step K for the sand and silt fractions were close to those for acid-extractable K (Table 7.2) but were lower for the clay fractions. This was not unexpected as step K was obtained by subtracting K<sub>cx</sub> from acid-extractable K, and K<sub>cx</sub> was higher for the clays than for the sands and silts.

**Table 7.4** Relative contribution of soil separates to whole soil acid-extractable potassium

Soil No.	Soil name	Relative contribution of soil separates to whole soil acid-extractable K (%)		
		Sand	Silt	Clay
S6	Marion	7	38	55
S9	Raumai	45	40	15
S11	Matapiro	15	34	51
S12	Wharekaka	4	27	69
S13	Pirinoa	6	31	63
S18	Opuha	5	10	85

When the step K was expressed as the percent contribution from the textural fractions on a whole soil basis (calculated using the formula in section 7.2.5) the contribution from the clays among the 6 soils ranged from 13 % (S9) to 84 % (S18). In the majority of the soils (5 out of 6), however, more than 40 % (42 % for S11, 51 % for S6, 55 % for S13, 64 % for S12, and 84 % for S18) of the contribution was from the clay fraction. The remainder was accounted for by the sand and silt fractions. Of interest is the 87 % contribution of step K from the sand and silt fractions of the Raumai (S9) soil (sand, 46 % and silt, 41 %). Haylock (1956b) showed that the majority of  $\text{HNO}_3$ -soluble K was extracted from clay fractions. For loam and sandy soils of New Zealand the proportion of "step K" derived from the clay fractions varied from 44-95 % for the loams and 11-24 % for the sands (Haylock, 1956b).

There was no consistency in the amount of acid-extractable K and step K removed from the soil separates after removal of  $K_{ex}$  (Table 7.3). For example, while there was a drop for S12 and S18 clays (14 % and 13 % drop in acid-extractable K, and 8 % and 4 % drop in step K, respectively) there was an increase in step K for S9 (26 %), S11 (25 %), and S13 (23 %) clays. Furthermore, acid-extractable K of the sands and silts either remained unchanged or increased slightly. This contrasts with the trend observed for the corresponding soils in Chapter 6 (section 6.3.4), where the acid-extractable K and step K values decreased after  $K_{ex}$  removal. Thus it appeared that the leaching technique used to remove  $K_{ex}$  from the soils (Chapters 4 and 6) had an overall greater impact on the reduction of the K than the equilibration shaking technique used to achieve the same objective for their textural separates in this chapter.

### 7.3.2 Potassium supplying power of soil separates

#### 7.3.2.1 *Dry matter yields*

Comparison of dry matter yield of ryegrass tops grown on the soil separates showed significant differences between the clays and the sands and silts (Table 7.5). The clays supported significantly higher dry matter yields than the sand and silt fractions for all the three harvests (Appendix 7.1), the total dry matter being 1.7 to 2.8 and 1.5 to 2.2

times greater than for the sands and silts, respectively. In most cases there were no significant differences in the total dry matter yields between the sand and the silt fractions of the soils. The exception to this trend was the Raumai soil (S9) for which the silt recorded significantly higher dry matter ( $0.316 \text{ g pot}^{-1}$ ) than the sand ( $0.245 \text{ g}$ ). This could be due to the high step K of the silt of S9 soil.

While there were differences in the total dry matter yields from the clay and the silt separates of the 6 soils, the dry matter yields of the sands were on par with one another. For example, the clay and the silt separates of the Raumai (S9) soil supported significantly higher dry matter yields than those of the Marton (S6) soil. Pirinoa (S13) clay produced a higher dry matter yield than Matapiro (S11) and Wharekaka (S12) clays. The S12 silt produced a statistically similar dry matter yield to that of S11 and S13. Furthermore, the Opuha (S18) clay recorded a significantly higher dry matter yield than the clays of S6, S11, and S12.

From the above comparisons it is evident that differences in dry matter yields recorded in Chapter 4 for the unleached soils (section 4.3.2) and in this chapter for the whole unperoxidised soils, were better reflected by the clay fractions than by sands and silts (Table 7.5).

The dry matter yield of roots grown in clays (Table 7.6) followed a similar trend to that of the shoots (Table 7.5) with the clays of S9, S13, and S18 supporting higher yields than S6, S11, and S12. The roots in the sand and silt separates and in the control pots grew so poorly that they could not be harvested.

### 7.3.2.2 *Potassium content of herbage*

The herbage K contents of each harvest for each soil and for each soil separate are assembled in Table 7.7. The K concentrations of herbage are highest for that grown in clays followed by the sand and silt separates.

There were considerable differences in the K concentration of the ryegrass tops among

**Table 7.5** Total dry matter (g pot<sup>-1</sup>) of ryegrass shoots grown on soil separates and on whole soils

Soil No.	Soil name	Sand	Silt	Clay	Unperoxidised soil	Chapter 4 data (Fig. 4.3)
S6	Marton	0.228	0.235	0.398	0.417	2.54
S9	Raumai	0.245	0.316	0.686	0.597	4.42
S11	Matapiro	0.254	0.290	0.446	0.519	3.40
S12	Wharekaka	0.258	0.253	0.448	0.463	2.82
S13	Pirinoa	0.252	0.259	0.553	0.574	4.28
S18	Opuha	0.277	0.275	0.549	0.683	4.84
LSD (0.05) SoilxTreatment		0.058			0.068	0.23

LSD = Least-squares difference

**Table 7.6** Dry matter, herbage K, and K uptake of ryegrass roots in the clay separate

Soil No.	Soil name	Dry matter (g pot <sup>-1</sup> )*	Herbage K (%)	K uptake (mg 100 g <sup>-1</sup> )
S6	Marton	0.035	0.40	2.80
S9	Raumai	0.232	0.86	39.90
S11	Matapiro	0.090	0.53	9.54
S12	Wharekaka	0.078	0.49	7.64
S13	Pirinoa	0.174	0.95	33.06
S18	Opuha	0.117	0.84	19.66

\* 5 g clay pot<sup>-1</sup>

**Table 7.7** Percent herbage K in ryegrass shoots for three harvests

Soil No.	Harvest 1 (3 week growth)			Harvest 2 (2 week growth)			Harvest 3 (3 week growth)		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
<b>S6</b>	0.19	0.18	0.21	0.17	0.18	0.20	0.14	0.16	0.15
<b>S9</b>	0.23	0.22	0.49	0.19	0.24	0.61	0.18	0.21	0.49
<b>S11</b>	0.20	0.19	0.25	0.17	0.19	0.30	0.15	0.19	0.25
<b>S12</b>	0.23	0.17	0.23	0.17	0.16	0.22	0.14	0.15	0.24
<b>S13</b>	0.19	0.18	0.41	0.18	0.17	0.64	0.15	0.16	0.55
<b>S18</b>	0.21	0.20	0.42	0.20	0.19	0.55	0.17	0.20	0.46
<b>Control</b>	0.18			0.17			0.18		

**Note:** Replicates pooled for the herbage K analysis



the soils for the three soil separates. For example, among the 6 soils, K contents of the tops grown in the clays of S9, S13, and S18 were about double those from the corresponding sand and silt separates for the 3 harvests.

The K concentration in the tops for the sands of all the soils was highest for the first harvest (the range being from 0.19-0.23 %) and then declined to lower values at the third harvest (0.14-0.18 %). It is interesting to note that there was no similar trend for silts and clays. Moreover, the K concentration in the ryegrass tops grown on the clays either increased or remained the same with progressive harvests, except for the Marton clay (S6). This could be a reflection of the clay fraction replenishing more plant available K than the sand and the silt separates. In Chapter 4 (section 4.3.3), however, the wide differences that occurred in the first harvest reduced to a narrow range in the final harvest.

Similar variation appeared in the K concentration of the roots among the 6 clays (Table 7.6) but the values were higher than for the shoot K.

### 7.3.2.3 *Potassium uptake*

The K uptake data for each harvest for each soil and its separates are given in Appendix 7.2.

#### 7.3.2.3.1 Uptake of K from the control pots

Ryegrass plants that were grown in the control pots (agar only) extracted 0.035 mg K pot<sup>-1</sup> (Table 7.8) over the three harvests. This value has been subtracted from the K uptake results for the treatments to obtain the actual K uptake from the soil separates and to calculate the comparative contributions of  $K_{ex}$  and  $K_{net}$  to plant uptake in section 7.3.2.3.4.

**Table 7.8** Total K uptake (less control) by ryegrass shoots from soil separates and from whole unperoxidised soil (mg 100 g<sup>-1</sup>)

Soil No.	Soil name	Sand	Silt	Clay	Whole soil	Chapter 4 data (Fig. 4.4)
S6	Marton	1.40	1.80	8.08	5.55	3.95
S9	Raumai	3.44	7.76	62.94	21.31	45.75
S11	Matapiro	2.40	4.88	17.26	12.57	18.90
S12	Wharekaka	2.76	1.90	14.36	7.01	7.90
S13	Pirinoa	2.28	2.62	52.90	16.85	41.25
S18	Opuha	4.34	4.78	45.48	33.22	62.35
control*		0.305 mg K pot <sup>-1</sup>				

\* K uptake by ryegrass from control pots (agar only)

### 7.3.2.3.2 Uptake of K from the soil separates

The total amounts of K taken up by ryegrass over 3 harvests from the soil separates are presented in Table 7.8. The range for sands was 1.40-4.34, silts 1.80-7.76, and clays 8.08-62.94 mg K 100 g<sup>-1</sup>. The mean values were 2.77, 3.96, and 33.50, respectively.

Thus the total K uptake from the clays is 3.5 to 23 times greater than the K uptake from sands and silts. While the clays of S9, S13, and S18 removed 63, 53, and 45 mg K 100 g<sup>-1</sup>, respectively, the remainder of the clays (S6, S11, and S12) provided less than 20 mg K 100 g<sup>-1</sup> to the ryegrass tops.

There were no major differences among the 6 soils in the K uptake of the sands and silts.

In general, the total uptake of K by the roots in the clay fractions was approximately half that of the shoots with similar differences between the soils (Table 7.6).

As in the case of dry matter yields the variations in the K uptake by ryegrass from the unperoxidised soils were better reflected by the clay fraction than sand and silt fractions (Table 7.8).

### 7.3.2.3.3 Exchangeable K after cropping

After the third harvest the  $K_{ex}$  in the soil separates ranged from 0.73 mg 100 g<sup>-1</sup> in S6 to 1.70 in S9 for sands, from 0.93 mg 100 g<sup>-1</sup> (S6) to 2.59 (S9) for silts, and from 5.02 mg 100 g<sup>-1</sup> (S6) to 21.52 (S18) for clays. Thus after cropping the  $K_{ex}$  levels had dropped except in the case of Raumai soil (S9) where the  $K_{ex}$  either increased (sand) or remained unchanged (silts and clays). This taken together with the higher K uptake from the separates of this soil (S9) highlights the rapidity at which K is being released to the bathing solution from the K bearing minerals.

#### **7.3.2.3.4 Comparative contribution of $K_{ex}$ and $K_{dex}$ uptakes to total K uptake from the soil separates**

There were considerable differences within the soil separates in the amounts of  $K_{ex}$  and  $K_{dex}$  contributed (Table 7.9). The wide differences in the  $K_{dex}$  contribution among the 6 soil clays could be a reflection of the rapidity with which K from 2:1 clay minerals is being released into the plant available pool. For example, the clays of the Raumai (S9), Pirinoa (S13), and Opuha (S18) soils contributed more  $K_{dex}$  to total plant K uptake than those of the Marton (S6), Matapiro (S11), and Wharekaka (S12) soils.

Thus the percent contributions of  $K_{dex}$  to total K uptake of ryegrass for the clays of S9 (99 %), S13 (84 %), and S18 (69 %) are considerably greater than that of the remaining soil clays (Table 7.10). Indeed, from Table 7.10  $K_{dex}$  appeared to be the major contribution to total plant uptake for the sands and silts of all the soils and for the clays of the 3 soils mentioned above.

#### **7.3.2.3.5 Predicted contribution of soil separates to K uptake of ryegrass grown in whole soil**

As in the case of K releasing power it is possible to predict the expected contributions of the textural fractions to total plant K uptake if ryegrass were grown on the whole soil. The predicted values are shown in Table 7.11 together with the percent contribution of  $K_{dex}$  by each fraction. Thus for the Marton soil (S6) it is predicted the sand would contribute 7 % of total K uptake but 11 % of the  $K_{dex}$ , the silt 31 % and 52 %, and the clay 62 % and 37 %. For 4 soils (S6, S9, S11, and S12) the sand and silt fractions combined would contribute 38 %, 42 %, 41 %, and 25 %, respectively, of the total K uptake by ryegrass shoots.

Furthermore, the predicted sand plus silt contribution to the  $K_{dex}$  uptake by these 4 soils would be 63 %, 46 %, 74 %, and 56 %, respectively. These fractions would therefore be expected to play an important role in the field with regard to K nutrition. The  $K_{dex}$  contributed by the sand plus silt fractions of the Pirinoa (S13) and Opuha (S18) soils

**Table 7.9** Actual contribution of  $K_{ex}$  and  $K_{nex}$  to total K uptake of ryegrass tops from the soil separates ( $mg\ 100\ g^{-1}$ )

Soil No.	Sand		Silt		Clay	
	$K_{ex}$	$K_{nex}$	$K_{ex}$	$K_{nex}$	$K_{ex}$	$K_{nex}$
S6	0.31	1.09	0.37	1.43	5.76	2.32
S9	-0.86	4.30	0.12	7.64	0.61	62.33
S11	0.32	2.08	1.02	3.86	13.37	3.53
S12	0.66	2.10	0.42	1.48	11.27	3.09
S13	0.21	2.07	0.42	1.48	8.53	44.37
S18	2.28	2.06	0.71	4.07	13.91	31.57

**Table 7.10** Percent contribution of  $K_{ex}$  and  $K_{nex}$  to total K uptake of ryegrass tops from the soil separates

Soil No.	Sand		Silt		Clay	
	$K_{ex}$	$K_{nex}$	$K_{ex}$	$K_{nex}$	$K_{ex}$	$K_{nex}$
S6	22	78	21	79	71	29
S9	0	100	2	98	1	99
S11	13	87	21	79	80	20
S12	24	76	22	78	78	22
S13	9	91	13	87	16	84
S18	53	47	15	85	31	69

**Table 7.11** Percent contribution of total plant K uptake (shoots) from the soil separates on whole soil basis (calculated as described in section 7.2.7)

Soil No.	Soil name	Sand	Silt	Clay
S6	Marton	7 (11)	31 (52)	62 (37)
S9	Raumai	23 (28)	19 (18)	58 (54)
S11	Matapiro	11 (21)	30 (53)	59 (26)
S12	Wharekaka	5 (12)	20 (44)	74 (44)
S13	Pirinoa	1 (1)	8 (6)	91 (93)
S18	Opuha	3 (2)	8 (10)	89 (88)

**Note:** Values in brackets indicate the percent contribution of  $K_{\text{nex}}$  uptake from the soil separates after weighting according to sand, silt, and clay composition in the whole soil

would be low (7 % and 12 %, respectively) despite these textural fractions together dominating the 2 soils (Table 3.2).

### **7.3.3 Validity of the computational method used to arrive at the relative contribution of soil separates to whole soil K releasing and supplying power**

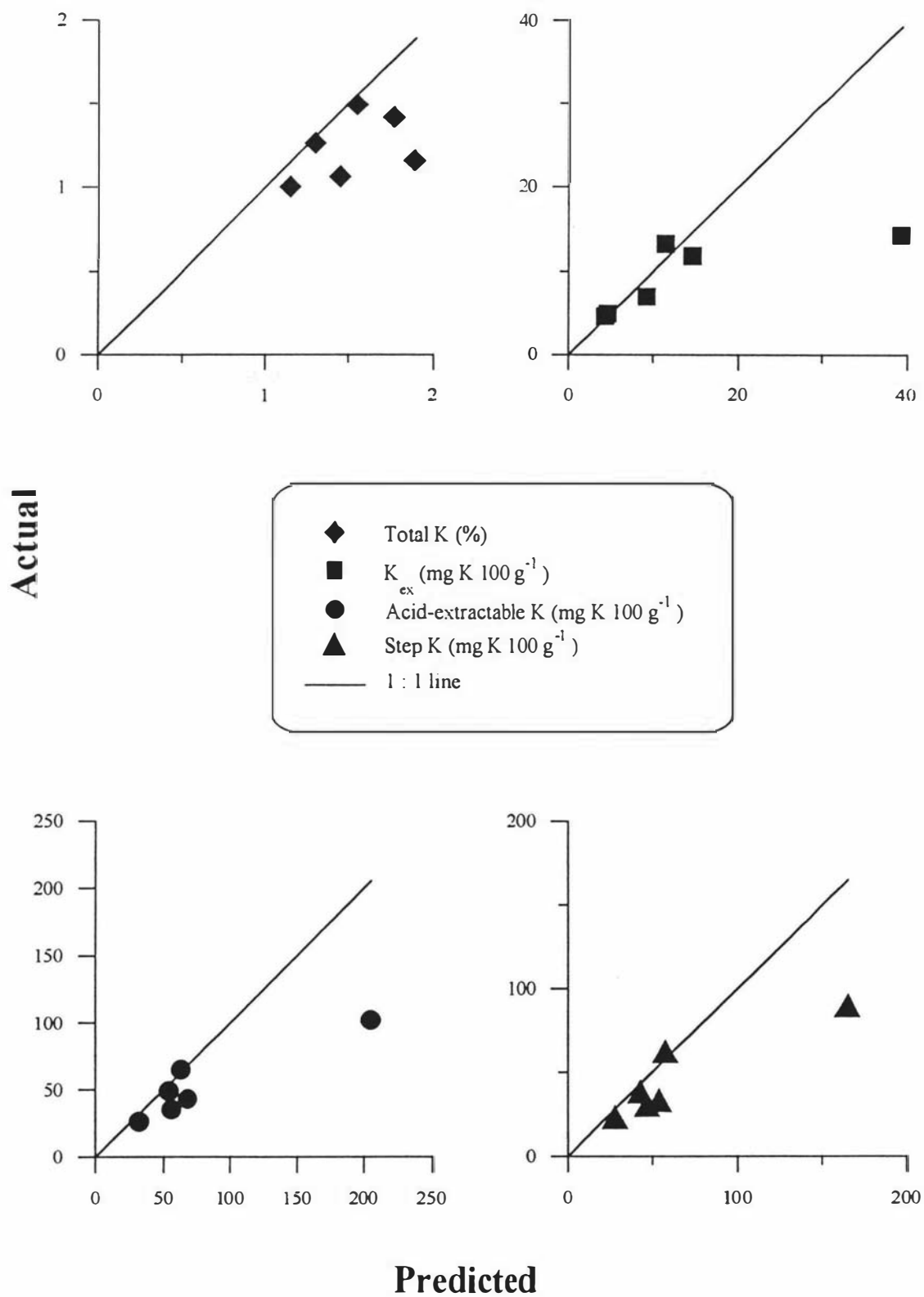
Figure 7.2 and 7.3 shows that the actual K release and supply data for the whole soil (unperoxidised soil for total K content; peroxidised soil for  $\text{NH}_4\text{OAc}$ -extractable K, acid-extractable K, and step K; and untreated peroxidised soil for K supply) do not consistently match with the predicted (computed) data of its separates on a whole soil basis. For example, the predicted values for  $K_{\text{ex}}$  of S18, and for acid-extractable K and step K of S12, S13, and S18 were considerably higher than the actual values (Fig. 7.2). Hence the relative contributions of soil separates to whole soil K releasing power in these soils (section 7.3.1) were of little significance.

Of some interest is the proximity of the acid-extractable K value for soil separates on whole soil basis to that of peroxidised whole soil in S6, S9, and S11. This confirms the potential K releasing power of sand plus silt fraction in these soils.

Similarly, the predicted K uptake values for the separates on whole soil basis for S9, S13, and S18, and the predicted  $K_{\text{nex}}$  values for almost all the soils were higher than that of the whole peroxidised (untreated) soils (Fig. 7.3) i.e., the performance of 3 fractions together in whole soil is different. This points to the difficulty of obtaining reliable estimates of relative contributions of textural fractions to whole soil K supply in these soils. The reason for these overestimates is most likely due to extra K release/supply from the clay fraction as a result of alterations during the separation procedure (e.g., freeze drying of clays).

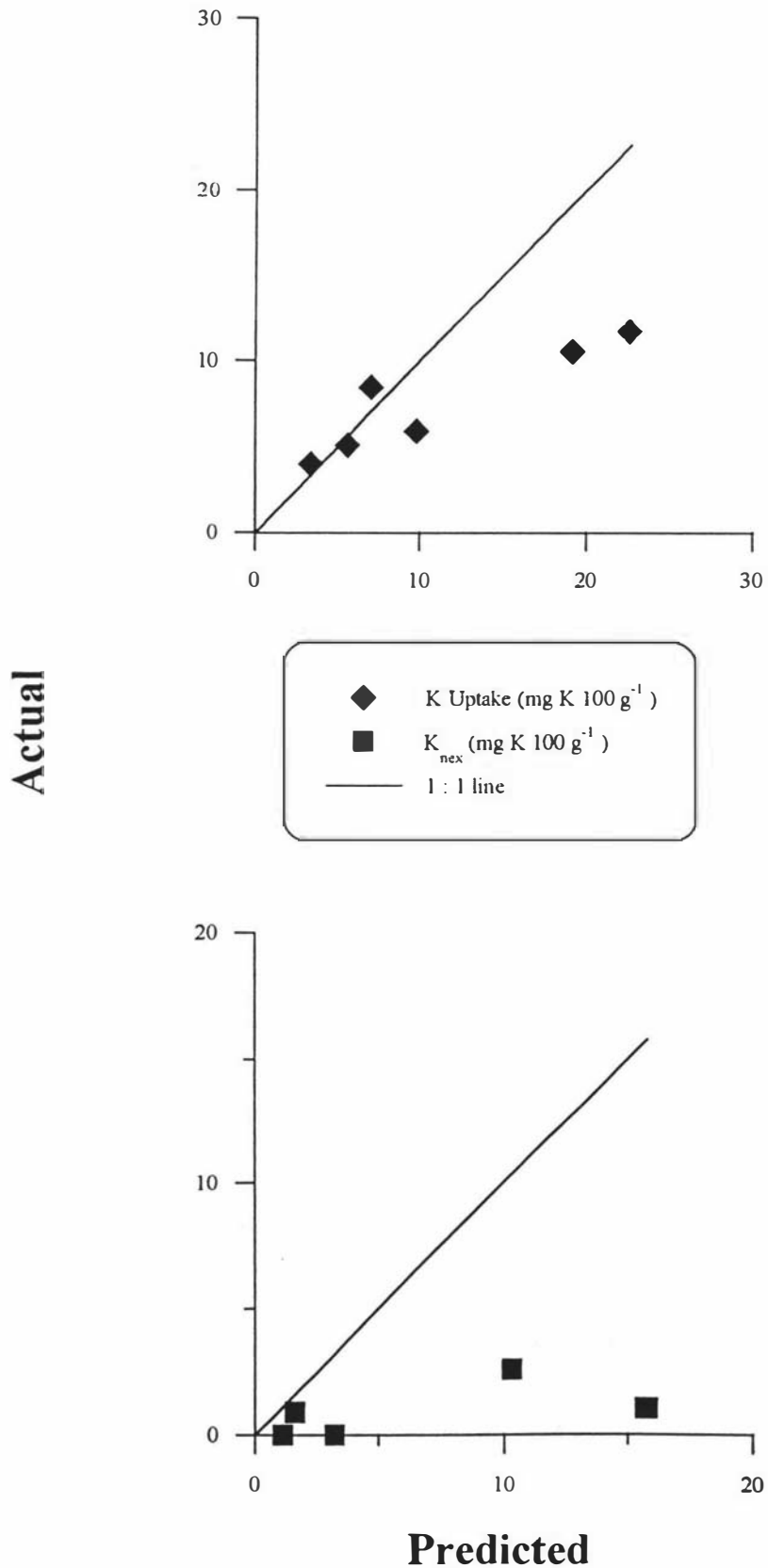
Thus most of the data in section 7.3.2.3.5 (Table 7.11) seems to be 'purely theoretical' and therefore it remains to be determined if the overestimation is acceptable, at least for the soils investigated. The predicted values of K uptake for S6, S11, and S12, however, remain valid and the data for the remainder of the soils can not be used to

**Fig. 7.2 Relationship between K releasing power for the whole soil (Actual) and for the soil separates on a whole soil basis (Predicted)**





**Fig. 7.3 Relationship between K supplying power for the whole soil (Actual) and for the soil separates on a whole soil basis (Predicted)**



emphasize the importance of coarser separates in plant nutrition.

It also remains to be determined if the differences in the total K uptake and  $K_{\text{dex}}$  uptake by ryegrass from the clays (Table 7.8 and Table 7.9) and the relative contribution of the separates to plant K uptake for S6, S11, and S12 (Table 7.11) reflect the mineralogy and the degree of difficulty with which K is weathered out of the mineral lattices.

It would be interesting to discover how valid are the relative contributions of soil separates to the chemical extraction procedures cited in the literature. Because in all the earlier studies (section 7.1), no attempt was made to separate the clay fraction (e.g., Lee and Gibson, 1974; Lee and Widdowson, 1977), to measure the actual K release from the whole soil (e.g., Munn *et al.*, 1976; Simard *et al.*, 1992), or to match the K release value for the whole soil (actual) with that of the separates on a whole soil basis (computed) e.g., James and Weaver, 1975; Al-Kanani *et al.*, 1984). McLean and Brydon (1963), however, reported that the computed amounts of  $K_{\text{dex}}$  of soil separates (measured by H-resin and boiling  $\text{HNO}_3$ ) together as whole soil were in accord with actual amounts determined.

#### 7.3.4 Relationship between acid-extractable K and plant K uptake

Figure 7.4 shows the correlation between acid-extractable K, and K uptake by ryegrass from the soil separates and from the whole (peroxidised and unperoxidised) soils.

If the K release to growing plants as measured by dry matter production and K uptake is a function of acid-extractable K (Chapter 6), there should be a significantly higher K uptake for Opuha (S18) clay when compared to Pirinoa (S13) clay because S18 clay released at least twice as much K as S13 to the acid extraction. Also, the K uptake from Raumai (S9) clay was about 4 times greater than that for Matapiro (S11) and Wharekaka (S12) clays (Table 7.8), even though all three had comparable levels of acid-extractable K (Table 7.3). This indicates that acid-extractable K release from the individual separates may not be a good indicator of plant available K. Nevertheless, the values of the acid-extractable K of the clay fraction arrived at by difference (Table 7.1)

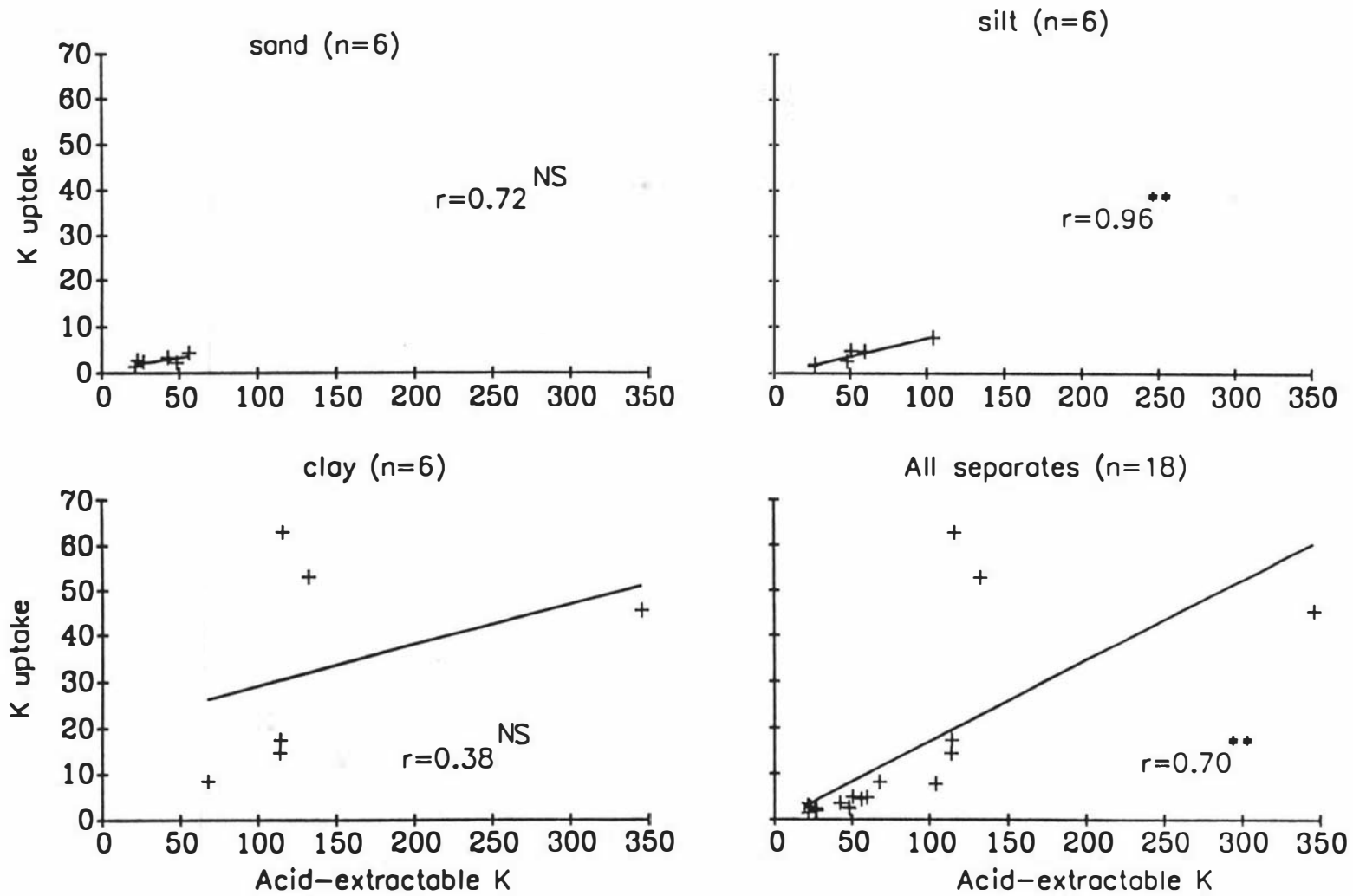


Fig. 7.4 Relationship between acid-extractable K (mg 100 g<sup>-1</sup>) and K uptake by ryegrass (mg 100 g<sup>-1</sup>) from the soil separates and soils

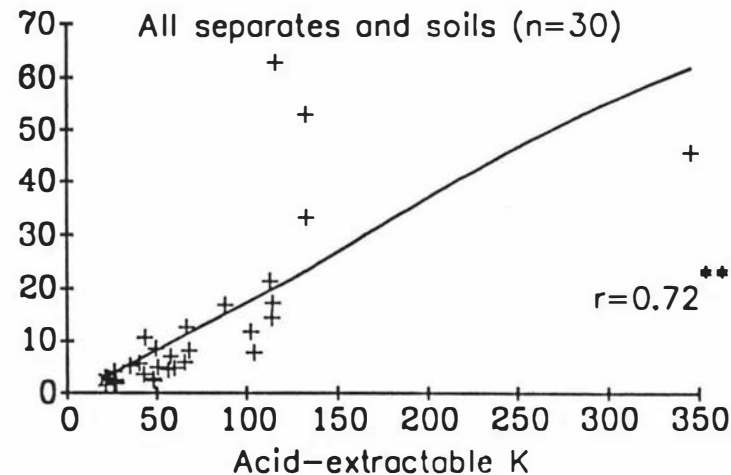
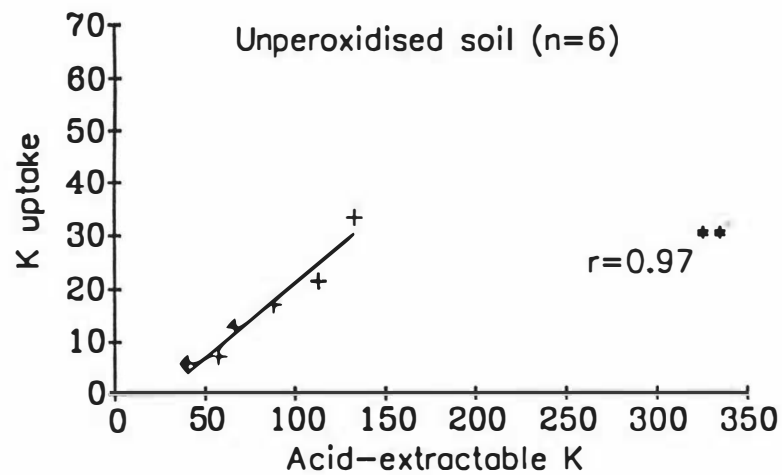
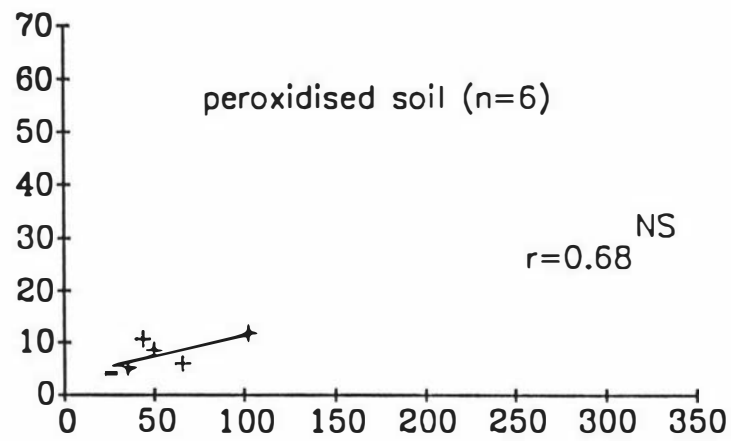
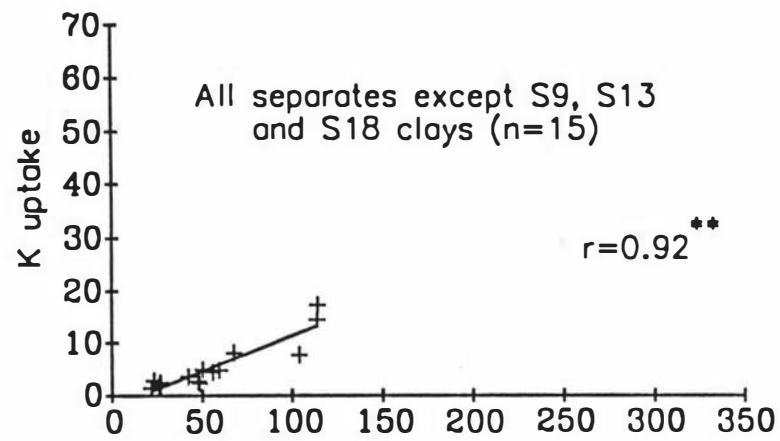


Fig. 7.4 (contd.) Relationship between acid-extractable K ( $\text{mg } 100 \text{ g}^{-1}$ ) and K uptake by ryegrass ( $\text{mg } 100 \text{ g}^{-1}$ ) from the soil separates and soils

explained 77 % of the variation in the K uptake. This indicates that it is very difficult to obtain reliable estimates for K releasing power of the separated clay fraction. It remains to determine the cause for the variable acid-extractable K release from the separated clays as a result of freeze drying. Probably the behaviour of hydrogen ions as a metal cation is more pronounced in the separated clays rather than in the whole unperoxidised soil.

A significant  $r$  value was obtained when the acid-extractable K values of all the three separates ( $n=18$ ) were correlated against their respective K uptake values. When, however, the clays of S9, S13, and S18 were excluded ( $n=15$ ), the  $r$  value increased from 0.70 to 0.92.

These results demonstrate that the acid-extractable K (a quantity factor) was only one factor affecting K release to plants. The rate factors may also be important in explaining the variations in K supply and in predicting K availability (Shaw *et al.*, 1983). In a review on the non-exchangeable K in soils, Martin and Sparks (1985), stated that the most important aspect of soil  $K_{\text{nex}}$  is the rate at which it is released to the exchangeable and solution forms which are readily available for plant uptake. It appears that the rate of K supply to growing plants in this study is considerably higher for S9 and S13 than for the remainder of the clays.

#### 7.4 CONCLUSIONS

1. Although on a unit weight basis the clay separates showed a much greater activity than the other fractions on a weighted basis, the contributions of the sand plus silt fraction to the total K uptake for the Marton (38 %), Matapiro (41 %), and Wharekaka (25 %) soils is of considerable importance. This suggests a need to focus attention on the mineral composition of sand and silt separates in these three soils as an important factor in determining the K fertility level.
2. It is evident that the K supplying power varied for the different soils, the variation being more pronounced for the clay fractions presumably due to

differences in the clay mineralogy. Since intensive farming requires continual replenishment of depleted resources,  $K_{\text{ex}}$  present in the interlayer positions of 2:1 clay minerals of the Raumai (S9), Pirinoa (S13), and Opuha (S18) soils would be more important for such replenishment than  $K_{\text{ex}}$  present in the clay minerals of the Marton (S6), Matapiro (S11), and Wharekaka (S12) soils.

3. This study emphasizes the general difficulty of obtaining reliable estimates of the relative contribution of soil separates to whole soil K release and supply. Although this study confirmed the potential K releasing power of sand plus silt fractions of the Marton (S6), Raumai (S9), and Matapiro (S11) soils, it reconfirmed this only for S6 and S11 soils with respect to K supplying power.
4. Acid-extractable K of the soil separates was significantly correlated with plant K uptake. Acid-extractable K is not all that effective with the K uptake by ryegrass from soil separates when compared to that from whole (unperoxidised) soil.

## CHAPTER 8

### MINERALOGY OF YGE AND RELATED SOILS IN RELATION TO NON-EXCHANGEABLE K RELEASING AND SUPPLYING POWER

#### 8.1 BACKGROUND

The mineralogy presented in this chapter is sequential upon information presented in previous chapters (2, 4, 6, and 7) which indicated that:

- (a) The  $K_c$  method of measuring  $K_{\text{dex}}$  releasing power may reflect soil mineralogy (Chapter 2, section 2.7.2.3). Thus  $K_c$  levels are expected to be highest in soils containing large amounts of K bearing primary minerals in sands and silts and in secondary minerals (clays). Since a substantial part of the plant available K in many soils is present in K bearing minerals of the clay fraction, an understanding of the clay mineralogy should provide an insight into the K releasing and supplying power of the soils.
- (b) Only soils with a  $K_c$  value greater than 10 mg 100 g<sup>-1</sup> contributed to  $K_{\text{dex}}$  supply (Chapter 4) thus permitting a grouping of the YGE and related soils in the present study into two categories (i) a  $K_c$  range of 8-10 and (ii) a  $K_c$  range of 12-19 mg 100 g<sup>-1</sup> (Table 8.1). The step K method of measuring  $K_{\text{dex}}$  releasing power on the other hand correlated well with  $K_{\text{dex}}$  supplying power (Chapter 6).
- (c) The clay fractions released most acid-extractable K on a unit weight basis (Chapters 6 and 7) indicating that the  $K_{\text{ex}}$  and  $K_{\text{dex}}$  releasing power of clay is higher than that of the sand and silt separates. Thus the  $K_c$  of the whole soil may reflect the  $K_c$  of the clays rather than the  $K_c$  of the silts and sands.

**Table 8.1**  $K_c$ , Step K, and  $K_{dex}$  supply ( $\text{mg } 100 \text{ g}^{-1}$ ) of the unleached YGE soils of different regions (data from Chapters 4 and 6)

Soils		$K_c$		Step K	$K_{dex}$ uptake	
<b>South Island</b>						
Timaru (a)	S14	17	12-19 range	75	27	
Timaru (b)	S15	15		62	8	
Claremont (a)	S16	13		60	16	
Claremont (b)	S17	12		42	3	
Opuha (a)	S18	18		101	35	
Opuha (b)	S19	14		60	11	
<b>North Island</b>						
Pirinoa	S13	19		70	26	
Raumai	S9	17		106	41	
Te Arakura	S10	16		50	5	
Tokorangi	S1	13	53	7		
Wharekaka	S12	15	49	4		
Matapiro	S11	9	8-10 range	44	0.93	
Ohakea	S8	10		35	Nil	
Tokomaru (a)	S2	9		28		
Tokomaru (b)	S3	9		30		
Halcombe	S7	10		29		
Milson	S4	8		26		
Marton (a)	S5	8		24		
Marton (b)	S6	8		31		

- (a) Undeveloped site  
 (b) Developed site



- (d) The total uptake of K by ryegrass shoots (a measure of K supplying power) from the clay fraction was significantly higher than that from the sand and silt fractions, and variations occurred in the  $K_{\text{nex}}$  supplying power of the clays (Chapter 7).
- (e) The sand and silt fractions of only 2 soils, the Marton (S6) and Matapiro (S11), could be expected to play an important role in the field with regard to K nutrition (Chapter 7).

The overall objective of the study described in this chapter is to identify the clay minerals in the YGE and associated soils with a view to relating the K bearing mineral patterns to the  $K_{\text{nex}}$  releasing and supplying power. Specifically, clay mineralogy was determined to ascertain if there are differences between the clays with the  $K_c$  ranges of 8-10 and 12-19 mg 100 g soil<sup>-1</sup>.

## 8.2 MATERIALS AND METHODS

### 8.2.1 Clay mineralogy

#### 8.2.2.1 *Procedure for identification of clay minerals by X-ray diffraction analysis*

To enable valid comparisons to be made among the 19 YGE and related soils, it is important that the clay samples be treated in precisely the same manner. In the present study  $\text{NH}_4$  saturated clays were used to obtain the XRD patterns based on the methodology of Kirkman and Pullar (1978). Whole soil was peroxidised to remove organic matter, suspended in water, raised to pH 10.0 by addition of 1:1  $\text{NH}_4\text{OH}$ , and dispersed ultrasonically at 20 kHz for 2 min. The clay fraction ( $< 2 \mu\text{m}$ ) was decanted after centrifugation at 1000 rpm for the appropriate period of time based on the temperature of the suspension. Subsamples of  $\text{NH}_4$  clay suspension were used to saturate the clay with (a) K (1 M KCl) and (b) Mg (1 M  $\text{MgCl}_2$ ). In each instance 0.5 ml chloride solution was added to 2 ml of  $\text{NH}_4$  clay suspension. Excess chloride was

removed by distilled water washing. The  $\text{NH}_4$ , K, and Mg suspensions were mounted on glass slides, dried overnight at  $20^\circ\text{C}$ , and 5 % glycerol in ethanol was fine sprayed on to the dry Mg clay sample only after an initial XRD irradiation. The clay specimens were irradiated with Fe filtered X-rays ( $\text{Co K}\alpha$ ) from  $4^\circ - 16^\circ 2\theta$  using a Phillips XRD diffractometer. The K saturated clay was sequentially heated at  $200^\circ\text{C}$ ,  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ , and  $500^\circ\text{C}$  for 30 min to assist identification and characterization of vermiculite.

Thus, for each clay 8 XRD patterns were obtained viz,  $\text{NH}_4$ , Mg, Mg plus glycerol, K, (all at room temperature) and K plus heating to 4 temperatures.

#### **8.2.2.2 *Interpretation of XRD patterns for clay mineral identification***

The XRD patterns were examined for a 1.00 nm mica peak, a 1.48 nm vermiculite or chlorite peak, a 1.80 nm smectite peak, and 0.70 nm peak that may be due to a second order reflection (002) of 1.48 nm material or to a first order reflection of a kaolin mineral (kaolinite/halloysite).

Weathering proceeds by a process of removal of interlayer K followed by the invasion of the interlayer space by a variety of cations including hydroxylated Al and hydrated Mg. This results in expansion of the lattice and modification of the chemical properties of the clay. The clay species undergoing this process display a continuum of hydroxy interlayered forms depending on the degree of in-filling of interlayer spaces with hydroxy polymers.

The 1.48 nm reflection in the XRD pattern of the  $\text{NH}_4$  saturated clay could be due to vermiculite or chlorite. Smectite dried at room temperature gives a reflection in the 1.20-1.40 nm region. When vermiculite forms under weakly acid conditions, the interlayer space is most commonly occupied by hydrated Mg ions. Subsequent K saturation, with or without heat, causes the c-spacing to collapse from approximately 1.48 nm towards 1.0 nm as Mg is replaced by K. This vermiculite may be called "magnesium vermiculite".

When vermiculite forms under more acid conditions, the proportion of hydroxy-Al ions in the interlayer space increases at the expense of Mg, and the lattice collapses on K saturation only with difficulty. Heat treatment over the temperature range of 200°C to 500°C may be needed to bring about a collapse (to near 1.00 nm). This vermiculite may be termed "heat collapsible vermiculite".

When the in-filling of the interlayer space with hydroxy-Al material is complete, the mineral is regarded as chlorite. This mineral, if present, will not collapse on K saturation plus heat treatment and the c-spacing remains at approximately 1.48 nm.

Thus K saturation and sequential heating treatment causes lattice collapse in the region of 1.00 to 1.48 nm which reflects the completeness of the hydroxy-Al intercalating layer.

If after Mg saturation plus glycerol treatment, a reflection shifts from 1.20-1.40 nm to approximately 1.80 nm smectite is present.

A strengthening of the 0.70 nm reflection and concomitant weakening of the 1.48 nm reflection indicates chlorite. The 0.70 nm reflection disappears at 500°C if it is due to kaolin.

### 8.2.2.3 *Transmission electron microscopy*

Selected clays were investigated by transmission electron microscopy (TEM). Specimens were prepared after dilution of the original  $\text{NH}_4 < 2 \mu\text{m}$  suspension. One drop of the diluted suspension was dried at 60°C for 10 min after mounting on a carbon film supported by a copper grid 3 mm in diameter. The TEM investigation aimed to determine if halloysite was present. This material has a characteristic and easily recognized morphology in the soils of New Zealand (Kirkman, 1977).

### 8.2.2 Sand and silt mineralogy

Sands ( $> 63 \mu\text{m}$ ) and silts ( $2\text{-}63 \mu\text{m}$ ) from Chapter 6 (section 6.2.4) were used to obtain XRD patterns. A non-oriented powder sample of each of these separates was irradiated with X-rays from  $4^\circ - 74^\circ 2\theta$ . Oriented samples of silts were irradiated from  $2^\circ - 16^\circ 2\theta$  to assist identification of the micaceous minerals.

Sands ( $> 63 \mu\text{m}$ ) and coarse silts ( $20\text{-}63 \mu\text{m}$ ) of selected soils (Raumai, Matapiro, and Pirinoa) were investigated for primary minerals using optical microscopy. The fine silts ( $2\text{-}20 \mu\text{m}$ ) of these soils were irradiated with X-rays from  $4^\circ - 74^\circ 2\theta$ .

## 8.3 RESULTS AND DISCUSSION

### 8.3.1 Clay mineral identification

Smectite and chlorite minerals were found to be absent from all the clays investigated.

There was a general similarity of the XRD patterns in the 1.00 and 0.7 nm regions of Tokomaru, Marton, Wharekaka, and Timaru clays with the respective Ah horizon clay XRD patterns of Pollok (1975).

The reflection in the region of 1.03-1.17 nm indicated the presence of micas at different stages of weathering.

The 1.48 nm reflection that is indicative of vermiculite was found to be absent from most of the soils in this study. This is contrary to the results of clay mineral analyses conducted by Pollok (1975) and New Zealand Soil Bureau (New Zealand Soil Bureau National/Overseas Soil Databases) on selected YGE soils. Possibly the 1.48 nm material in this study collapsed due to  $\text{NH}_4$  saturation, a treatment not used in the studies reported earlier.

Where a 1.48 nm reflection was present K saturation without heat treatment did not

result in a shift of the reflection towards 1.00 nm indicating absence of Mg vermiculites in the soils that contained 1.48 nm material (S17, S19, S13, and S12).

Sequential heating of K saturated clay samples on the other hand caused ongoing collapse of the lattice from 1.48 nm towards 1.00 nm and therefore vermiculite clays with a range of Al-hydroxy interlayering may be present.

The 0.70 nm peak could be due either to the second order reflection of hydroxy interlayered vermiculite or to halloysite or to both. The peak at 1.00 nm due to mica sharpened and tended to intensify after sequential heating of the samples.

### **8.3.2 XRD patterns of the clays with $K_c$ ranges of 8-10 and 12-19 mg 100 g soil<sup>-1</sup>**

The profiles of the 1.00 nm and 0.70 nm reflections were different for the soil clays of the two  $K_c$  ranges (Table 8.2, and Figures 8.1 & 8.2).

The 1.00 nm reflections increased in sharpness with increasing  $K_c$  value. Increased sharpness of the reflection may imply increased crystallinity, decreased weathering, and thus increased K content and therefore could account for increased  $K_c$ . Typical central YGE soils fall in the 8-10  $K_c$  range and their southern counterparts in the 12-19 range. The exceptions to this trend were Tokorangi (S1) and Wharekaka (S12) soils.

For clays of soils in the  $K_c$  range 8-10 heating of the K saturated clay to 200°C resulted in a sharpening of the 0.70 nm reflection. Since a 1.48 nm peak was absent, the sharpening of the 0.70 nm peak was probably due to dehydration of halloysite. The presence of halloysite was confirmed by TEM which showed curled flakes and tubular particles typical of this material. Further heating to 400°C caused no further sharpening of the reflection but at 500°C it disappeared presumably due to destruction (dehydroxylation) of the halloysite phase.

For clays of soils in the  $K_c$  range of 12-19, the 0.70 nm peak was smaller and did not sharpen with the heat treatment. This indicated the absence of halloysite in these soils.

**Table 8.2** Differences in the clay mineralogy and the amounts (subjective assessment), and in K releasing/supplying power of the YGE and related soils in the two  $K_c$  ranges

		$K_c$ (8-10 mg 100 g soil <sup>-1</sup> )	$K_c$ (12-19 mg 100 g soil <sup>-1</sup> )
1	Profile of 1.0 nm peak See peak (b) in Fig. 8.1 and 8.2	Blunt and low	Sharp and tall
2	Profile of 0.7 nm peak See peak (c) in Fig. 8.1 and 8.2	Sharp and tall	Blunt and low. S9 is exception*
3	Mica/illite/hydrous mica (2:1 minerals)	++	+++
4	Spectrum of vermiculite/interstratified clays (mixed clays) (2:1 minerals)	+++	++
5	Kaolinite/halloysite (1:1 minerals)	+++	+ (S9 and S10 are exceptions**)
6	Step K range (Table 8.1)	24-44	42-106
7	$K_{ex}$ supply range (Table 8.1)	0-0.93	4-35

+++ Large amount  
++ Moderate amount  
+ Small amount

- \* 0.7 nm peak intensifies after K Heat 200°C even though it was blunt after  $NH_4$  and K saturation
- \*\* TEM studies revealed appreciable amounts of halloysite and kaolinite in S9 (Table 8.4)
- \*\* Possibly no halloysite in S10 (NZ Soil Bureau National/Overseas Soil Databases)

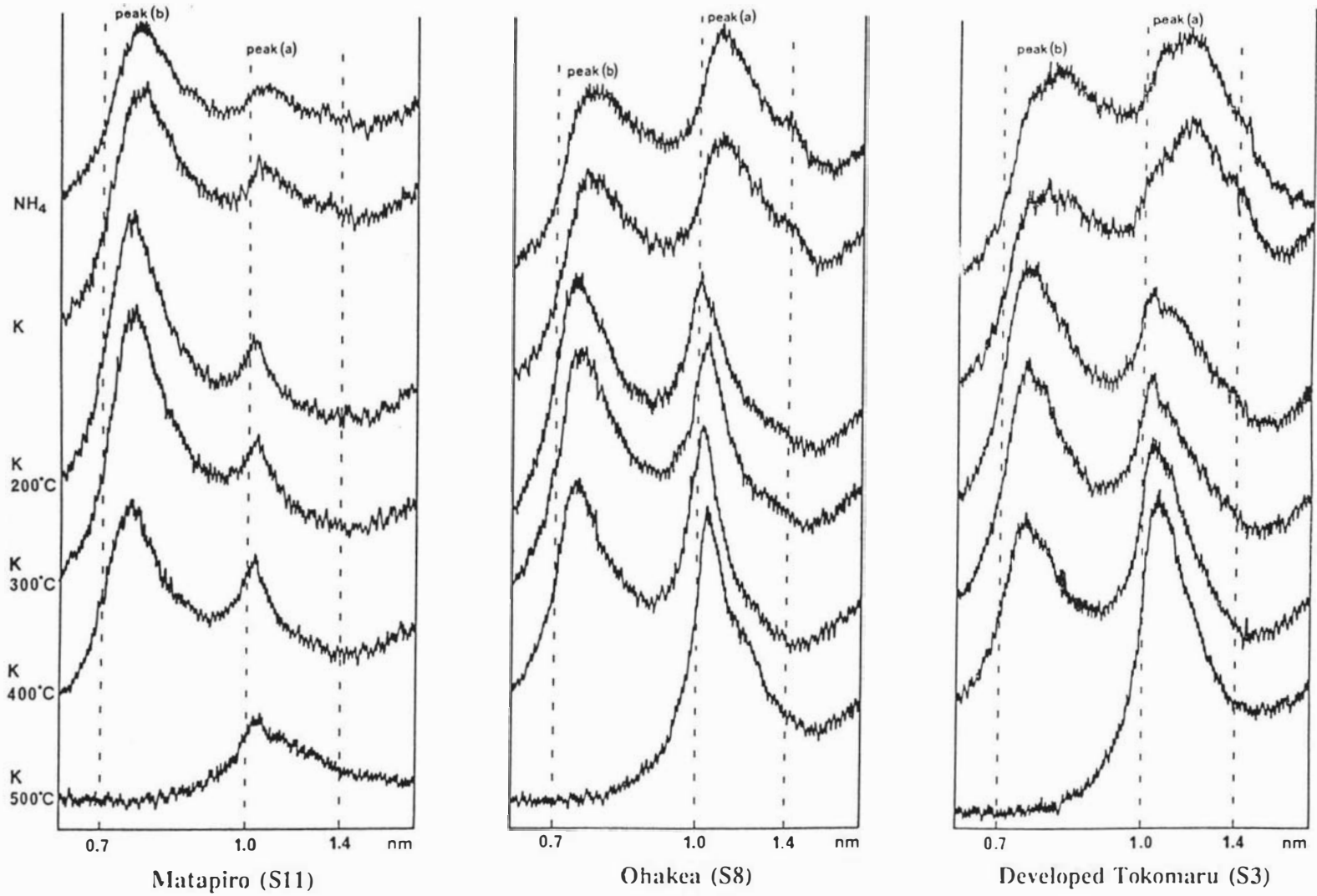


Fig. 8.1 X-ray diffractograms of soil clays ( $< 2 \mu\text{m}$ ),  $K_c$  range 8-10 mg 100 g soil<sup>-1</sup>

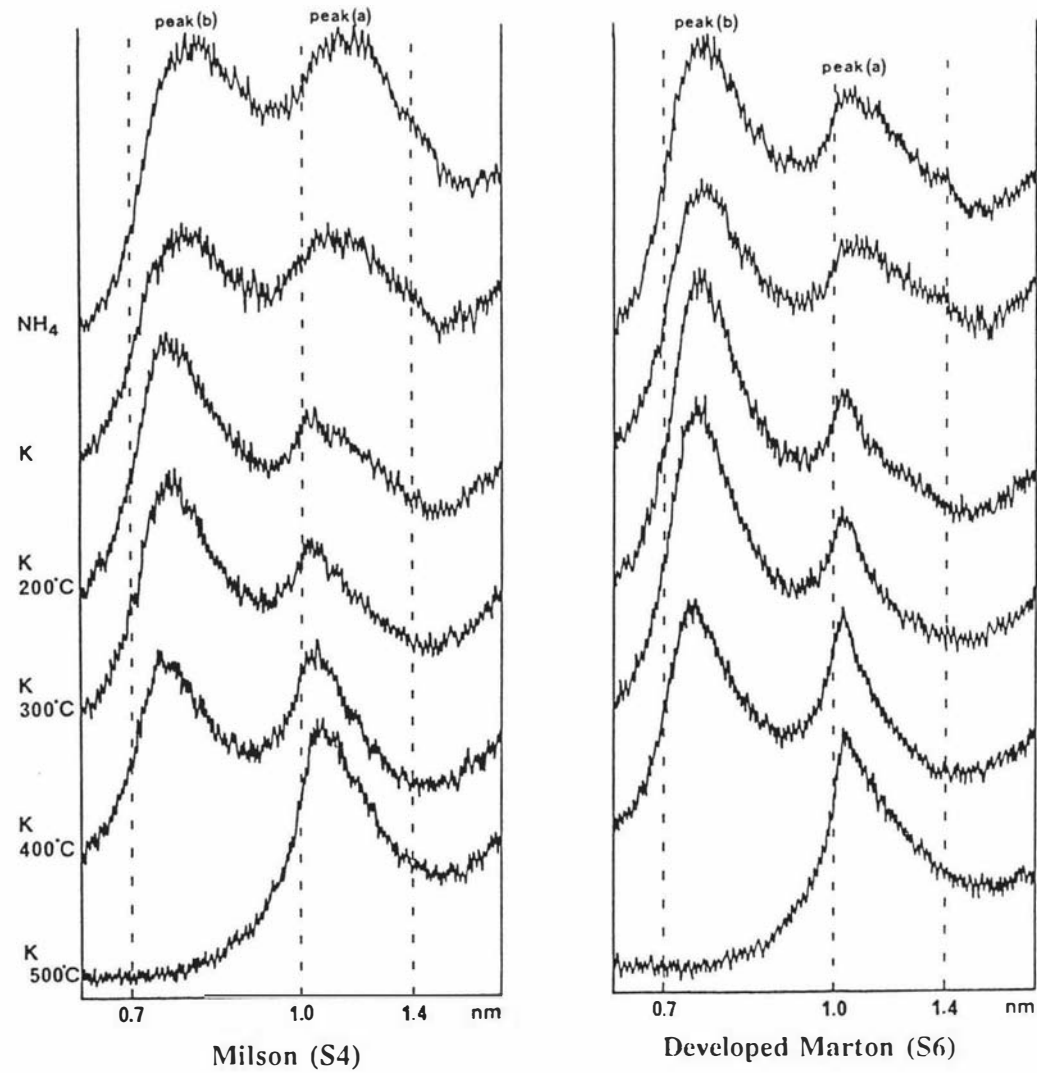


Fig. 8.1 contd.



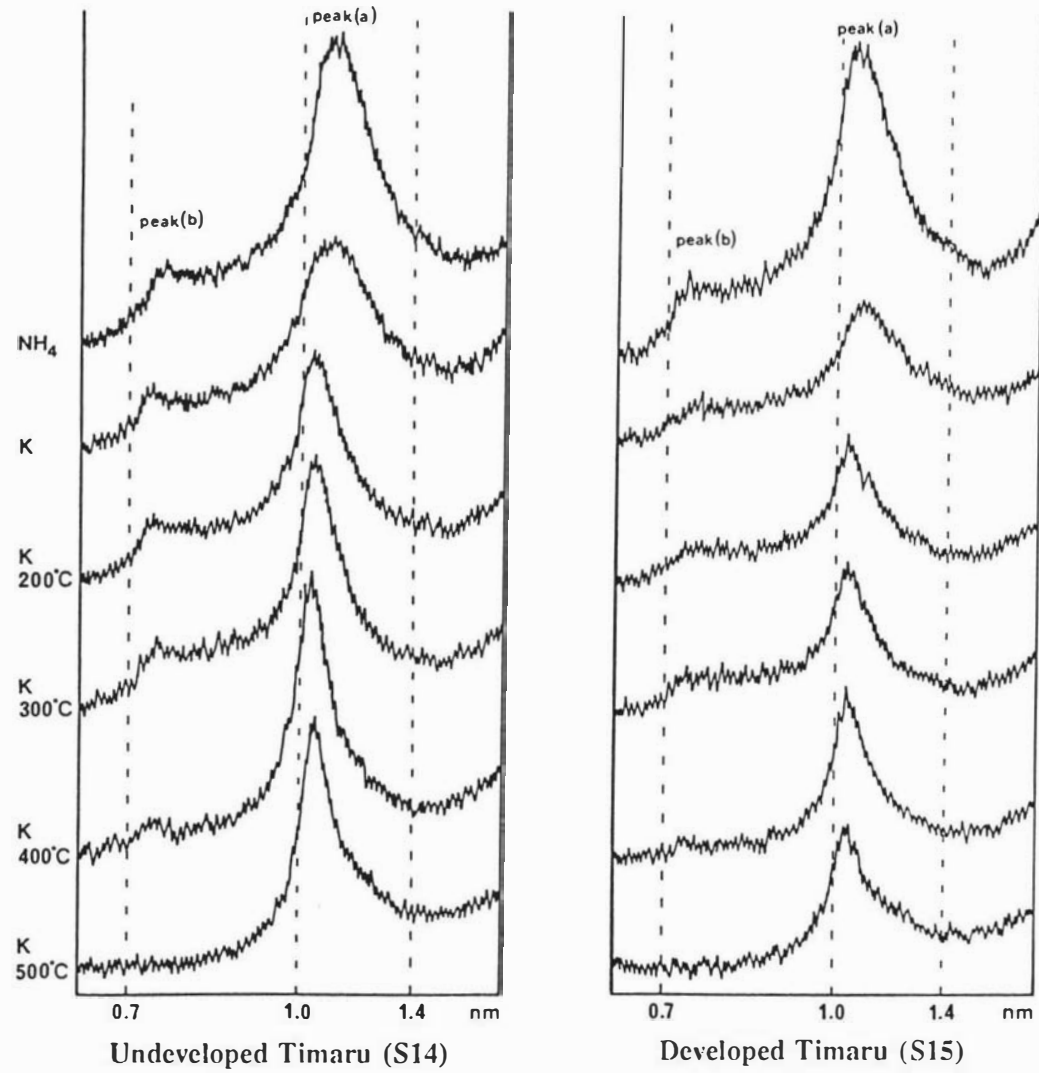


Fig. 8.2 X-ray diffractograms of soil clays (< 2  $\mu\text{m}$ ),  $K_c$  range 12-19 mg 100 g soil<sup>-1</sup>

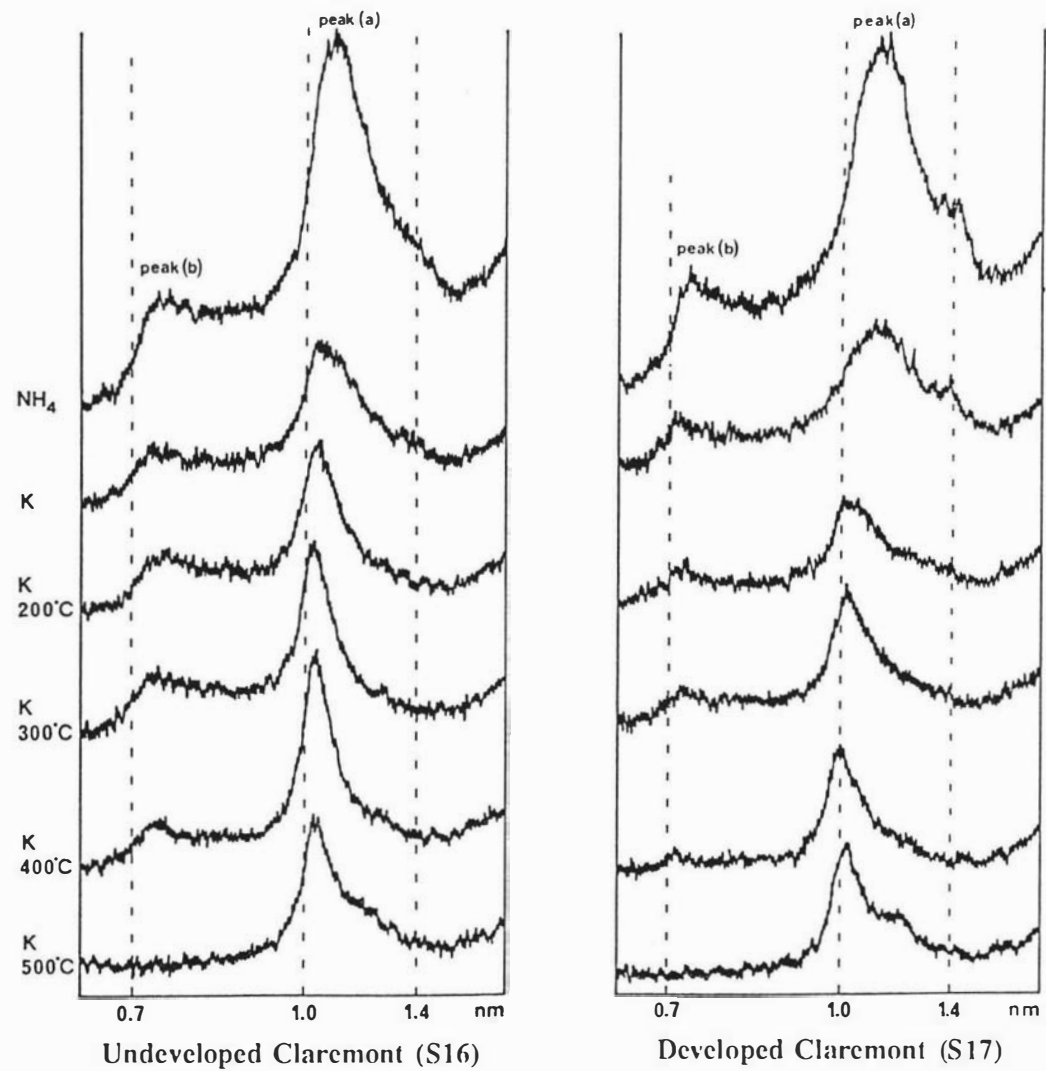


Fig. 8.2 contd.

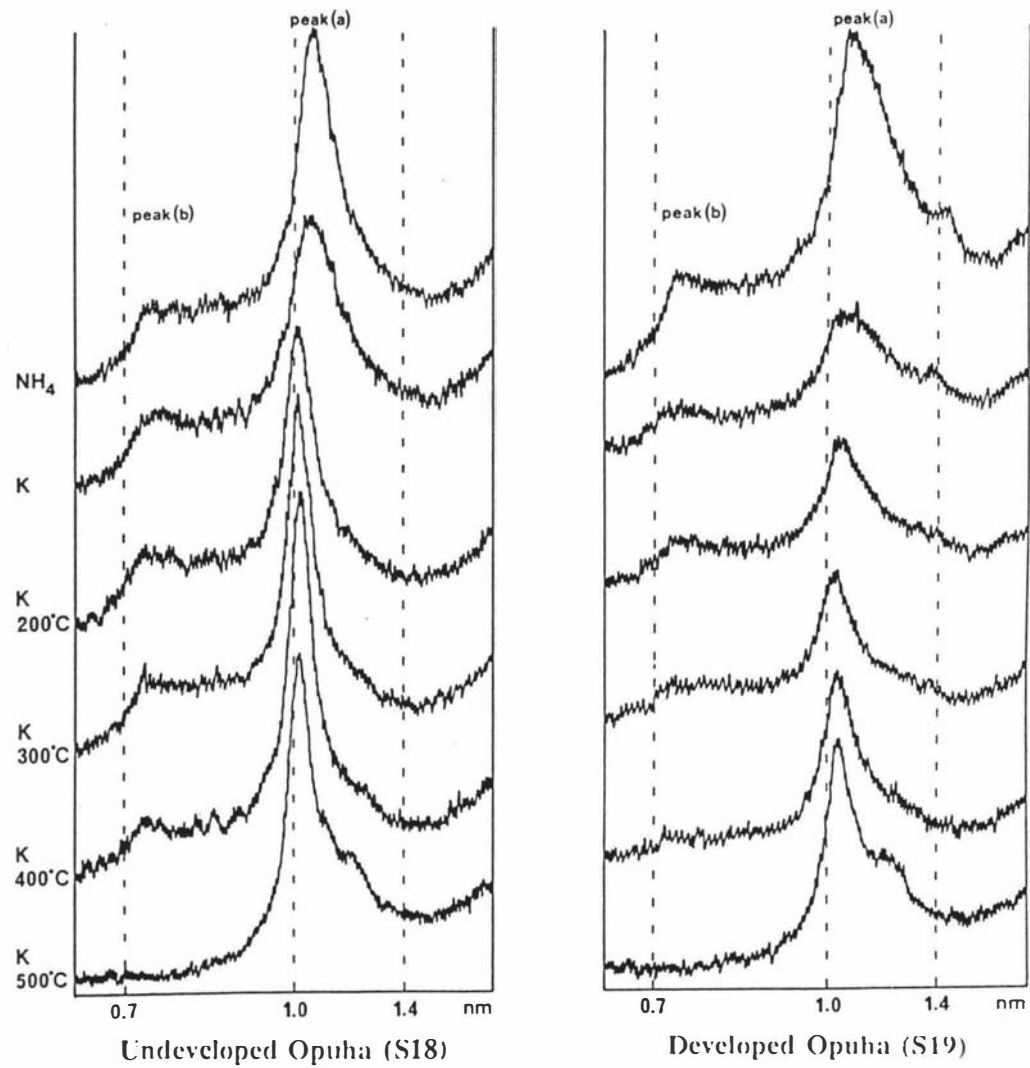


Fig. 8.2 contd.

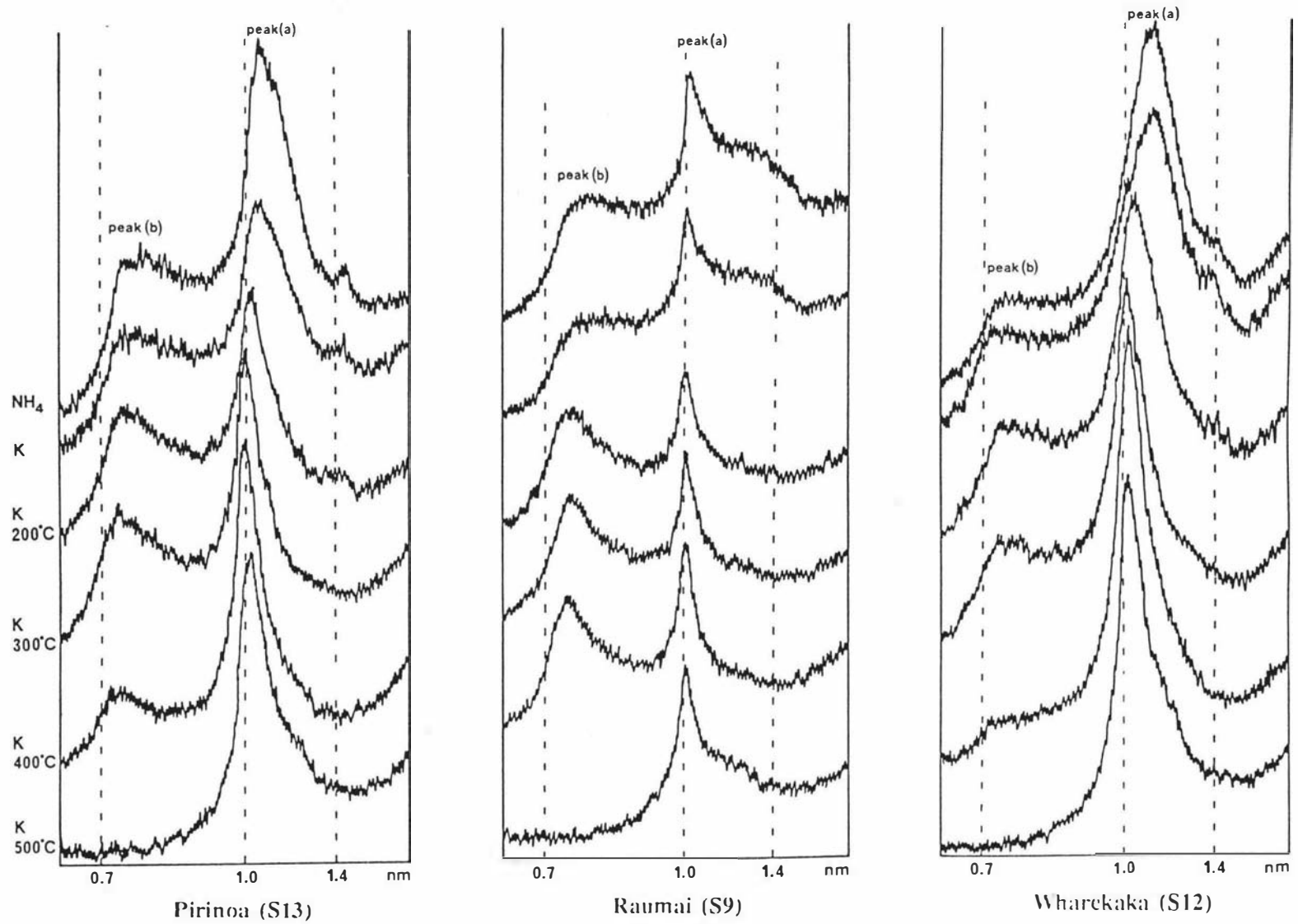


Fig. 8.2 contd.

The exceptions were Raumai (S9) and Pirinoa (S13). The presence of halloysite in S9 (dominant) and S13 (very few particles) was confirmed by the TEM study (Table 8.3).

In general, the 0.70 nm clay material of soils of  $K_c$  8-10 was mostly halloysite, and hydroxy interlayered vermiculite was insignificant or absent. For clays of soils of  $K_c$  12-19, hydroxy interlayered vermiculite was present together with mica and halloysite was, at best, a minor component.

### 8.3.3 Relationship between mineralogy and $K_{n_{ex}}$ releasing and supplying power of soils

It appears that clays from soils in the  $K_c$  range 12-19 are dominated by mica and expanded micaceous material whereas those in the  $K_c$  range 8-10 contain expanded micaceous materials together with halloysite. Thus the  $K_c$  values reflect the soil mineralogy. On this basis it would be more appropriate to rank Tokorangi (S1), Wharekaka (S12), and the YGE intergrades (S9, S10, and S13) as "high"  $K_c$  soils rather than "medium"  $K_c$  soils as suggested by Cornforth and Sinclair (1984).

The  $K_c$  range 12-19 soils released more step K and gave a higher  $K_{n_{ex}}$  supply than soils with a  $K_c$  range of 8-10 (Table 8.2). The wide variations in the step K and  $K_{n_{ex}}$  supply of the soils in the  $K_c$  range of 12-19 (Table 8.1), however, could not be explained by the mineralogy. For example, the XRD patterns of clays from developed sites did not differ significantly from their undeveloped counterparts (see Fig. 8.2) even though their  $K_{n_{ex}}$  uptake varied considerably (Table 8.1).

The differences in the  $K_{n_{ex}}$  uptake by ryegrass between the developed and undeveloped YGE soils from the southern region, however, owe more to the step K values than the  $K_c$  values (see Table 8.1). Thus step K is a better measure of  $K_{n_{ex}}$  releasing power than  $K_c$  as already indicated in Chapter 6 (section 6.3.3).

Table 8.4 shows that the Wharekaka (S12) clay supplied little  $K_{n_{ex}}$  to plants compared to the clays of S9, S13, and S18 yet all fall in the  $K_c$  range of 12-19. Presumably the

**Table 8.3 Summary of clay minerals of 3 soils identified using XRD patterns in conjunction with TEM**

Soil	K <sub>c</sub> range	Clay minerals identified	Dominant mineral
Raumai (S9)	12-19	(a) Unexpanded mica (1.03 nm) (b) Expanded mica weathering to vermiculite (1.28 nm) which collapses to 1.02 nm on K + Heat 200°C (c) Halloysite	Mica (but less than for Pirinoa)  (Fig. 8.2)
Pirinoa (S13)	12-19	(a) Expanded mica (1.06 nm) (b) Vermiculite (1.41 nm) which collapses to 1.03 nm on K + Heat 300°C. Therefore may vermiculite of S13 may contain slightly more Al than that of S9. (c) Halloysite and kaolinite	Mica  (Fig. 8.2)
Matapiro (S11)	8-10	(a) Expanded mica (1.06 nm) (b) Small amounts of vermiculite (1.33 nm) which collapses on K + Heat 200°C (c) Halloysite	Halloysite  (Fig. 8.1)

Note: Vermiculite in Raumai > Pirinoa > Matapiro

**Table 8.4** Non-exchangeable K releasing power and supplying power (mg 100 g<sup>-1</sup>) of clay fraction (Chapter 7 data)

<b>K<sub>c</sub> range of soils</b>	<b>Soil</b>	<b>Step K of the clay fraction (Table 7.3)</b>	<b>K<sub>ncx</sub> supply of the clay fraction (Table 7.9)</b>
12-19 mg 100 g <sup>-1</sup>	Wharekaka (S12)	95	3.1
	Pirinoa (S13)	111	44.4
	Opuha undeveloped (S18)	311	31.6
	Raumi (S9)	101	62.3
8-10 mg 100 g <sup>-1</sup>	Marton developed (S6)	57	2.3
	Matapiro (S11)	93	3.5

Note: K<sub>c</sub> of clays was not measured

rate of recharge of K from interior lattice sites of the Wharekaka (S12) clay was insufficient, possibly due to low rate factors. More information is needed to characterize the expanded (1.12 nm) mica material of the S12 clay in relation to K supplying power. At another site, the Ah horizon of this soil contained large amounts of interstratified clays and mica/illite (Pollok, 1975).

Table 8.3 shows that the mica content is less in Raumai (S9) when compared to Pirinoa (S13). Despite this the  $K_{\text{nex}}$  supply from the clay fraction of the former soil was considerably higher than that of the latter, indicating the importance of rate factors in governing K release from clay minerals.

#### 8.3.4 Sand and silt mineralogy

XRD analyses showed that the sands and silts consisted of mainly quartz and feldspars. The XRD pattern of the oriented sample of Raumai silt (S9), however, showed a 1.02 nm reflection indicative of mica.

Table 8.5 shows some of the minerals in the sand and coarse silt fractions of Raumai (S9), Matapiro (S11), and Pirinoa (S13) soils as identified by optical microscopy. These minerals were expressed on weight basis as percentage of total sample. For example, 10.08 % (6.55 + 3.53) of the total sample is volcanic glass in the sand plus silt (coarse) fractions of Matapiro soil (S11). The remainder (89.92 %) constitutes the other minerals identified by optical microscopy viz, minerals in Table 8.5 as well as clear quartz, secondary quartz plus feldspars, volcanic quartz, and volcanic mafics; and minerals in fine silt and clay fractions.

The sand and coarse silt fractions of Matapiro (S11) thus had higher amounts of volcanic glass than those of Raumai (S9) and Pirinoa (S13). Micas were more abundant in the Raumai (S9) sand than in the sands of S11 and S13.

Quartz and feldspars were identified from the XRD patterns of fine silts of S9, S11, and S13. The fine silt of Raumai (S9), however, contained some mica.



**Table 8.5 Primary minerals in sand and coarse silt fractions expressed as percentage of total sample (soil after removal of organic matter, amorphous materials, and water)**

Soil	SAND			
	Volcanic glass	Greywacke fragments	Micas	Total
<b>Raumai (S9)</b>	0.16	25.85	3.09	<b>29.10</b>
<b>Pirinoa (S13)</b>	0.52	3.87	0.05	<b>4.44</b>
<b>Matapiro (S11)</b>	6.55	9.01	0.04	<b>15.60</b>

Soil	SILT (coarse silt only)			
	Volcanic glass	Greywacke fragments	Micas	Total
<b>Raumai (S9)</b>	0.15	0.37	0.72	<b>1.24</b>
<b>Pirinoa (S13)</b>	0.42	0.62	0.31	<b>1.35</b>
<b>Matapiro (S11)</b>	3.53	0.00	0.18	<b>3.71</b>

**Note:** Greywacke is a type of sedimentary rock. It is not a mineral. It consists of sand and silt fragments held in micaceous matrix (illite-mica matrix) and hence may be a potential source of K

The probable sources of K from clay, and sand plus silt fractions of S9, S11, and S13 are presented in Table 8.6. Possibly other K bearing minerals (sericite and K feldspars) are present in the coarser fractions but only in small amounts.

**Table 8.6** Probable sources of K from the clay and sand plus silt fractions

Soil	$K_c$ range of soil	Clay	Sand + Silt
Raumai (S9)	12-19	Mica + Vermiculite	Micas
Pirinoa (S13)	12-19	Micas Possible contribution from vermiculites	Micas Volcanic glass
Matapiro (S11)	8-10	Mica Possibly little or no contribution from vermiculites	Mainly from volcanic glass Very little from micas

#### 8.4 CONCLUSIONS

The soils in the 12-19 mg 100 g<sup>-1</sup>  $K_c$  range were distinct from those in 8-10 mg 100 g<sup>-1</sup>  $K_c$  range not only in the  $K_{ex}$  release and supply but also in the XRD patterns. The former group of clays appeared to contain more K bearing minerals than the case for the latter. The differences in the  $K_{ex}$  release and supply among the soils in either  $K_c$  range could not be explained by mineralogy.

## CHAPTER 9

### ASSESSMENT OF THE K SUPPLYING POWER OF YGE SOILS

#### 9.1 BACKGROUND

As mentioned in Chapter 2 (section 2.9), the most widely used method for assessing the potassium fertilizer requirement of pasture farming systems in New Zealand is the Computerized Fertilizer Advisory Services (CFAS) mass balance model of Cornforth and Sinclair (1984) currently used by AgResearch. This is a simplified version of an earlier model by Campkin (1985).

The mass balance model is based on the assumption that the flow of K through the plant available pool of nutrients in the soil is in steady state and the plant and/or animal requirements can be maintained if K losses from the system are equalled by K gains (Campkin, 1985; Williams, 1988).

Potassium fertilizer requirements for a specific farming system are calculated as the difference between the "losses of K" from the system and the "gains of K" to the cycling K pool from the weathering of soil minerals. While the K losses are calculated by the "animal loss" and the "leaching loss" parameters of the CFAS model, the gains (contribution of soil K) are estimated empirically from the long term K supplying power of the soil or reserve K pool (based on  $K_c$ ) and the immediate K supply from  $K_{ex}$  forms (based on QTK). The CFAS model is therefore a depletive model rather than a true maintenance model. This is because soil  $K_{ex}$  and  $K_c$  only help to offset the losses of K. Thus total soil K is gradually depleted.

A true maintenance (sustainable) model on the other hand would disregard the K supply from soil and all the K losses are "made good" by addition of K fertilizers. This approach would incur unnecessary expenditure on K fertilizers in high reserve K soils in the short term.

There is, however, evidence (Williams *et al.*, 1986; Williams *et al.*, 1990) that shows that the estimate of "soil K supply" using the CFAS model is not a good predictor of the K supplying power of the soils in which the plant available non-exchangeable K is a major component. This reflects the lack of appropriate methods (chemical measurements) to estimate reliably soil K supplies.

It is evident, from the equation for the fertilizer K requirement (section 2.9), that the soil QTK and  $K_c$  values are central to the calculation of fertilizer requirement. This chapter deals with the assumptions made as to the plant availability of exchangeable K (in terms of quick test units) and reserve K ( $K_c$ ) on an annual basis. At present  $K_c$  values are assigned on the basis of soil group (0.70, 0.30, and 0.10 meq % for high, medium, and low  $K_c$  soils, respectively).

The present study is not intended to test the validity of the fertilizer equivalents of QTK and  $K_c$ , which are estimated to be 0.75 kg ha<sup>-1</sup> and 0.40 kg ha<sup>-1</sup> for each unit of QTK and  $K_c$ , respectively (Campkin, 1985). Rather it examines the limitations imposed by using an assigned  $K_c$  value instead of measuring the actual  $K_c$  for each soil. The study also aims to test the accuracy of the predicted soil K supply, using different soil K supply equations (section 9.2) against the K availability to ryegrass grown in the glasshouse trial (Chapter 4).

The overall objective of the study reported in this chapter is therefore to examine the practical implications of the measured differences in K supplying power of 19 YGE and related soils in the pot trial using the "soil K supply" parameter of the CFAS model.

## 9.2 THEORY

The "soil K supply" parameter of the original model (Campkin, 1985) and that of the current AgResearch model (Comforth and Sinclair, 1984) assumes the following forms.

$$\text{Soil K supply (kg ha}^{-1} \text{ yr}^{-1}) = \{10 (\text{QTK}-3) + 100(K_c)\} \quad (9.1)$$

(Campkin, 1985)

$$\text{Soil K supply (kg ha}^{-1} \text{ yr}^{-1}) = 10 (\text{QTK} - D) \quad (9.2)$$

Where  $D = 0$  for medium  $K_c$  soils  
 and  $D = 2$  for low  $K_c$  soils  
 (Cornforth and Sinclair, 1984)

The QTK is expressed in quick test units (parts per 250,000 of extracting solution) and  $K_c$  is expressed in meq %. The constants 10 and 100 in Eq. 9.1 represent the estimates of the K supplied from QTK and  $K_c$  as kg K ha<sup>-1</sup> yr<sup>-1</sup> for one unit of QTK and for one meq % of  $K_c$ , respectively.

Equation 9.2 is a simplified version of Eq. 9.1 and is intended to estimate soil K supplies for low and medium  $K_c$  soils only (section 2.9). To obtain estimates of soil K supply for high  $K_c$  soils Eq. 9.1 can be used by substituting an assigned value of 0.70 meq % for  $K_c$  (Campkin, 1985). A detailed explanation of the calculation involved in estimating the soil K supply in the format used in Eq. 9.1 is reported in Chapter 2 (section 2.9). Both Eq. 9.1 and Eq. 9.2 will be referred to as "AgResearch equations" in this chapter.

The  $K_c$  values for Eq. 9.1 can be obtained either by (a) assigning constant  $K_c$  values to the designated soil groups (0.30 meq % for the North Island YGE soils and 0.70 meq % for the South Island YGE soils) as presently followed by the AgResearch (Cornforth and Sinclair, 1984), or (b) measurement, or (c) rating the measured  $K_c$  values based on the Campkin rating procedure (Campkin, 1985 and Table 9.1) followed by assigning the respective  $K_c$  values (0.10, 0.30, and 0.70 meq % for low, medium, and high  $K_c$  soils, respectively).

When the assigned  $K_c$  values (Campkin, 1985) are used, Eq. 9.1 assumes the forms given in Table 9.1 for low (Eq. 9.3), medium (Eq. 9.4), and high (Eq. 9.5)  $K_c$  soils.

For soils in the Recent New Zealand soil group that contain relatively large amounts of non-exchangeable K (Jackson, 1985), the following equation was developed by Cornforth and Sinclair (1984) to predict the soil K supply.

$$\text{Soil K supply (kg ha}^{-1}\text{ yr}^{-1}\text{)} = 50 (\text{NaTPB K} + 0.10) \quad (9.6)$$

Where NaTPB K is K removed by sodium tetraphenyl boron (NaTPB) reagent (Jackson, 1985).

Also available is the equation developed by A. Metherell (pers. comm.) based on NaTPB K and QTK. The K supplied from non-exchangeable but available potassium (NEAP) in the Metherell equation is calculated using NaTPB K and QTK, and replaces  $K_c$  in Eq. 9.1. The K supplied from NEAP is estimated as 50 kg ha<sup>-1</sup> yr<sup>-1</sup> per one meq % of NEAP (A. Metherell, pers. comm.). This means that NEAP has a fertilizer equivalent of 18.86 % that is annually plant available compared to 40 % for  $K_c$ .

$$\text{Soil } K_{\text{nex}} \text{ supply (kg ha}^{-1} \text{ yr}^{-1}) = (50 \text{ NaTPB K} - 3.5 \text{ QTK}) \quad (9.7)$$

Therefore,

$$\begin{aligned} \text{Soil K supply (kg ha}^{-1} \text{ yr}^{-1}) &= 10 (\text{QTK} - 3) \\ &+ \\ & (50 \text{ NaTPB K} - 3.5 \text{ QTK}) \end{aligned} \quad (9.8)$$

The K supply from the 19 unleached YGE and related soils (described in Chapter 3) was estimated using the equations 9.1-9.8. The measured QTK and the measured  $K_c$  values are presented in Table 9.2. The plant K uptake from the unleached soils in the pot trial (Chapter 4) was used to test the accuracy of the model predictions using a range of K supply equations.

**Table 9.1** Simplified equations to estimate soil K supplies (kg ha<sup>-1</sup> yr<sup>-1</sup>) for low, medium, and high  $K_c$  soils (Campkin, 1985)

$K_c$			Equation	Equation No.
Rating	Range (meq %)	Assigned (constant) value (meq %)		
Low (L)	<0.21	0.10	10(QTK-2)	9.3
Medium (M)	0.21-0.45	0.30	10(QTK+0)	9.4
High (H)	>0.46	0.70	10(QTK+4)	9.5

Table 9.2  $K_c$  rating and measured  $K_c$  and QTK values of 19 soils

Soil No.	Soil name	Classification using		Measured $K_c$ values (meq %)	QTK
		Assigned $K_c$ values for soil groups (Cornforth and Sinclair, 1984)	Campkin (1985) rating procedure (Table 9.1) based on measured $K_c$ values of soils		
North Island YGE and related soils		<b>MEDIUM</b>			
S1	Tokorangi		M	0.34	14
S2	Tokomaru (a)		M	0.23	8
S3	Tokomaru (b)		M	0.24	4
S4	Milson		L	0.20	18
S5	Marton (a)		L	0.20	2
S6	Marton (b)		L	0.21	2
S7	Halcombe		M	0.24	7
S8	Ohakea		M	0.26	7
S9	Raumai		M	0.44	2
S10	Te Arakura		M	0.40	3
S11	Matapiro		M	0.23	6
S12	Wharekaka		M	0.38	2
S13	Pirinoa	H	0.48	6	
South Island YGE soils		<b>HIGH</b>			
S14	Timaru (a)		M	0.43	23
S15	Timaru (b)		M	0.37	4
S16	Claremont (a)		M	0.34	11
S17	Claremont (b)		M	0.32	3
S18	Opuha (a)		M	0.45	11
S19	Opuha (b)	M	0.35	7	

- (a) Undeveloped site  
(b) Developed site

### 9.3 RESULTS AND DISCUSSION

#### 9.3.1 Soil K supply from exchangeable sources

The predicted K supply of the 19 YGE soils from exchangeable sources (as measured by QTK) using the first half of Eq. 9.1 ranged from -10 to 200 kg ha<sup>-1</sup> yr<sup>-1</sup> (Table 9.3).

The negative or zero soil QTK supply resulted from assuming that QTK levels rarely fall below 3 for most New Zealand soils (Campkin, 1985). Calculations based on the model therefore show that soils can supply 10(QTK-3) kg K ha<sup>-1</sup> annually from their exchangeable pool.

The negative or zero QTK supply in Marton (S5 and S6), Raumai (S9), Te Arakura (S10), Wharekaka (S12), and developed Claremont (S17) soils indicated that during a year these soils theoretically cannot supply K from the exchangeable pool. Thus all the K taken up by the plants is derived from  $K_{\text{ncx}}$  sources. If this situation existed on a dairy farm it would mean that either the  $K_{\text{ncx}}$  sources are releasing sufficient K to maintain maximum pasture production or K deficiency is reducing pasture yield. The possibility of no contribution from QTK is unlikely as for all soils in the pot trial, the contribution of  $K_{\text{ex}}$  to plant uptake is positive (Chapter 4).

#### 9.3.2 Predicted soil K supply from non-exchangeable sources based on the assigned and measured $K_c$ values

The soil  $K_{\text{ncx}}$  supply currently assigned (Cornforth and Sinclair, 1984) to the 13 North Island and the 6 South Island soils under investigation is 30 and 70 kg ha<sup>-1</sup> yr<sup>-1</sup>, respectively (column A in Table 9.3). This means that the less weathered YGE soils in the South Island are predicted to supply 40 kg ha<sup>-1</sup> more K from the reserve K pool annually than their counterparts in the North Island irrespective of the variations in  $K_{\text{ex}}$  availability within the soils of either region.

The predicted reserve K supply of South Island YGE soils based on measured  $K_c$  values (column B in Table 9.3) are on average 33 kg ha<sup>-1</sup> yr<sup>-1</sup> lower than those based on the



**Table 9.3** Predicted soil K supply from  $K_{ex}$  and  $K_{nex}$  sources

Soil No.	Soil name	Soil K supply (kg ha <sup>-1</sup> yr <sup>-1</sup> ) from $K_{ex}$ and $K_{nex}$ pools (Eq. 9.1)			
		$K_{ex}$ pool	$K_{nex}$ pool		
			100 ( $K_c$ )		
		10(QTK-3)	A	B	C
S1	Tokorangi	110	30	34	30
S2	Tokomaru (a)	50	30	23	30
S3	Tokomaru (b)	10	30	24	30
S4	Milson	150	30	20	10
S5	Marton (a)	-10	30	20	10
S6	Marton (b)	-10	30	21	10
S7	Halcombe	40	30	24	30
S8	Ohakea	40	30	26	30
S9	Raumai	-10	30	44	30
S10	Te Arakura	0	30	40	30
S11	Matapiro	30	30	23	30
S12	Wharekaka	-10	30	38	30
S13	Pirinoa	30	30	48	70
S14	Timaru (a)	200	70	43	30
S15	Timaru (b)	10	70	37	30
S16	Claremont (a)	80	70	34	30
S17	Claremont (b)	0	70	32	30
S18	Opuha (a)	80	70	45	30
S19	Opuha (b)	40	70	30	30

- A = Based on the current categorisation of the North Island YGE and related soils as medium  $K_c$  soils (0.30 meq % as an assigned  $K_c$  value) and their southern counterparts as high  $K_c$  soils (0.70 meq % as an assigned  $K_c$  value)
- B = Based on measured  $K_c$  values
- C = Based on measured  $K_c$  values of the soils, rating the  $K_c$  of the soils using Campkin's ranking procedure (Table 4.1 and Table 9.1), and thereafter estimating soil  $K_{nex}$  supply using the respective assigned  $K_c$  values of Campkin (Table 9.1)

Cornforth and Sinclair (1984) rating (column A in Table 9.3). The difference in the reserve supply estimated by using the measured  $K_c$  values and the assigned  $K_c$  value in the YGE soils in the North Island was less than or equal to  $18 \text{ kg ha}^{-1} \text{ yr}^{-1}$ . The variations in  $K_{\text{nex}}$  supply within the soils of either North Island YGE group or South Island YGE group may be economically significant enough to invalidate applying a single  $K_c$  value to either of the groups.

The average predicted  $K_{\text{nex}}$  supply from these North Island soils is, however, similar to that of the assigned supply ( $30 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ).

It should be noted that the measured  $K_c$  ratings of the soils in Table 9.2 are based on measurement, and ranking according to the Campkin (1985)  $K_c$  rating procedure. Indeed, the rating procedure of Campkin (Table 9.1) was the basis on which the assigned  $K_c$  values (0.10, 0.30, 0.70 meq % for low, medium, and high  $K_c$  status soil, respectively) were obtained. Using this criterion, 4 of the North Island YGE soils did not fall into the medium  $K_c$  category whereas all the South Island soils fell into the medium  $K_c$  group (Table 9.2) as against the medium and high categories in the current scheme, respectively (Cornforth and Sinclair, 1984). This misranking will lead the current model (using AgResearch equations) to overestimate soil K supply by  $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$  in S4, S5, and S6 and underestimate by  $40 \text{ kg}$  in S13 (Comparing A and C in Table 9.3). The predicted K supply from the South Island soils will be higher by  $40 \text{ kg ha}^{-1} \text{ yr}^{-1}$ . This casts some doubt as to the classification of the South Island YGE soils in the current scheme as high  $K_c$  soils. It may be that if the rated  $K_c$  for South Island YGE soils is "medium" then the estimation that no K fertilizer is required for these soils (Cornforth and Sinclair, 1984) may be in error.

It is not clear why in the current CFAS model for determining K fertilizer requirements the South Island YGE soils were rated as "high"  $K_c$  soils while none of the YGE soils in this study (Table 9.2) and in the literature (New Zealand Soil Bureau, 1968; Metson, 1980) approach this figure. The  $K_c$  of the Claremont soil, however, in one separate study (Jackson, 1985) is reported to be 0.76 meq %, thus reflecting the extent of variability in  $K_c$  measurement even within a soil type. Both the undeveloped (S16) and the developed (S17) Claremont soils in the present study, on the other hand, have the

same  $K_c$  value of 0.33 meq % (Table 9.2).

Campkin (1985) may have assigned a value of 0.70 meq % to high  $K_c$  soils so that the model could cater for recent alluvial soils with very high  $K_c$  (Cornforth and Sinclair, 1984).  $K_c$  values of more than 0.70 meq % are infrequent in New Zealand soils. The soils reported to have  $K_c$  values higher than 0.70 meq % are listed in Table 9.4.

The suggestion by AgResearch that no K fertilizer is required on high  $K_c$  soils implies that the amounts of K being released from minerals in these soils are sufficient to replace the annual K loss from a farming system. It is not known, however, how long the rate of supply of  $K_{\text{ex}}$  continues to replace the losses of K.

### 9.3.3 Relationship between observed K uptake by plants and predicted soil K supply

Table 9.5 shows the soil K supply of the 19 YGE soils (X-variable) estimated using different models (section 9.2) regressed against observed K uptake (Y-variable) by ryegrass grown on the unleached soils (Chapter 4). The assumptions as to bulk density and rooting depth made for converting pot trial K uptake data to  $\text{kg ha}^{-1}$  were similar to those used when the original soil K supply model was developed (Campkin, 1985).

As seen from the slopes of the regression equations (Table 9.5), the pot trial extracted 2-3 times as much K as predicted by various models developed from field trial data, reflecting the capacity of the Stanford and DeMent technique of pot culture to exhaustively extract a plant nutrient. The larger K uptakes per unit weight of soil in the pot trial can be explained by the large amounts of dry matter produced. On a per hectare basis the dry matter (shoots) ranged from 84660 to 164560 kg. These values are based on the weight of the soil and assuming a soil depth of 75 mm. Havlin and Westfall (1985), Weber and Grimme (1986), and Portela (1993) all reported that the rate of K removal per unit soil mass under glasshouse conditions is much higher than in the field.

Other pot experiments in New Zealand that are less exhaustive than the pot trial in

**Table 9.4** List of New Zealand soils that have  $K_c$  values of more than 0.70 meq % as reported in the literature

Reference	Soil Name	Depth (mm)	New Zealand genetic soil group	$K_c$	
				Measured (meq %)	Assigned rating based on soil group (Cornforth and Sinclair, 1984)
Jackson (1985)	Claremont	0-75	Yellow-grey earth	0.76	High
	Hurunui	0-75	Yellow-brown earth	0.76	Medium
New Zealand Soil Bureau (1968)	Conroy sandy loam	0-102	Brown-grey earth	0.88	High
	Waikakahi clay loam	0-152	Rendzina	0.75	High
	Waiareka clay	0-76	Brown granular clay	1.30	High
	Ahuriri clay	0-76	Gley recent soil	0.82	High

**Table 9.5** Regression analyses between K uptake ( $\text{kg ha}^{-1}$ ) from the pot trial (Y-variable) and the soil K supply ( $\text{kg ha}^{-1} \text{ yr}^{-1}$ ) predicted using existing models (X-variable)

Model	$K_c$ based on	Regression equation	r
10 (QTK-3) + 100 ( $K_c$ )  (Eq. 9.1)	Assigned $K_c$ values for soil groups	$Y = 16.6 + 1.99X$	0.82**
	Measured values	$Y = 13.8 + 2.31X$	0.86**
	Measured and assigned values using Campkin's rating procedure	$Y = 22.0 + 2.27X$	0.84**
50 (NaTPB K+0.010)  (Eq. 9.6)	-	$Y = -12.5 + 3.10X$	0.92**
10 (QTK-3) + (50 NaTPB K- 3.5 QTK)  (Eq. 9.8)	-	$Y = 30.7 + 2.05X$	0.97**

Chapter 4 have shown that the observed K uptake by ryegrass plants was 2-4 times more than that predicted by the model using QTK and the measured  $K_c$  (Table 9.6).

The observed  $K_{\text{ex}}$  supply in the pot trial is 8.90 and 2.32 times more than that predicted annually using the second half of Eq. 9.1 (measured  $K_c$ ) and Metherell's equation (Eq. 9.7), respectively (see regression coefficients in Table 9.7). The former value may be a little misleading because of the large negative intercept obtained in the regression equation.

It appears from the correlation coefficients ( $r$ ) (Table 9.5) that the predicted total soil supply of K is reasonably good irrespective of how the  $K_c$  value is obtained. In contrast, table 9.7 shows that the  $r$  values for the supply of  $K_{\text{ex}}$  improved considerably when the  $K_c$  values are measured. Replacing  $K_c$  with the NaTPB K improved the fit.

#### 9.3.4 Development of a model for predicting soil K supply from the pot trial

In the original Campkin model (Eq. 9.1), the K supplied from QTK and  $K_c$  was estimated as 10 and 100 kg ha<sup>-1</sup> annually for one unit of QTK and for one meq % of  $K_c$ , respectively (Chapter 2, section 2.9). These estimates were based on one year K response field trials conducted at 38 sites throughout New Zealand (Campkin, 1983). For these trials, 100 percent clippings were returned. The major soil groups of New Zealand covering a wide range of  $K_c$  values were included. The  $K_c$  values, however, were not measured at the time, but were taken from Soil Bureau data (New Zealand Soil Bureau, 1968) for each soil group but not necessarily the same location and site conditions.

It is possible a significant linear fit could have been obtained with Campkin data based on the relationship between K uptake from the control plots (minus K treatment) and the measurements of K releasing power (QTK and  $K_c$ ). The estimates for QTK and  $K_c$  were, however, obtained on the basis of slopes derived from the regression analyses between these measurements of K releasing power and the fertilizer K required to produce 90 % maximum yields (Chapter 2).

**Table 9.6** Relationship between observed and predicted uptake in other pot experiments in New Zealand using Campkin equation (9.1)

	Reference	Soil:plant ratio (g plant <sup>-1</sup> )	No. of soils	Regression equation	r
1	Table 9.5	1	19	$Y = 13.8 + 2.31X$	0.86**
2	Jackson (1985) (Trial A soils)	8.33	13	$Y = -13.0 + 2.76X$	0.72**
3	Jackson (1985) (Trial B soils)	8.33	25	$Y = -19.3 + 4.26X$	0.85**
4	Hay (1971)	8.33	16	$Y = 43.0 + 1.80X$	0.53*
5	Campkin (1972)	66.66	13	$Y = 65.8 + 1.60X$	0.90**

Y = Observed K uptake (kg ha<sup>-1</sup>) in pot trial

X = Predicted K uptake (kg ha<sup>-1</sup> yr<sup>-1</sup>) using QTK and measured K<sub>c</sub> (Eq. 9.1)

**Table 9.7** Regression analyses between K<sub>ex</sub> uptake (kg ha<sup>-1</sup>) observed in the pot trial (X-variable) and that predicted (kg ha<sup>-1</sup> yr<sup>-1</sup>) by models (Y-variable)

Model	K <sub>c</sub> based on	Regression equation	r
100 (K <sub>c</sub> ) (Second half of Eq. 9.1)	Assigned K <sub>c</sub> values for soil groups	$Y = -32.5 + 2.08X$	0.41 <sup>NS</sup>
	Measured values	$Y = -227.7 + 8.90X$	0.85**
	Measured and assigned values using Campkin rating procedure	$Y = -55.3 + 3.85X$	0.49*
50 NaTPB K-3.5 QTK (Eq. 9.7)	-	$Y = -20.3 + 2.32X$	0.92**

On the other hand, the slopes obtained by the regression analyses between K uptake and the measurements of K release (Chapter 6) should give the amounts of K supplied to plants in the pot trial. Therefore, with the information available in Chapter 6 (Table 6.2) the following equations were developed using a conversion technique (to convert QTK units and meq % of  $K_c$  to  $\text{kg K ha}^{-1}$ ) similar to that of Campkin (1985).

$$\text{Soil K supply (kg ha}^{-1}\text{)} = 16 (\text{QTK}-3) + 994 (K_c) \quad (9.9)$$

$$\text{Soil K supply (kg ha}^{-1}\text{)} = 16 (\text{QTK}-3) + 175 (\text{step K}) \quad (9.10)$$

Equation 9.9 is based on the measured  $K_c$  values because K uptake is poorly correlated with the assigned  $K_c$  values. Furthermore, since step K was better correlated with K uptake (Table 6.2) and  $K_{\text{ncx}}$  uptake (Table 6.3) than  $K_c$ , Eq. 9.10 may be more valid and useful than Eq. 9.9.

An attempt was made to test the soil K supply model based on the pot trial study i.e., Eq. 9.9, against the data from other pot trials reported in the New Zealand literature (Table 9.8). It is evident from the regression slopes and intercepts that the equation developed from the present pot trial relates reasonably well with only one pot trial (Jackson, 1985; trial B soils) where maximum K uptake was  $1224 \text{ kg ha}^{-1}$ . The lack of general agreement is probably a reflection of different methodologies of measuring K uptake with different durations of cropping and with different planting densities.

## 9.4 GENERAL DISCUSSION

By considering the "soil K supply" parameter of the CFAS K model, it is possible to identify the factors which cause variations in the predicted soil K supply.

### 9.4.1 Variations due to reserve K supply

Currently quantifying the amount of annual reserve soil K ( $K_c$ ) supply is dependent on the ranking of soils by AgResearch into  $K_c$  categories (low, medium, or high) and subsequently assigning the corresponding  $K_c$  values (0.1, 0.3, and 0.7 meq %, respectively). No allowance is made for variations in "real"  $K_c$  within soil group.



**Table 9.8** Relationship between the observed and the predicted K uptake by ryegrass using equation 9.9 in the other pot experiments in New Zealand

	Reference	Soil:plant ratio (g plant <sup>-1</sup> )	No. of soils	Regression equation	r
1	Jackson (1985) (Trial A soils)	8.33	13	$Y = -104.9 + 0.72X$	0.75**
2	Jackson (1985) (Trial B soils)	8.33	25	$Y = -54.4 + 0.87X$	0.72**
3	Hay (1971)	8.33	16	$Y = -420.2 + 1.07X$	0.77**
4	Campkin (1972)	66.66	13	$Y = 33.8 + 0.57X$	0.85**

Y = Observed K uptake (kg ha<sup>-1</sup>) in pot trial

X = Predicted K uptake (kg ha<sup>-1</sup>) using QTK and measured K<sub>c</sub> (Eq. 9.9)

Indeed, measurements of  $K_c$  revealed that actual  $K_c$  may be well removed from assigned  $K_c$ . From the fertilizer requirement perspective the differences could cause errors in fertilizer recommendations (0.1 meq % of  $K_c$  has a fertilizer equivalent of 10 kg K ha<sup>-1</sup> yr<sup>-1</sup>). Furthermore, none of the soils under investigation has a measured  $K_c$  of greater than 0.48 meq %, yet some are ranked as high  $K_c$  soils (0.70 meq %).

#### 9.4.2 Variations due to soil $K_{ex}$ supply

The estimation of soil  $K_{ex}$  supply based on the equations 9.1 and 9.2 has been used to address the validity of the assumptions made by Campkin (1985). It can be seen from the first half of the Eq. 9.1 i.e.,  $10(QTK-3)$ , that each increase in the QTK of one unit above a value of 3 decreases the K requirement by 10 kg ha<sup>-1</sup> yr<sup>-1</sup>. Unfortunately, the 30% coefficient of variation associated with QTK values (Edmeades *et al.*, 1985) due to spatial return of excretal K by grazing animals in pasture soils, and possibly other factors, is inevitable. This results in an uncertainty of test values and a consequent uncertainty in fertilizer recommendations. Thus a 1, 2, or 4 unit change in the QTK value will change the fertilizer recommendation by 10, 20, 40 kg ha<sup>-1</sup> or a fertilizer cost by approximately \$7.50, \$15.00, and \$30.00 per hectare (M.J. Hedley, pers. comm.). This variability associated with the soil test result and the recommendations does not engender confidence for the grower, farmer or consultant.

Yet another problem with the QTK measurements is that it may be difficult to measure the changes in the quantity of  $K_{ex}$  (as measured by QTK) to indicate the depletion of soil K over a period of time in the grazed pastures. For example, the determination of the amount of QTK in the 0-75 mm depth of Massey University No. 4 dairy farm soil over the last 5 years (Table 9.9) has shown little indication of decline (M.J. Hedley, pers. comm.), despite an estimated 87 kg K annual loss per hectare (based on the CFAS model). If real, this is assumed to be due to the continuous replenishment of  $K_{ex}$  from the large pool of  $K_{min}$  in the K-bearing minerals (Williams, 1988; Williams *et al.*, 1990). Also errors in measurement of QTK due to spatial variability could mask any downward trend.

In contrast to the field situation, changes in the quantity of  $K_{ex}$  were observed in the pot

**Table 9.9** Quick test K values (parts per 250,000 of extract) of reference paddocks on No. 4 dairy farm on Massey University (M.J. Hedley, pers. comm.)

Year	Paddock No.			
	6	21	38	48
1988	6	10	5	8
1989	4	5	4	4
1990	2	5	3	6
1991	6	13	5	6
1992	5	4	5	5

experiment (Chapter 4) where  $K_{ex}$  levels dropped significantly after cropping ryegrass. The drop in  $K_{ex}$  is less than the plant uptake on many soils (Chapter 4), indicating release from  $K_{nec}$  sources. It is difficult therefore to compare over time the estimated net losses or gains of K with changes in the soil K using either  $K_{ex}$  or QTK measurements in soils containing K bearing minerals that permit release of K in variable amounts. Williams (1988), concluded that an organic soil might be one of the few soil types suitable for the purpose of comparison both because of the lack of soil minerals that release  $K_{nec}$ , and the low native K content.

#### 9.4.3 Possible improvements to the CFAS soil supply model

- (1) The current CFAS model for predicting soil K supply (using AgResearch equations) clearly would gain value if the designated  $K_c$  values of the major soil groups (Cornforth and Sinclair, 1984; Campkin, 1985) are replaced with the measured  $K_c$  values. Another possible issue is related to the South Island YGE soils. These soils are currently recognised as "high"  $K_c$  soils with an assigned value of 0.70 meq %. But the evidence appears to rest only on the published information by Cornforth and Sinclair (1984) and Campkin (1985). In this study somewhat lower values were observed. Measurement of  $K_c$  and the subsequent rating using the rating procedure of Campkin (1985) revealed that the South Island YGE soils fall into the "medium"  $K_c$  category (section 9.3.2).
- (2) As a result of finding a variable supply of QTK and  $K_{nec}$  from soils in the YGE soil group the soil K supply parameter of the K model would benefit from rigorous field test verification of the fertilizer equivalents of QTK and  $K_c$  (75 and 40 %, respectively) for at least soils in the YGE soil group. Variability could also occur in other important major soil groups. The percent utilisation values determined were not based on assessing variability within soil groups, nor for periods longer than one year. Moreover, the trials on which the fertilizer equivalents for QTK and  $K_c$  were based included a range of application rates of K in order to predict the amount of fertilizer required that would maintain 90 % of maximum pasture (ryegrass-clover), but did not involve grazing animals. The maintenance rate of K fertilizer that is required for 90 % relative yields

may be less for the grazed trial than for the 100 % clippings returned trial (Morton, 1981) at least in the short term (less than one year). The reason for this difference in responsiveness to K fertilizer is thought to be due to a more rapid recycling of K and N via excreta in the grazing trial compared to the mowing with clippings returned trial (Williams, 1988). The fertilizer equivalents of QTK and  $K_c$  would therefore be expected to exceed 75 and 40 %, if obtained from grazing trials.

- (3) Campkin (1985) assumed soil K will be available from only the top 75 mm. Williams (1988), however, found approximately 35 % of the pasture roots can explore soils to depths greater than 75 mm. Thus one meq % of  $K_c$  may be equivalent to larger quantities of K on a hectare basis than the 100 kg presently estimated by the AgResearch model based on a root depth of 75 mm. In any future work associated with assessing soil K supply consideration should be given to assessing the effect of soil depth.
- (4) The soil K supply parameter of the K model could be improved by using measurements of K supply that correlated well with the plant uptake in the pot trial (Chapter 6, Table 6.2). For example, step K could be used to replace  $K_c$ , because it better explained the variations observed in both total K and  $K_{ex}$  uptake by ryegrass from the 19 soils.

Furthermore, the step K method, in contrast to  $K_c$ , enabled monitoring of the expected soil K depletion due to farming practices as is evidenced by lower step K levels in the developed (pasture) sites when compared to the undeveloped (virgin) sites of the South Island YGE soils (section 6.3.4 and Table 9.10). Over a period of time,  $K_{ex}$  as measured by step K, may be lowered in the absence of K fertilizers indicating the depletion of plant available K. This depletion will be more rapid in an arable cropping system than under grazed pastures, because of the more rapid K recycling in the latter. While this drop in step K, due to artificial leaching of the  $K_{ex}$  and subsequent cropping with ryegrass, was observed in the majority of the soils in the pot trial (Table 9.10 and Fig. 6.7), no attempt was made to study the changes in step K over a period

Table 9.10 Changes in step K (kg ha<sup>-1</sup>) due to leaching and cropping

Soil No.	Soil name	Original unleached soils	After leaching	After leaching and cropping
S1	Tokorangi	363	353	335
S2	Tokomaru (a)	191	203	198
S3	Tokomaru (b)	205	206	227
S4	Milson	177	172	185
S5	Marton (a)	167	162	165
S6	Marton (b)	210	203	204
S7	Halcombe	196	216	202
S8	Ohakea	240	242	241
S9	Raumai	723	635	436
S10	Te Arakura	340	314	303
S11	Matapiro	299	295	278
S12	Wharekaka	330	305	291
S13	Pirinoa	475	428	359
S14	Timaru (a)	511	430	332
S15	Timaru (b)	423	374	329
S16	Claremont (a)	410	327	263
S17	Claremont (b)	285	252	237
S18	Opuha (a)	686	595	456
S19	Opuha (b)	405	339	317

of time in the field situation. The existing method of determining  $K_{\text{dex}}$  supply based on the  $K_c$  on the other hand, conceptually does not estimate soil K depletion due cropping and grazing (Metson, 1980).

- (5) Development of prediction equations to obtain the fertilizer equivalents of acid-extractable K under field conditions could also be considered.

Ultimately, whether a depletive (CFAS model) or K maintenance (sustainable) model best meets the future requirements of New Zealand's growers and the community at large will be determined by economic factors and the sense of responsibility to future generations.

## 9.5 CONCLUSIONS

1. The North Island YGE and related soils have been assigned by AgResearch to the medium  $K_c$  group which implies that  $30 \text{ kg } K_{\text{dex}} \text{ ha}^{-1}$  is annually available to plants. The measured  $K_{\text{dex}}$ , however, ranges from  $20\text{--}48 \text{ kg ha}^{-1}$ . The difference between expected and measured  $K_{\text{dex}}$  may be economically significant to the point that it is not valid to apply a single assigned  $K_c$  value to the North Island YGE soil group. Further work may reveal that a single assigned  $K_c$  value is also invalid for other soil groups.
2. None of the South Island YGE soils under investigation had a measured  $K_c$  value of more than  $0.45 \text{ meq } \%$ , despite AgResearch treating them as high  $K_c$  soils. On the basis of the measured  $K_c$  values and the  $K_c$  rating procedure adopted by Campkin (1985), these soils fall into the "medium"  $K_c$  category, in which case the estimation that no K fertilizers is required for grazed pastures on these soils (Cornforth and Sinclair, 1984) may be in error.
3. Plants in the pot trial extracted twice as much K as was predicted by the soil K supply model of Cornforth and Sinclair (using AgResearch equations) indicating that the rate of K removal per unit soil weight under glasshouse conditions is much higher than in the field. A model similar to that of Campkin (1985)

developed on the basis of the Stanford and DeMent pot trial indicated that the efficiencies of utilisation of K by ryegrass plants from QTK and K<sub>c</sub> were more than those predicted by Campkin (1985) using field trial data.



## CHAPTER 10

### SUMMARY

The work presented in this thesis may be summarised as follows:

1. A review of the literature indicated that low levels of  $K_{cx}$  do not always indicate lack of plant available K i.e., responses do not always occur where  $K_{cx}$  is low. This is because measures of exchangeable  $K_{cx}$  (e.g., QTK) fail to account for  $K_{necx}$ , which is sometimes also plant available. In New Zealand,  $K_c$  is used to measure the potential amount of non-exchangeable, but plant available, K.

The  $K_c$  method was originally developed as an index of long term K supply. It was intended to be specific to a soil genetic group, and was dependent on the mineralogy. Soils within a genetic group may well contain variable reserves of micaceous minerals, which release K at different rates. Thus  $K_c$  is not a totally reliable parameter for estimation of the short or medium term  $K_{necx}$  supply, because it disregards the more soluble portion of non-exchangeable K. Hence there is a need for a short term index for measuring  $K_{necx}$  in the soils of New Zealand.

2. It was also apparent from the literature review that the CFAS model used to estimate annual K requirements of pastures and crops in New Zealand is based in part on a routine soil test (QTK) and a single estimate of  $K_c$  assigned to the appropriate soil group. All YGE soils and intergrades in the North Island have been assigned a medium reserve of K ( $K_c$  value of 11.7 mg 100 g<sup>-1</sup>), while the southern YGE soils have a  $K_c$  of 27.3 mg 100 g<sup>-1</sup>. No allowance is made for any variation of reserve K within a soil group.

Therefore any variation in the  $K_{necx}$  supply within the YGE soils of either the North or South Islands would undermine the validity of the  $K_c$  method as an

index of  $K_{nex}$  supply and hence its place in the CFAS K model.

3. An investigation was conducted to compare the  $K_{nex}$  supply of the YGE soils in the North and South Islands, using a modified Stanford and DeMent pot trial. There was a wide variation in the measured  $K_c$  of the YGE soils from each island. The measured  $K_c$  of the North Island YGE soils ranged from 7.8-18.6 mg 100 g<sup>-1</sup>, and the southern YGE soils had a narrower range of 12.3-16.8 mg 100 g<sup>-1</sup>. The corresponding assigned  $K_c$  values are 11.7 and 27.3.

The results also showed large differences in  $K_{nex}$  supply within the YGE group of each island. The  $K_{nex}$  supply of the soils in the North Island ranged from 0 to 41 mg 100 g<sup>-1</sup> and that of in the South Island soils ranged from 3 to 35 mg 100 g<sup>-1</sup>.

4. With respect to the South Island YGE soils, there were consistent differences in the  $K_{nex}$  supply between the undeveloped (virgin) and developed (pasture) sites of a particular soil type. This must have implications for the soil group concept currently used to estimate  $K_{nex}$  supply. Because, though the measured  $K_c$  was more or less the same for both the developed and undeveloped soils, the actual  $K_{nex}$  taken up by plants grown to K exhaustion in the glasshouse varied markedly.
5. An experimental attempt to explain the differences in the  $K_{nex}$  supply of the soils, using the "threshold K level" concept, was not satisfactory. The threshold K levels (in terms of equilibrium concentration of K in solution,  $K_{ex}$ , and  $AR^K$ ) were not related to the  $K_{nex}$  supply and release. The lack of agreement may be due to differences in the  $K_{nex}$  release mechanisms of the laboratory experiment, created by an equilibrated CaCl<sub>2</sub> soil solution and a pot experiment, that involved rhizospheric soil solution.

The above finding has an important implication to the concept behind the mechanism of K release from  $K_{nex}$  (interlayer) sources. The supply and release

of  $K_{\text{nex}}$  by the soils of the present study seemed to reflect an interlayer penetration that was due more to hydronium ions than hydrated Ca ions.

6. Soil chemical tests based on the extraction of  $K_{\text{ex}}$  plus  $K_{\text{nex}}$  provided a better measure of available K when compared to those based on separate extractions of  $K_{\text{ex}}$  and  $K_{\text{nex}}$ . The highest simple correlation with plant available K was obtained from boiling nitric acid-extractable K. This test requires less time and cost than the NaTPB K method.

The results also showed that the step K method of measuring  $K_{\text{nex}}$  (obtained by subtracting the  $\text{NH}_4\text{OAc}$  extractable  $K_{\text{ex}}$  from the acid-extractable K value) was better than the  $K_c$  method for explaining the variations among the soils in the amount of  $K_{\text{nex}}$  taken up by ryegrass plants.

7. The 7 YGE soils of the North Island, supplied little or no  $K_{\text{nex}}$  to ryegrass plants in the pot trial, had  $K_c$  and step K values of 10 and 35 mg 100 g<sup>-1</sup>, respectively. All other soils with  $K_c$  and step K values of more than 10 and 35 mg 100 g<sup>-1</sup> supplied  $K_{\text{nex}}$  to the plants grown to K exhaustion in the pot trial. The 7 YGE soils that did not supply  $K_{\text{nex}}$  to plants can be designated as soils with low  $K_{\text{nex}}$  supplying power, in relation to the remainder of the soils in the study.
8. Depletion of soil K by plant growth was more clearly shown by change in the acid-extractable K level than by a change in  $K_{\text{ex}}$  measurement. Unlike acid-extractable K, the  $K_{\text{ex}}$  of the soils was found to decline to more or less constant levels (below 7.2 mg 100 g<sup>-1</sup>) under cropping.

Thus for soils that supplied  $K_{\text{nex}}$  to ryegrass, a reduction in step K was observed. For soils that did not supply  $K_{\text{nex}}$  step K levels remained unchanged. This indicated that, unlike  $K_c$  (which is reported to be constant after short term cropping), the step K method was sensitive to changes in  $K_{\text{nex}}$  status caused by plant uptake. Furthermore, step K measurement better differentiated undeveloped soils from developed counterparts than did  $K_c$ .

9. After it was demonstrated that acid-extractable K was a better index of K supplying power, the test was used to assess the K releasing power of soil textural separates. The results indicated that the acid-extractable K was highest for the clay separate on a per weight basis in all the 19 soils studied.

When calculated on a whole soil basis, the contributions of the sand and silt separates represented approximately 50 % of the K released. The exceptionally high percent contributions observed for the sand and silt separates of the Marton (S5 and S6), Raumai (S9), and Matapiro (S11) soils, indicated that these separates may deserve more consideration in estimating potential supply of K plants. The corresponding values were 64, 69, 83, and 66 %, respectively.

10. A more detailed investigation into 6 selected soils using chemical analyses of soil separates and a novel agar pot trial, especially designed to grow plants on the soil separates, confirmed the potential K releasing and supplying power of the clay separates.

With respect to the K releasing power the sand plus silt separates of three soils (Marton, S6; Raumai, S9; and Matapiro, S11) contributed substantially to the acid-extractable K. These percent contributions were 45, 85, and 49, respectively. The acid-extractable K data for these whole soils were in accord with the computed data of their separates on a whole soil basis.

With respect to K supplying power (K uptake), the percentage contribution data for the whole soils of only Marton (S6) and Matapiro (S11), were in accord with the computed data of their separates on a whole soil basis. The study demonstrated therefore the difficulty of obtaining reliable estimates of the relative contributions of soil separates to the whole soil K releasing and supplying power.

11. Contrary to expectation, the acid-extractable K of the clay fraction did not correlate well with plant K uptake. Nevertheless, a significant  $r$  value was obtained when the acid-extractable K data of all the three separates were correlated against their respective K uptake data.
12. That  $K_c$  values reflected soil mineralogy was demonstrated by clay mineralogical studies. The XRD patterns for the clays of soils in the 12-19 mg 100 g soil<sup>-1</sup>  $K_c$  range were distinct from those in the 8-10  $K_c$  range. The soils in the former  $K_c$  range appeared to have more K bearing minerals in the clay fraction than was the case for the latter. The differences in the  $K_{nex}$  supply of soils within each  $K_c$  range, however, could not be explained by differences in mineralogy.

Micas and volcanic glass were identified in the coarser fractions (sand and silt) of Raumai (S9) and Matapiro (S11) soils, respectively. These primary minerals could serve as potential sources of K to plants.

13. The assigned  $K_c$  values for the soils of the North Island and the South Island translate to an annual  $K_{nex}$  supply to pasture plants of 30 and 70 kg ha<sup>-1</sup>, respectively. The measured  $K_c$  values of the 13 North Island soils result in different annual K fertilizer recommendations to that using assigned values. Underestimations of the annual  $K_{nex}$  supplies as predicted by the CFAS K model (using assigned  $K_c$  values) were in the range of 4-18 kg ha<sup>-1</sup> (4 soils) while the range of overestimation was 4-10 kg ha<sup>-1</sup> (9 soils). The variations in the  $K_{nex}$  supply within a soil group may be significant enough to economically invalidate applying a single  $K_c$  value to a soil group.
14. AgResearch has placed South Island YGE soils in the high  $K_c$  category. The CFAS model therefore indicates these soils do not need K fertilizers unless used excessively for hay or silage. High  $K_c$  soils currently are presumed to replace K losses from the grazed pastures while maintaining productivity at acceptable level, but it is not known for how long these losses can be sustained.

In the present study none of the South Island YGE soils had a  $K_c$  value of more than 0.45 meq % which places them in the medium  $K_c$  category. Thus fertilizer K may be necessary for some of these soils, and K losses may be depleting the soils more readily than hitherto suspected.

15. In the Stanford and DeMent pot trial, ryegrass extracted twice as much K as would be released in a pasture annually on the basis of the field based CFAS soil K supply model. This was attributed to the rapid rate of K removal per unit soil weight under glasshouse conditions when compared to the field.
16. A soil K supply estimate based on QTK and a calculated value of  $K_{nex}$  using NaTPB K better predicted the variations in K uptake by ryegrass in the pot trial than did the current method based on QTK and the assigned value of  $K_c$  (CFAS approach). Given the conclusion in 6 (above) this finding supports the replacement of  $K_c$  values in the CFAS model by other methods of  $K_{nex}$  determination. There seems to be a great potential for the step K method of determining  $K_{nex}$ .
17. The findings reported in this thesis lead to the conclusion that the CFAS model for K fertilizer recommendations in New Zealand would benefit from more investigations in respect of the soil K supply component. The use of measured  $K_{nex}$  values based on  $HNO_3$  extraction ( $K_c$  method) would be more meaningful than the assigned values, and the soil K supply component of the model would benefit from field test verification.
18. As a result of good correlation of acid-extractable K with plant K uptake, prediction equations to obtain pasture utilisation of K from acid-extractable K and step K under New Zealand field conditions should be developed.

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**Appendix 4.1** Dry matter (g pot<sup>-1</sup>) of ryegrass grown on unleached (UL) and leached (L) soils

SOILS	CUT1		CUT2		CUT3		CUT4	
	UL	L	UL	L	UL	L	UL	L
S1	0.66	0.56	1.24	1.01	0.97	0.68	1.51	1.08
S2	0.59	0.51	1.07	0.89	0.68	0.48	1.25	0.76
S3	0.54	0.48	0.94	0.75	0.56	0.44	0.86	0.64
S4	0.65	0.51	1.13	0.83	0.81	0.51	1.36	0.69
S5	0.49	0.49	0.84	0.84	0.44	0.46	0.72	0.69
S6	0.52	0.46	0.80	0.80	0.46	0.38	0.75	0.69
S7	0.55	0.46	1.06	0.84	0.62	0.49	1.07	0.77
S8	0.60	0.51	0.96	0.90	0.61	0.49	1.06	0.83
S9	0.61	0.54	1.27	1.28	0.95	0.93	1.60	1.66
S10	0.53	0.50	0.95	0.98	0.52	0.54	0.82	0.77
S11	0.58	0.49	1.08	0.83	0.66	0.52	1.08	0.82
S12	0.53	0.51	0.94	0.94	0.47	0.57	0.88	0.83
S13	0.61	0.55	1.27	1.23	0.96	0.80	1.44	1.29
S14	0.60	0.59	1.37	1.23	1.01	0.83	1.87	1.31
S15	0.57	0.55	1.03	0.96	0.62	0.55	0.92	0.93
S16	0.65	0.56	1.18	1.15	0.84	0.77	1.64	1.33
S17	0.58	0.52	0.97	0.87	0.55	0.43	0.95	0.70
S18	0.68	0.60	1.34	1.15	1.07	0.80	1.75	1.35
S19	0.61	0.56	1.18	0.96	0.72	0.59	1.24	1.04
CONTROL	0.47		0.67		0.34		0.54	
LSD (0.05) soilxtrt*	0.06		0.10		0.08		0.16	
C.V (%)	8.0		6.9		9.4		10.9	

\* Treatment

LSD = Least-squares difference

C.V = Coefficient of variation

**Appendix 4.2**      **Percent K content of ryegrass tops grown on unleached (UL) and leached (L) soils during four cuts**

SOILS	CUT1		CUT2		CUT3		CUT4	
	UL	L	UL	L	UL	L	UL	L
S1	0.52	0.30	0.29	0.22	0.29	0.21	0.20	0.17
S2	0.30	0.22	0.26	0.19	0.22	0.21	0.16	0.15
S3	0.23	0.19	0.21	0.18	0.20	0.20	0.16	0.15
S4	0.54	0.23	0.28	0.19	0.24	0.19	0.20	0.15
S5	0.19	0.21	0.19	0.18	0.21	0.19	0.15	0.14
S6	0.21	0.22	0.18	0.19	0.19	0.19	0.16	0.15
S7	0.27	0.26	0.23	0.20	0.21	0.20	0.17	0.15
S8	0.24	0.24	0.23	0.20	0.22	0.20	0.17	0.15
S9	0.40	0.51	0.31	0.36	0.33	0.42	0.22	0.25
S10	0.24	0.25	0.21	0.19	0.21	0.20	0.16	0.16
S11	0.30	0.22	0.25	0.20	0.21	0.21	0.17	0.16
S12	0.22	0.24	0.21	0.20	0.20	0.21	0.16	0.17
S13	0.43	0.39	0.31	0.27	0.29	0.27	0.19	0.18
S14	1.19	0.53	0.50	0.26	0.43	0.25	0.24	0.19
S15	0.32	0.28	0.22	0.20	0.20	0.21	0.18	0.17
S16	0.58	0.45	0.29	0.24	0.33	0.24	0.20	0.17
S17	0.23	0.21	0.20	0.18	0.20	0.19	0.16	0.16
S18	0.60	0.45	0.32	0.25	0.38	0.28	0.23	0.18
S19	0.36	0.28	0.26	0.21	0.25	0.22	0.18	0.16
CONTROL	0.19		0.19		0.22		0.17	
LSD (0.05) soilxtrt	0.05		0.03		0.03		0.02	
C.V (%)	11.0		12.4		8.3		7.9	

## Appendix 4.3

Uptake of K (mg pot<sup>-1</sup>) by ryegrass tops grown on unleached (UL) and leached (L) soils

SOILS	CUT1		CUT2		CUT3		CUT4	
	UL	L	UL	L	UL	L	UL	L
S1	3.24	1.68	3.59	2.19	2.79	1.43	2.97	1.81
S2	1.78	1.11	2.77	1.69	1.45	1.01	2.02	1.15
S3	1.23	0.88	1.98	1.31	1.12	0.85	1.33	0.96
S4	3.46	1.15	3.14	1.55	1.19	0.94	2.69	1.01
S5	0.92	1.00	1.56	1.53	0.90	0.87	1.07	0.94
S6	1.10	1.01	1.46	1.48	0.87	0.71	1.19	1.01
S7	1.48	1.18	2.43	1.66	1.30	0.99	1.77	1.17
S8	1.43	1.21	2.17	1.79	1.35	0.99	1.73	1.26
S9	2.37	2.73	3.91	4.63	3.17	3.90	3.53	3.65
S10	1.25	1.25	2.02	1.83	1.06	1.08	1.25	1.24
S11	1.75	1.07	2.66	1.64	1.39	1.10	1.84	1.31
S12	1.13	1.24	1.96	1.90	0.93	1.20	1.33	1.39
S13	2.60	2.13	3.93	3.27	2.78	2.12	2.77	2.31
S14	7.01	3.14	6.79	3.19	4.36	2.05	4.33	2.45
S15	1.80	1.51	2.26	1.89	1.25	1.16	1.60	1.58
S16	3.72	2.46	3.37	2.72	2.80	1.83	3.29	2.27
S17	1.33	1.09	1.88	1.54	1.09	0.81	1.49	1.10
S18	4.04	2.70	4.26	2.88	4.08	2.30	3.92	2.36
S19	2.18	1.57	3.00	2.00	1.77	1.26	2.23	1.67
CONTROL	0.89		1.27		0.75		0.92	
LSD (0.05) soilxtrt	0.29		0.43		0.33		0.34	
C.V (%)	10.8		12.4		14.4		12.8	

**Appendix 7.1      Dry matter (mg pot<sup>-1</sup>) of ryegrass shoots for the three harvests**

Soil No.	Harvest 1 (3 week growth)			Harvest 2 (2 week growth)			Harvest 3 (3 week growth)		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
<b>S6</b>	64	61	118	46	43	82	118	130	198
<b>S9</b>	66	76	134	48	64	177	131	177	376
<b>S11</b>	69	80	119	44	56	100	141	153	228
<b>S12</b>	73	72	132	50	52	91	136	130	226
<b>S13</b>	65	73	148	49	51	122	138	136	284
<b>S18</b>	81	76	159	62	58	130	134	141	260
<b>LSD (0.05) Soilx Treatment</b>	20			23			28		



**Appendix 1.2**

**Potassium uptake (less control) by ryegrass tops from the soil separates for the 3 harvests ( $\mu\text{g pot}^{-1}$ )**

Soil No.	Harvest 1 (3 week growth)			Harvest 2 (2 week growth)			Harvest 3 (3 week growth)		
	Sand	Silt	Clay	Sand	Silt	Clay	Sand	Silt	Clay
S6	36	24	162	34	33	120	00	33	122
S9	64	81	450	47	11	1030	61	197	1667
S11	52	66	212	31	62	256	37	116	395
S12	82	36	195	41	39	156	15	20	367
S13	38	45	521	44	43	737	32	043	1387
S18	84	66	582	80	66	671	53	107	1021
*	86			44			175		

\* K uptake by ryegrass from control pots (agar only)