A description of the soil potassium fertility of steepland pastures in the southern North Island 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.

Sally Jane Officer

1999

Abstract

The pattern of soil K fertility was investigated in two typical steepland pastures, located in the southern North Island of New Zealand. The parent materials of soils in this area are predominantly derived from sedimentary rocks. The soils have medium to high K reserves, and K fertilisers are not normally applied to the areas of steepland pasture. The study sites are part of well-established mixed stock grazing farms and have received regular aerial topdressing with superphosphate for at least 30 years. Grazing animals in steepland tend to favour the flatter areas, which are mainly on the crests of the ridges, and to spend relatively short periods of time grazing the steep slopes. Concerns have arisen as to the development of K deficiencies on the steep slopes, as stock are expected to graze these areas, and then to excrete most of the K ingested in the herbage onto the flatter areas.

Two surveys were made of the K fertility patterns in two steepland paddocks. The first study was made over one paddock, by collecting soil samples along vectors of random direction, from points that were between 0.25 m and 25 m apart. The second survey targeted the main trends, sampling at regular intervals along the ridge crests and down the transects of the main slopes, at two paddocks. The tests on the soil samples included exchangeable K (Quick test K), acid extractable K and the difference between the two factors, which was thought to provide a measure of plant available nonexchangeable K (Step K).

The Quick test K values in one pasture alone ranged from 0.07 to 1.34 mg K/g soil, which was a range between very low and extremely high values for New Zealand soils. There was a similar wide range of values for other parameters. The frequency distributions of the soil test values were skewed, so that the arithmetic mean of the results was higher than 60-70% of the values. Spatial variability was at a maximum at a sampling distance of 0.25 m. The results indicated that the bulking of soil samples was a poor practise when sampling for exchangeable and plant available nonexchangeable K at these sites.

Some relationships could be discerned between the soil K fertility patterns and the position of the topsoil in a steepland landscape, despite the high spatial variability. On the steep slopes, the Step K value of a soil was related to the soil moisture pattern, as determined by aspect and water seeps, and also to the pattern of the soil parent materials. Quick test K had no similar relationship to position in the landscape on the steep slopes. The spatial variability of both tests increased as the ground slope decreased. The mean and variability of Quick test K increased sharply on both well drained shoulder slopes and ridge-tops that were animal campsites. In contrast, the mean and variability of Step K increased markedly only on the well drained ridge-top campsites. The different behaviour of cattle and sheep, the relatively large amounts of K deposited in excreta compared to P, and the slower rate of breakdown and dispersal of excreta in drier conditions, were all thought to contribute to these effects.

The mineralogy of the topsoils at the two sites was also investigated. The clay mineralogy was dominated by a complex of 2:1 layer silicates, accompanied by lesser quantities of quartz, feldspars and kandites. The topsoils formed a sequence, which ranged from a 2:1 layer silicate clay complex that was dominated by mica and interlayered mica smectite (MS), to a 2:1 layer silicate clay complex that was dominated by vermiculite and hydroxy interlayered vermiculite (HIV).

There was a very strong relationship between the Step K value and the mica content of a soil on the steep slopes. The relationship indicated that the dominance of either mica and MS, or vermiculite and HIV, in the clay fraction of a soil on the steep slopes depended on the original composition of the soil parent materials, the age of the soil profile, and the soil moisture conditions. On the shoulder slope and ridge-tops, there was a similar range of clay mineralogy, but Step K value now had a poor relationship to the mica content. This effect was mainly associated with soils under the well drained animal campsites, which had a distinctive mica and irregularly interstratified MS dominated clay mineralogy. The results were consistent with a reversal of the 2:1 layer silicate weathering processes under well drained animal campsites.

Concentrations of total K and P were investigated in the topsoils of the two steepland pastures. The average difference between the total P of slope and ridge-top samples was about 200 kg P/ha, indicating a relatively small accumulation of P on the ridge-tops after many years of aerial topdressing and grazing. The expected accompanying increase in total K was not found. The marked effect of animal transfer processes on the plant available chemistry and mineralogy of the well drained ridge-top soils was thought to be a disproportionate indicator of the relatively small extent of total nutrient accumulation that appeared to have occurred on the ridge-top campsites.

The plant response to K fertiliser was measured at the two steepland pastures sites. No K uptake response or growth response was identified at either site, despite low exchangeable K values in some areas and a low K content in some of the pasture samples, even after fertiliser was applied. In contrast, an exhaustive pot trial, using a selection of soils from the two sites, revealed a considerable range in the ability of the soils to supply K.

Cation and anion concentrations were measured in the leachates of "stove pipe" soil cores collected from the ridge-tops and steep slopes. K concentration in the leachates of soil from the steep slopes were relatively low and reasonably consistent over time, compared to the Ca and Mg concentrations that were more sensitive to changes in the ionic strength. K concentration in the leachate of soils from different ridge-top locations varied markedly between the different locations. The increased leaching of K under animal campsites was identified as a significant loss mechanism for the K that is transferred to these areas. However, it was thought that an exact quantification of this process would be difficult, because the spatial variability of the concentration of K leaching from the topsoil into the subsoil under campsites was expected to be even higher than the spatial variability of exchangeable K in these soils.

In conclusion, animal transfer losses of K from the steep slopes to the flatter areas at these sites appeared to be in the low range for New Zealand steepland pastures. No significant depletion of the K fertility appeared to have developed on the steep slopes, although the measurements were confounded by the very high degree of spatial variability found in all aspects of the K fertility patterns. The current conventional practice of not applying K fertiliser to these and similar sites was thought to be sustainable.

Acknowledgments

My grateful thanks to all the people who helped me along the path to completing this study, in particular:

Prof. Russell Tillman, for his patient coaching and encouragement through the many ups and downs of this study.

Mr Joe Whitton, for going beyond the call of duty with his assistance and teaching.

Dr Alan Palmer, Dr Dave Scotter and Mrs Denise Brunskill, for their encouragement and assistance.

SpectraChem Analytical Ltd, Dr Aravind Surapaneni, Dr Harry Percival and Sylvia Weil, who very ably carried out the analysis work commissioned for this study.

Bob Toes, Mike Bretherton, Ian Furkert, Ross Wallace and James Hanly for technical assistance in the laboratory and the field. Also, Toby Officer, for building the frames for the leaching experiment.

Mr Terry Clare, for the use of Bernwood farm as a research site.

Massey farms, for access to the Tuapaka farm site.

Canpotex, Pacific Raw Materials Ltd, the N.Z. Fertiliser Manufacturers' Research Association, Massey University, the Leonard Condell scholarship fund, the Helen E. Akers scholarship fund and MUSA for their financial support of this study.

My parents, Barry and Raewyn Officer, for their financial support and steadfast encouragement.

Table of Contents

Chapter 1

Chapter 2

Literature review

Chapter 3

Spatial variability of soil K in steepland pasture

Chapter 4

Topsoil mineralogy in steepland pasture

Chapter 5

Relationship between plant growth and K fertility in steepland pasture and glasshouse trials

Chapter 6

Soil K leaching under steepland pasture

Chapter 7

List of Figures

Page

Chapter 2: Literature Review

Chapter 3: Spatial variability of soil K in steepland pasture

Chapter 4: Topsoil mineralogy in steepland pasture

Chapter 5: Relationship between plant growth and K fertility in steepland pasture and glasshouse trials

Chapter 6: Soil K leaching under steepland pasture

List of Tables

Page

Chapter 3: Spatial variability of soil K in steepland pasture

Chapter 4: Topsoil mineralogy in steepland pasture

Chapter 5: Relationship between plant growth and K fertility in steepland pasture and glasshouse trials

Chapter 6: Soil K leaching under steepland pasture

Chapter 7: Summary and conclusions

Appendix 1

Appendix 2

Introduction

Chapter 1

The objective of this study was to investigate soil potassium (K) fertility in a typical steepland pasture in the southern North Island of New Zealand. The parent materials of soils in the lower North Island are predominantly derived from sedimentary rocks that are often rich in K. K fertilisers are not normally applied to steepland pastures in this area and concerns have arisen as to the possible development of K deficiencies caused by small but constant losses of K. In particular, the grazing animals will transfer the K ingested in pasture from the slopes to more favoured parts of a paddock, particularly the flatter ridge-tops, effectively concentrating the K in a smaller area. Gillingham and During (1973) examined a steepland site developed in volcanic soil parent materials, which generally have low reserves of K. After more than 30 years of pasture growth, with regular topdressing, the transfer process had created a K deficiency on the steeper slopes. Much of the steepland in the lower North Island has been under pasture since early this century and many areas have received regular applications of superphosphate fertiliser (supplying phosphate and sulphur) since the 1950's. Fifty years of continuous losses of K from the soil on the slopes may have now caused the development of similar K deficiencies in these topsoils on the slopes. This study takes the approach of thoroughly characterising the K fertility patterns in two typical steepland pasture sites, in order to create a clear picture of the cumulative effect of the transfer processes to date, which will enable the prediction of future trends.

The potassium fertility of soil is a very well established subject. The following excerpt from Bray and DeTurk (1938) introduces the basic concepts.

"Of the various forms of potassium (K) which occur in the soil it is difficult to point to one of them as being of greatest importance to plant growth under all conditions. The plant physiologist would consider the K occurring in the soil solution as being the most important, pointing out that only dissolved material can pass through the membranes of the feeding roots and that K is not available to the plant until it has dissolved or been brought into the soil solution. The soil chemist, familiar with soil solution research and the base-exchange equilibria, would point out that the amount of K occurring in the soil solution at any one time is negligible compared to the total amount needed by the plant and might justly claim that the (salt) replaceable K is of greater importance since without it the soil solution K could not be continually renewed at a rate sufficiently fast to supply all the K needed by the plant. At this point, therefore, we have the picture of several pounds per acre of K in the soil solution being continually renewed through release of the replaceable K, at first practically as fast as the soil solution K is removed by the plant. As the replaceable K immediately surrounding the feeding root tip is diminished, replenishment in this area from the replaceable form becomes more difficult and the K concentration in the soil solution is lowered. Diffusion of K from more distant areas helps in part to overcome this decrease since in effect a diffusion potential for K is created. This diffusion, however, will not be rapid enough in most cases to supply all the K needs. The root tip, however, is continually pushing into new areas which contain less diminished amounts of replaceable K. In effect the soil solution is of direct immediate importance to the plant but the replaceable K is essential to the continued renewal of soil solution K. It so happens that the amount of K in the soil solution, because of base-exchange equilibria, is not directly proportional to the amount of replaceable K or to the K-fertility of the soil and its measure does not give a correlation with K needs. On the other hand, the replaceable K value in many studies has been found to be definitely related to the K-fertility of the soil and its measurement has, therefore, been used as a measure of the "available K" in the soil.

"The above soil processes, however, take care only of the more immediate needs of the plant. The water-soluble K is present in amounts sufficient at most for a few hours' to a few days' feeding by the plant, and the replaceable K is present in amounts sufficient for a few months to a few years. In spite of this, the decrease in replaceable K over a period of years caused by growing crops is not the same as the amount of K removed in the crops, but usually much less. Often, the replaceable K level will have decreased only slightly during the crop growth and the level will rise significantly between the time the crop is removed and the time the next crop is planted. Of the existence of this renewal process or processes there can be no doubt, for without it we could not have the yearly removal of large amounts of replaceable K caused by cropping, without bringing about its complete exhaustion. The renewal process or processes are, therefore, necessary for the continued maintenance of replaceable K which must be kept at a sufficiently high level to supply the soil solution with adequate amounts for plant growth, failing which, the soil becomes K-deficient."

Deturk et al. (1943) continued to develop these concepts, exploring the phenomenon of K fixation, which is a reversal of the K release processes described above. K fixation was defined as a change of water soluble, or replaceable K, into forms that are not replaceable by salt leaching. Also defined was difficultly-replaceable K, as K that cannot be displaced from a soil by salt leaching but which, under soil conditions, is known to pass into the replaceable form. After quantifying soil solution K, replaceable

K, and difficultly-replaceable K, the remaining soil K was expected to exist largely in the form of primary minerals, usually termed mineral K.

The same basic concepts and observations are still relevant today, although the terminology has changed somewhat. In this thesis, the term replaceable K has become exchangeable K, usually referring to soil K that can be exchanged with NH_4^+. By default, all other K in the soil is nonexchangeable K, including difficulty replaceable K, which is now termed plant available nonexchangeable K. These terms are explored further in the literature review (Chapter 2).

The literature review also examines, in some detail, soil mineralogy with respect to 2:1 layer silicate clays (which dominated the soils in this study). Animal – plant interactions in a pasture system are also examined, with respect to K, and the general terminology and conditions associated with steepland pasture systems are reviewed.

The study then moves on to examine the K fertility patterns in steepland pastures in a series of increasingly detailed scales. The relevant statistical techniques are first reviewed (Chapter 3.2). Exchangeable and nonexchangeable K fertility patterns are then surveyed in one steepland pasture (Chapter 3.3). The main K fertility trends identified in the initial survey are then explored in more depth at the same site and at a second site on a different farm (Chapter 3.4). The mineralogy of these soils is then examined, with particular attention to the difference between soils on the slopes and soils on the ridge-top areas that are well frequented by the grazing animals (campsites) (Chapter 4). The elemental composition of the soils is also examined, with particular attention to the accumulation of nutrients under campsites (Chapter 4.3.5). The study then moves on to examine the response of pasture to K fertiliser at specific sites within the two steepland paddocks (Chapter 5.2). The plant availability of K in selected soils from the two paddocks is then examined in more detail in a subtractive pot trial (Chapter 5.3). Finally, an in-depth study was made of the K leaching processes in soil from various points around the two steepland pasture sites (Chapter 6).

Literature review

Chapter 2

2.1 Introduction

Potassium (K) is the seventh most common element in the earth's crust, and has been recognised as an essential element for plant growth since 1840. K salt deposits, which are mainly formed by the evaporation of seawater, have been recognised as a valuable fertiliser and mined since 1861. The global fertiliser reserves are expected to last for many centuries (Sheldrick, 1985; Stewart, 1985).

As a relatively abundant and mobile cation, K fulfils a wide range of mainly electrochemical roles in soil, plant and animal systems. The numerous roles have generated a vast associated literature that cannot be exhaustively reviewed here and only topics relevant to the current research will be covered in depth. For more general information on soil K, the reader is directed to the seminal "Potassium in Agriculture" published by the American Societies of Agronomy, Crop Science and Soil Science, in 1985.

K has been described as a "nomadic" element, with a behaviour in soil that is "often perplexing and enigmatic" (Sparks and Huang, 1985). As plants remove K in pasture systems, K diffuses from the soil parent materials to replenish the soil solution (as described in Chapter 1). Grass species in particular remove large quantities of K from the soil. K remains highly mobile in the plant and in grazing animals, and so is readily recycled back to the soil as the organism excretes or dies (Figure 2.1). This cycle replenishes the soil pool with K, although imbalances can be created if K is not returned to the soil system at the same point from which it was lost. Soil systems tend to be

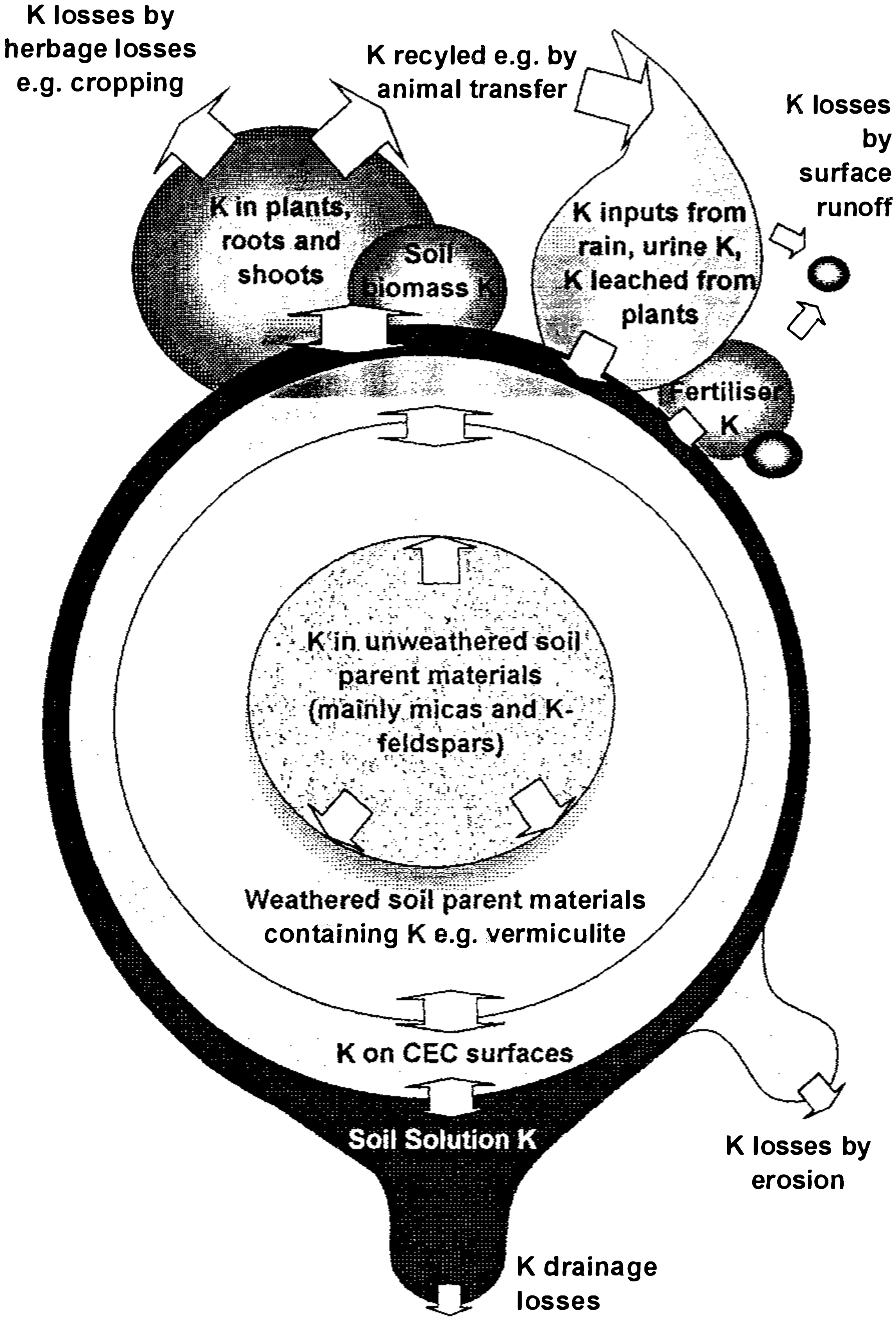


Figure 2.1: Representation of the potassium pools, inputs and losses in a typical soil system under pasture. Arrows show the movement of K between the various pools.

highly conservative of K and excessive levels of K arriving back in the cation exchange system are efficiently retained in many soils. Leaching losses on a farm or regional scale are usually relatively small, and K has been regarded as a relatively self-contained nutrient. Total K reserves can be relatively large in soils developed in sedimentary parent materials and the current New Zealand model for K fertiliser requirements makes the assumption that a soil with appreciable K reserves can be indefinitely "mined" to replace any losses (Metson, 1980; During, 1984; Kirkman et al., 1994).

More recently, the validity of a fertiliser requirement model that deliberately exploits the soil reserves has been questioned. Also, demonstrations of the very rapid cycling of K, within the relatively closed soil- plant- animal system inside a catchment or a paddock, have shown the potential for localised imbalances or K deficiencies to develop. The implementation of models and soil tests that are more accurate has been proposed (Williams, 1988; Taylor and Velbel, 1991; Haynes and Williams, 1993; Surapaneni, 1994). This study centred on gaining an understanding of the spatial variability of K fertility patterns in order to improve the models, and also the accuracy of soil K testing procedures. A thorough understanding of the processes and chemistry that affect K fertility in pasture was also necessary, in order to correctly interpret the spatial variability results. This study examined soil K in the context of a New Zealand steepland pasture developed in soils mainly derived from quartzo-feldspathic greywacke and argillite rocks, and loess. The principal soil parent materials containing K were expected to be mica and feldspars. Mica and related minerals dominated the clay fraction of the soils in this study and appeared to control the plant available K chemistry. The chemistry of these minerals, and the related soil chemistry, is reviewed next in some depth, followed by a general review of the soil-plant-animal system, with respect to K chemistry. A more general review is then made of literature concerning steepland pasture.

2.2 K in the soil

Mica forms part of the 2:1 layer silicate family of minerals. A good understanding of the mineral structure and associated chemistry is essential to developing meaningful answers to the wider problems of K plant availability in this study, so the subject is reviewed in some detail.

2.2.1 Layer silicate structure

The structure of 2:1 layer silicate minerals is well established. Unless otherwise indicated, this review is drawn largely from Sparks and Huang (1985) who reviewed this topic with particular respect to K, and also Weaver (1989), for a more mineralogical perspective.

The classic structure of a 2:1 layer silicate mineral consists of a stack of firmly bonded, highly structured layers (Figure 2.2). The central sheet is formed by octahedra of four oxygen ions (O^{2-}) and two hydroxyl ions (OH^-) coordinated around an aluminium ion (Al^{3+}). Each O^{2-} also forms one point of a tetrahedron of four ions of O^{2-}, coordinated around a silica ion (Si^{4+}). The Si tetrahedra form hexagonal rings, knitting together to form Si sheets, which sandwich the Al octahedral sheet - hence, this mineral unit is termed a 2:1 layer silicate. The symmetry of the Si tetrahedral sheet is greater than the symmetry of the octahedral sheet, so the tetrahedral units tilt and shrink to fit the octahedral sheet, which is somewhat stretched. The whole 2:1 layer silicate forms a plate like structure 0.93 – 0.95 nm thick.[1]

Many cations can form substitutions into both the tetrahedral and octahedral sheets. In particular, Al^{3+} often substitutes for Si^{4+} in the tetrahedral sheets, and magnesium (Mg^{2+}) and ferrous ions (Fe^{2+}) often substitute for Al^{3+} in the octahedral sheet. These substitutions, and also Al^{3+} vacancies in the octahedral sheet, generate an overall negative charge. In 2:1 layer silicates with no vacancies in the octahedral sheet, Fe^{2+} and Mg^{2+} substituting for Al^{3+} usually generate the negative charge and the layer silicate sheet is termed trioctahedral. In 2:1 layer silicates where the negative charge is predominantly generated by vacancies of Al^{3+} in the octahedral sheet the layer silicate is termed dioctahedral.

---

[1] Ionic charge is fully specified in this section, hereafter, ions marked with the appropriate charge signify a fully hydrated and mobilised ion in soil solution, as opposed to ions that are absorbed onto the soil surfaces, or are part of a structure.

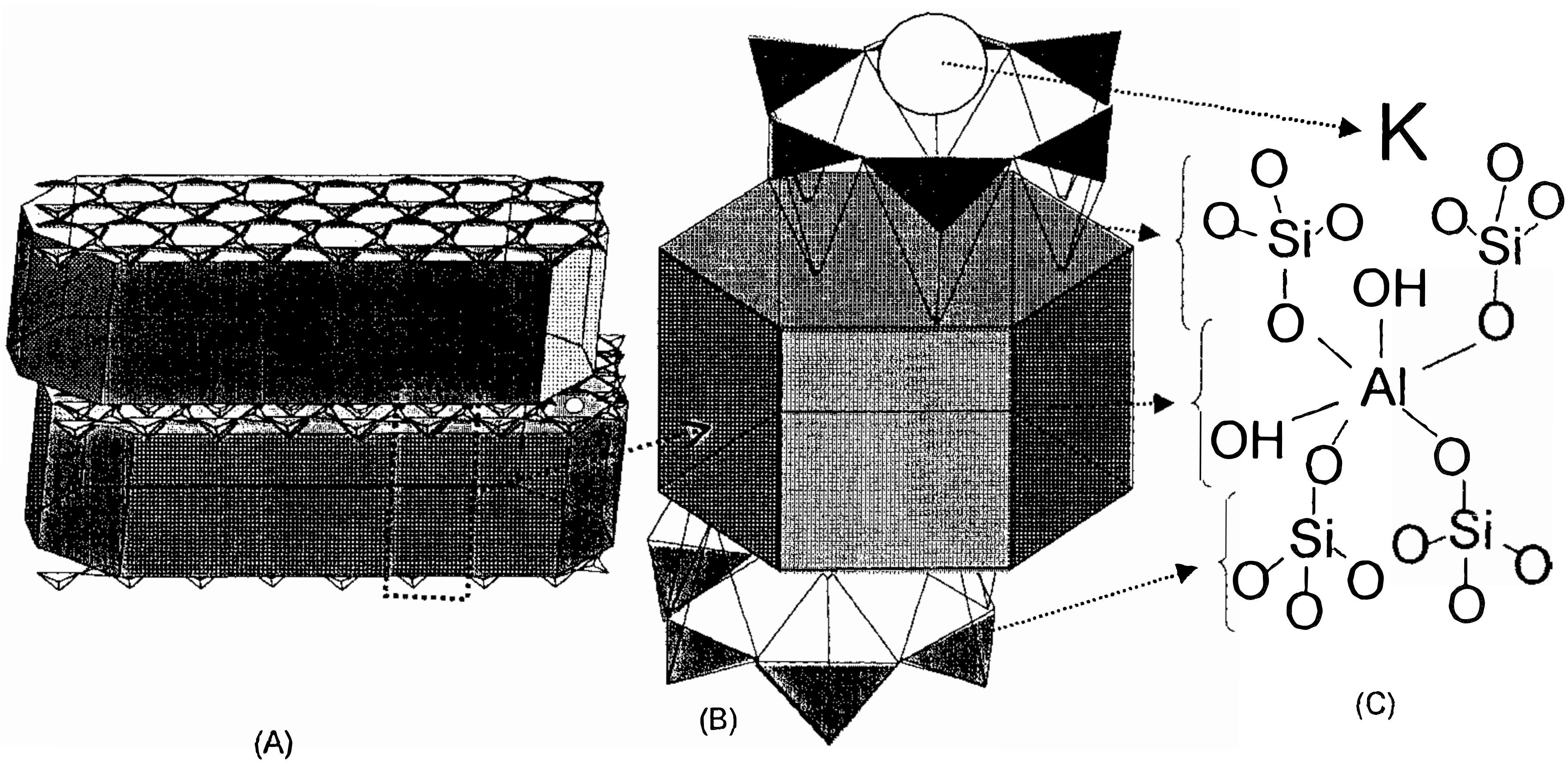


Figure 2.2: Illustration of the basic 2:1 layer silicate mineral structure: the clay stack formation, with K (white circle) in the interlayer spaces (A), a single 2:1 silicate layer, consisting of a central Al-octahedon sheet sandwiched by two rings of Si-tetrahedra and one interlayer K in the surface cavity formed by the hexagonal grouping of Si tetrahedra (B), and the individual molecules present in each unit (C).

On the outside of the 2:1 layers the hexagonal rings of Si tetrahedra form cavities, bounded by O^{2-}. These cavities can accommodate almost half of a K^+, which (when not hydrated) is the largest cation required by plants (0.13 nm diameter). If there is sufficient negative charge in an adjacent pair of 2:1 layers, and sufficient K^+ in solution between two 2:1 silicate layers, the layers move closer together. The positive - negative charge attractions between the K^+ and the two layers will increase with decreasing distance, to a greater extent than the repulsion forces between the layers will increase with decreasing distance (Verburg and Baveye, 1995). The weak hydrostatic bonding of K^+ allows the water molecules to be shed by the K^+ ion with relative ease, and water is then excluded in an ordered fashion from between the two closing silicate layers. As the two sheets align, some Al^{3+} may substitute for tetrahedral Si^{4+}, generating more negative charge on the surface of the tetrahedral sheets (Shibata et al., 1995). Finally, two adjacent hexagonal rings of O^{2-} on the surfaces of the silicate layers nearly surround an anhydrous K^+, leaving a gap of only 0.05 nm between the silicate layers.

Usually a number of 2:1 layer silicates will align together, forming the typical clay stacks found in soils and rocks. If anhydrous K^+ is the interlayer species, the mineral is termed mica. If the 2:1 layers are trioctahedral (e.g. forming the mineral biotite), the relatively tight packing of these layers causes the H^+ of the octahedral OH^- to move close to the K^+. The resulting charge repulsion makes the bonding of the K^+ ion less stable and the trioctahedral form more vulnerable to breakdown and loss of K^+. When the 2:1 layers are dioctahedral (e.g. muscovite), there is sufficient room for the H^+ to move away from the K^+, and so a more stable layer structure is created, which is more resistant to weathering processes. Hence dioctahedral micas are more common in soils, particularly in the upper horizons.

Mica is the dominant form of such anhydrous stack structures in natural systems, reflecting the relative abundance of K^+, the relative ease with which the ion can be dehydrated, and the relative stability of the structure. Other ions of similar anhydrous size, such as NH_4^+, can also form such structures. NH_4^+ is less abundant and the cation requires more energy to dehydrate than K^+, but does form a mica-like structure (Tobelite) with sufficient heating (Miklos and Cicel, 1993; Saha and Inoue, 1997). H_3O^+ mica structures can also be formed but appear to be quite short lived and unstable, possibly because, like similar structures formed with smaller ions, the interlayer cation can slip right into the cavity formed by the Si tetrahedrons, destabilising the mica structure (Nishimura et al., 1995).

2.2.2 Weathering processes of 2:1 layer silicates

Substitution, stripping by chelates of Fe and Al, redox reactions (particularly Fe), solid state and hydrated diffusion, can all modify or remove the metal ions in the 2:1 layer silicate sheets, and reduce the negative charge of the layer. The structural changes also distort the layers, causing buckling of the surfaces and curling at the edges. The structural distortions combine with environmental mechanical stresses, such as freezing expansion, to cause flaking, splitting and shearing of the stacks, and breakdown of the larger particles into clay sized particles (Aoudjit et al., 1996).

Breakdown of the 2:1 layer silicates generally results in less negative charge, so the requirement for interlayer cations is reduced. As repulsion forces between the cations start to dominate, the layer silicates start to separate, assisted by the shape distortions. Resistance to the initial hydration is expected to be quite high, because of the mechanical movement needed for the 2:1 silicate layers to separate (Laird and Shang, 1997).

When the interlayer gap is sufficiently wide to allow in water (about 0.25 nm), the water molecules are first attracted to the K, hydrating sufficiently exposed cations in groups of three (Figure 2.3). When the interlayer gap allows a full monolayer of water to be present the water molecules take on a strained and largely immobilised, hexagonal icelike structure. K is vulnerable to replacement by H, i.e. hydrolysis, at this stage by "jumping" between stations. Subsequent hydration of the interlayer fully hydrates the remaining K ions in an octagonal coordination. The hydrated cation is held in a fixed position until the interlayer opens beyond the width of the hydration shell (0.33 nm). Water molecules around the hydration shell of an interlayer cation in a fixed position are also ordered but are more mobile than water in the hydration shell (Sposito and Prost, 1982). If the interlayer opens beyond this width, the hydrated cation is able to tumble and diffuse more freely.

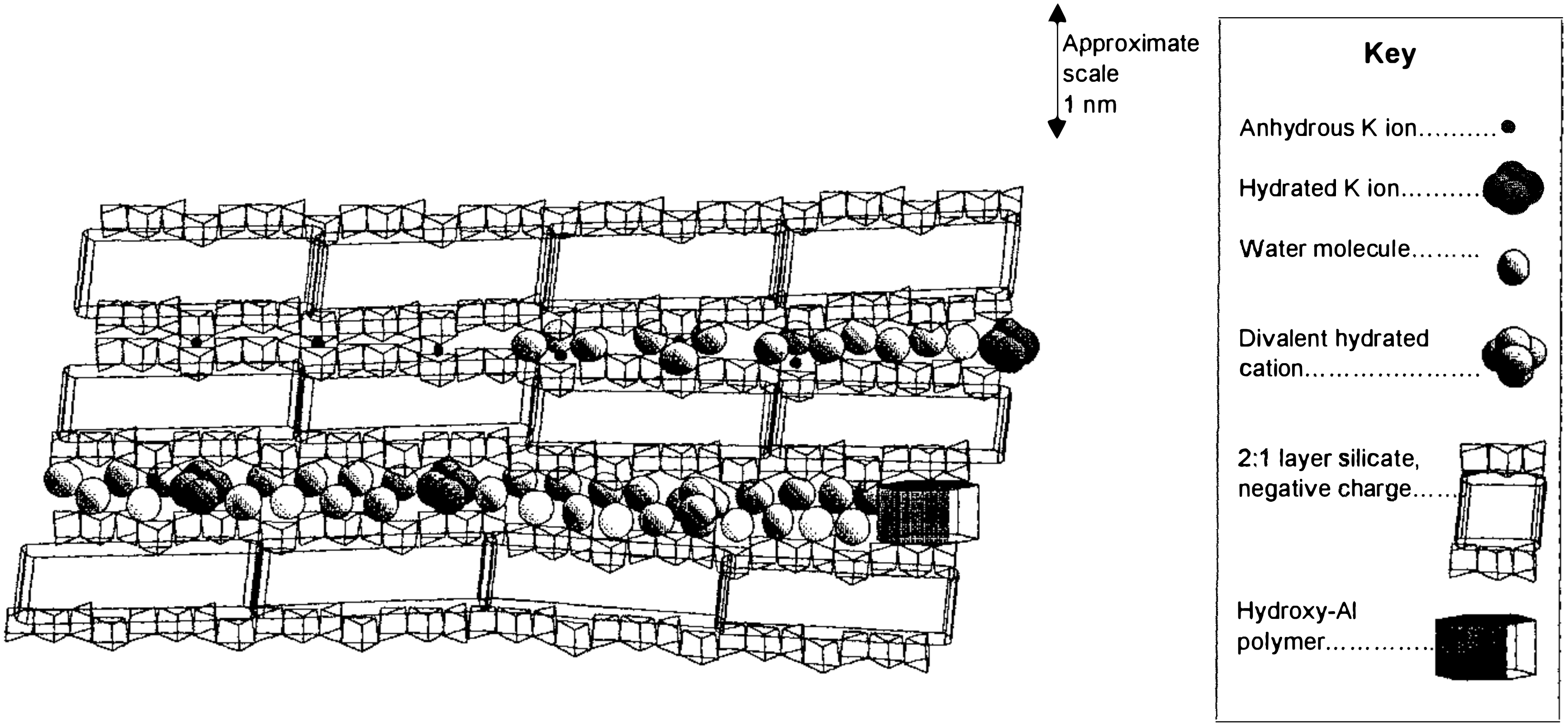


Figure 2.3: Illustration of the hydration processes in the interlayer space of mica weathering to vermiculite. The upper interlayer, from left to right, illustrates anhydrous K and then K in the initial hydration stages, first with three water molecules around each K, and then hydrated by water in a ice-like monolayer as the interlayer space widens near the edge. The lower interlayer illustrates, from left to right, hydrated K ions surrounded by a structured double layer of water, then hydrated Mg and a hydroxy-Al polymer replace K as the interlayer space widens.

Once the interlayer gap is sufficiently open, bivalent cations tend to displace K and dominate the interlayer space. These cations have larger hydration shells than K^+ (Ca^{2+} - 0.41 nm, Mg^{2+} - 0.42 nm) and open the interlayer space to sufficient width to allow K^+ and the other smaller hydrated cations to diffuse very freely. While the 2:1 layer silicate charge remains relatively high (~0.7 standard units of layer charge per unit of clay) and only one layer of cations is present in the interlayer space, re-collapse of the interlayers is possible if high concentrations of K^+ are re-introduced. Hydrated 2:1 layer silicates that can dehydrate interlayer K^+ and collapse are termed vermiculite. The collapse is not a simple reversal, and a marked hysteresis (compared to the expansion process) is expected, as the various resistances to movement and rearrangement are overcome (Laird and Shang, 1997).

As the 2:1 layer silicate structure becomes more disordered, and the clay plates increasingly buckled or curled, the layer charge drops to ~0.35 standard units of layer charge per unit of clay (termed smectite). The interlayer space increases, approaching one nm, and the interlayer cations can now move freely. Smectite is not expected to collapse if K^+ is re-introduced to the interlayer space under normal soil conditions.

Charge repulsions within a clay stack may also be resolved by occasional or regular interstratification of anhydrous layers with hydrated layers, which allow the K ions in particular to move farther apart. These interstratified structures are very common in soil environments. The edges of a clay stack are also commonly hydrated. The associated destabilising of the edges of the 2:1 layer silicates causes a typical curling of the silicate layers and forms scroll like hydrated "wedge zones" on the edges of a clay stack.

Wesselink et al. (1994) examined 2:1 layer silicates weathering in a soil environment and found that the processes affecting the mineral layers and the interlayer K could be quite different. Breakdown of the 2:1 layer silicate structure, was a steady, chemically controlled process, related to Si^{4+} and Al^{3+} soil solution concentrations and particularly to soil pH and temperature. In contrast, the release of interlayer K was diffusion controlled and could be initiated by low soil solution concentrations of K^+. The rate of release of K was dependent on the amount of K previously removed from the minerals. The early release rates (first 24 hours), of K from interlayer spaces newly exposed to solution, were rapid, and subsequent removal of K was relatively slow. Wesselink et al. (1994) predicted that, while a slow overall 2:1 layer silicate weathering rate was maintained over time, the actual weathering rate in a soil environment would fluctuate as the level of soil solution K^+ varied.

2.2.3 Definitions used in this study

2.2.3.1 Mica

In the mica group, the 2:1 lattice structure is well formed and the negative charge at a maximum. The interlayer cation is anhydrous K. While trioctahedral mica is usually regarded as highly unstable parent material, it may form a highly stable dioctahedral mica as a weathering product. The common trioctahedral form in soils is biotite. The common dioctahedral form is muscovite (Sparks and Huang, 1985). In soil a common mica form is illite, a dioctahedral mica with a layer charge that is characteristically slightly weaker than muscovite. H_2O and Ca may enter some of the interlayers, but the interlayer spacing is still mica-like (Whitton and Churchman, 1987).

2.2.3.2 Vermiculite

In vermiculite, the 2:1 layer silicate charge is reduced sufficiently so that the interlayer space becomes hydrated, although the size of the interlayer space remains restricted and able to recollapse to an illite structure, if sufficient K^+ is reintroduced to the interlayer spaces. Vermiculite interlayers can selectively adsorb smaller hydroxy-Al polymers and low Si/Al ratio hydroxy aluminosilicates, creating hydroxy interlayered vermiculite (HIV) (Whitton and Churchman, 1987; Sakurai and Huang, 1998).

2.2.3.3 Smectite

Smectites have heavily substituted 2:1 layers and a low charge density on the surfaces, so the interlayer forces are weaker than vermiculites and micas. By definition, smectite cannot re-collapse to a mica form under hydrated conditions. Hydroxy aluminium silicate polymers, which are bulkier than the polymers found in vermiculites, can be adsorbed in the interlayer spaces of smectite. Drying in the presence of high concentrations of K^+ or NH_4^+ can cause at least partial collapse of the interlayers (Sparks and Huang 1985; Lou and Huang, 1995).

2.2.3.4 Chlorite

In chlorites, a 2:1 layer silicate structure still exists, but the interlayer space is completely filled by a Mg, Fe, or Al hydroxide. The structure is very stable and non reactive, although chlorites formed at low temperatures are liable to have imperfectly formed interlayers, and to have some expandable characteristics (Whitton and Churchman, 1987; Weaver, 1989).

2.2.3.5 Interstratified layer silicates

The 2:1 layer silicates can form regular interstratifications, e.g. alternating layers of mica and smectite, or irregular interstratifications with no clear structure. The layers are not pure mixtures, with the amount of K increasing in the mica layers as the proportion of mica to smectite in the mixture increases. In fact, all 2:1 layer silicates in soils are thought to be interstratified to some extent (Whitton and Churchman, 1987; Weaver, 1989).

2.2.3.6 Feldspars

Feldspars consist of a very stable, honeycomb-like, framework of Si and Al tetrahedra. K and Na typically are trapped in the gaps in the structure, to balance negative charges generated by substitution of the Al and Si. K release from feldspars is thought to require complete dissolution of the framework structure. A restricted area of exposure of the feldspar structure to water can create channels that behave like the exchangeable surface of a 2:1 layer silicate. Feldspars are only expected to contribute significantly to the K supply of plants in temperate climates under conditions of strong leaching and podzolisation (Sparks and Huang, 1985; Goulding, 1987; Robert, 1992).

2.2.3.7 Kandites

Kandites are 1:1 layer silicates with alternate layers of silicon-oxygen tetrahedra and Al-hydroxide. The structure is stable but the two sheets do not match well, resulting in either flakes (kaolinite), or curled tubes (halloysite). Kandites are usually full of substitutions into the sheets or impurities, which can result in some layer charge. (Weaver, 1989).

2.2.4 Soil solution and exchangeable K

As previously indicated (Section 2.2.2) crystalline soil minerals generally have a negative charge resulting from the substitution, or vacancies, of ions in the mineral structure. Much of this negative charge is balanced "internally" by cations, such as anhydrous K in the interlayers. A range of cations in the soil solution surrounding the mineral particles can balance the negative charge on the outside of the mineral. In New Zealand soils, the dominant cation in soil solution is usually Ca^{2+} followed by Mg^{2+}, K^{+} and Na^{+} in that order. Therefore it is normally observed that Ca is also the dominant ion held on the negatively charged outer surfaces of the minerals. Al, Fe and Si hydroxy polymers and organic matter can also develop negative charge. The extent of this negative charge is dependent on the soil pH. As the pH increases, the amount of negative charge also increases. Such "variable charge" sites are also present on the edges of the 2:1 layer silicates, where the Al and Si sheets are breaking down. Otherwise, most of the negative charge on the 2:1 layer silicates is permanent, regardless of pH. The total amount of negatively charged surface exposed to soil solution is termed the cation exchange capacity (CEC). While much of the CEC is expected to be associated with charged surfaces that have adequate room for a diffuse double layer to form (interlayer space > 1nm), some negatively charged sites will be associated with size restrictions, generating a preference for the smaller cations such as K (Rich and Black, 1964).

A size restriction can be formed in the wedge zones on the edges of 2:1 layer silicate stacks, or by physical obstructions in the interlayer spaces. Al, Fe and Si hydroxy polymers are more positively charged when soil conditions are acid and are attracted to the 2:1 layer silicate surfaces. The polymers, ranging from single units to large, plate like structures, may be present in the interlayer space, depending on the width of the interlayer space and the width of the hydroxy polymer (Krisnamurti et al., 1995; Sakurai and Huang, 1998). The polymers tend to sit mainly in the frayed edges of the interlayers, forming a distinctive "atoll" around the edges of a 2:1 layer silicate stack (Lou and Huang, 1995). The presence of these polymers reduces the charged surface available for cation exchange and also creates size restrictions or obstructions for cations moving in and out of the interlayer space. If soil conditions cause the interlayers to close, without changing the pH dependant charge on the polymers, then the polymers may prop the interlayers open and prevent the "fixing" of K by re-collapse of the interlayers (Saha and Inoue, 1997). Larger more structured polymer species, like allophane, may also develop some permanent negative charge and the typical spiral formations may generate size-specific sites that hold K in preference to the larger cations.

The specificity of some cation exchange sites for K allows soils to be characterised by their K retention and release patterns, relative to the other cations. A full discussion of the chemistry and thermodynamics involved is beyond the scope of this study and the reader is directed to reviews such as Evangelou et al. (1994) and Bond and Verburg (1997). In terms of the practical issues of K^+ mobilisation into solution in field soils, a simplified relationship developed by Beckett (1964a) has been found to be applicable to many soils (Sparks and Huang, 1985). Mineral soils dominated by Ca on the CEC often maintain a characteristic ratio of K^+ in solution, in relation to the amount of Ca^{2+} and Mg^{2+} in solution (equation 1), under reasonably normal hydration and ionic strength conditions. If Ca^{2+} and Mg^{2+} are assumed to be mobilising into solution in the same way, then the concentration of these two cations can be combined and a characteristic ratio with respect to K^+ mobilisation, termed the activity or the intensity ratio (AR_k), can be found;

$$AR_k = \frac{a_K}{\sqrt{(a_{Ca} + a_{Mg})}} \tag{1}$$

where a_i denotes activity of each cation (i) in soil solution (Beckett, 1964a). If the cation concentrations are relatively low, as would be expected in a typical New Zealand pasture soil, the activity effects are expected to be minimal, so a simple concentration ratio (CR_k) can be calculated;

$$CR_k = \frac{K_l}{\sqrt{(Ca_l + Mg_l)}} \tag{2}$$

where $_l$ is concentration in mol/l. If Ca^{2+}, Mg^{2+}, K^+ and Na^+ constitute most of the cations in soil solution then the concentration of each cation will be a fraction of the total cation charge (z) in soil solution (equation 3) (Robbins et al., 1980).

$$z = K_l + Na_l + 2(Ca_l + Mg_l) \tag{3}$$

In soil solutions, changes in the concentration of anions are expected to control the overall concentration of cations (Tillman, 1991). In New Zealand pasture soils, variations in HCO_3^-, the dominant anion, are expected to mainly control cation levels (Parfitt et al., 1997), which may in turn be dependant on soil moisture levels (Bouma et al., 1997). Large fluctuations in NO_3^- may also be important, e.g. when nitrate fertilisers are in use (Yanai et al., 1996).

A substitution of the CR_k equation into a partial calculation of ionic strength [$z_p = K_l + 2(Ca_l + Mg_l)$] could predict the theoretical effect of anion flushes on the fraction of the total cation concentration occupied by Ca^{2+}, Mg^{2+} and K^+. Solving for K^+ concentration indicated that the relationship between the concentration of K^+ in solution and the partial ionic strength would be quadratic (equation 4), and that K^+ concentration may not be very responsive to anion flushes in a soil system.

$$z_p = K_l + 2\left(\frac{CR_k}{K_l}\right)^2 \tag{4}$$

In contrast, a highly responsive, linear relationship was predicted between the concentration of Ca^{2+} and Mg^{2+} in solution and partial ionic concentration, indicating that flushes of anions moving through a soil system could result in marked variations in the Ca^{2+} and Mg^{2+} concentrations.

Concentration ratio can also be related to the ratio of the same cations on the exchange surface (Quanitity ratio, equation 5) by a proportionality constant (k_g) (equation 6);

$$Q_k = \frac{K_{ex}}{(Ca_{ex} + Mg_{ex})} \tag{5}$$

$$k_g = \frac{K_{ex}}{(Ca_{ex} + Mg_{ex})} * \frac{\sqrt{(Ca_l + Mg_l)}}{K_l} \tag{6}$$

Where $_{ex}$ denotes exchangeable cations on the CEC surface (cmol(+)/kg soil) (Beckett, 1964b). Poss et al. (1997) found k_g values between 9.9 and 11.5 for kaolinitic soils containing small amounts of mica-smectite. Bar et al. (1987) found that intensive fertilisation of smectite dominated soils inside glass houses led to reduced selectivity for K^+ as exchangeable Kincreased, and k_g values of about 8.7 reduced to less than 2. Bar et al. (1987) also report that in soils containing illite, k_g values increased from 2 to 40 as K was depleted, while in a pure mica depleted of K, a k_g value of 2000 was found.

Manipulation of equation 6 under laboratory conditions often produces a distinct two phase curve for a soil system (Beckett, 1964b) (Figure 2.4). The two phases correspond to the energy with which K is held at the charged sites (Lee, 1973; Evangelou et al., 1994). Phase I (linear upper phase) corresponds to negatively charged sites that have little specificity for K and will readily supply K into solution if the amount of K^+ in solution is reduced, or the amount of bivalent cations is increased. These sites are expected to correspond to K held on the outer (planar) surfaces of clay particles, or in fully expanded interlayers, wherever a conventional diffuse double layer has been established. Once these sites have been depleted of K, only sites that have a greater specificity (or affinity) for K remain undisturbed (phase II). This second range of sites is expected to include any site that has a greater specificity for K than a 2:1 layer silicate surface that is fully exposed to soil solution. As discussed previously, this will include a very wide range of charged sites, with specificity for K ranging from simple size restrictions against larger ions, to only partially hydrated K in a partially open interlayer space, with an extremely high specificity for K. If all the phase I K has been removed and the only K potentially available for diffusion is on these selective sites, any depletion of the K^+ in solution will be replaced less readily. When the amount of K on the charged surfaces becomes very low, diffusion of K from nonexchangeable sources becomes significant, limiting the smallest CR_k that can be achieved (Beckett and Nafady, 1967b; Lee, 1973).

The amount of Phase I and II sites in a soil is generally equated with exchangeable K, which is the amount of K that can be displaced into solution by NH_4 in a fixed time period (Rich and Black, 1964; McClean and Watson, 1985). The test does create a rather arbitrary cut off point in terms of the site specificity, which can be different for different soils (Beckett and Nafady, 1967a). It must also be noted that the chemistry of the two ions, particularly when hydrated, is similar but not identical. NH_4 appears to coordinate to the 2:1 layer silicate surfaces somewhat differently, and to adsorb to some sites that do not adsorb K (Evangelou et al., 1994). The definition of nonexchangeable K is therefore also rather arbitrary. It is incorrect to assume that all nonexchangeable K is in mica-like interlayer spaces. The term will also include hydrated K that was not

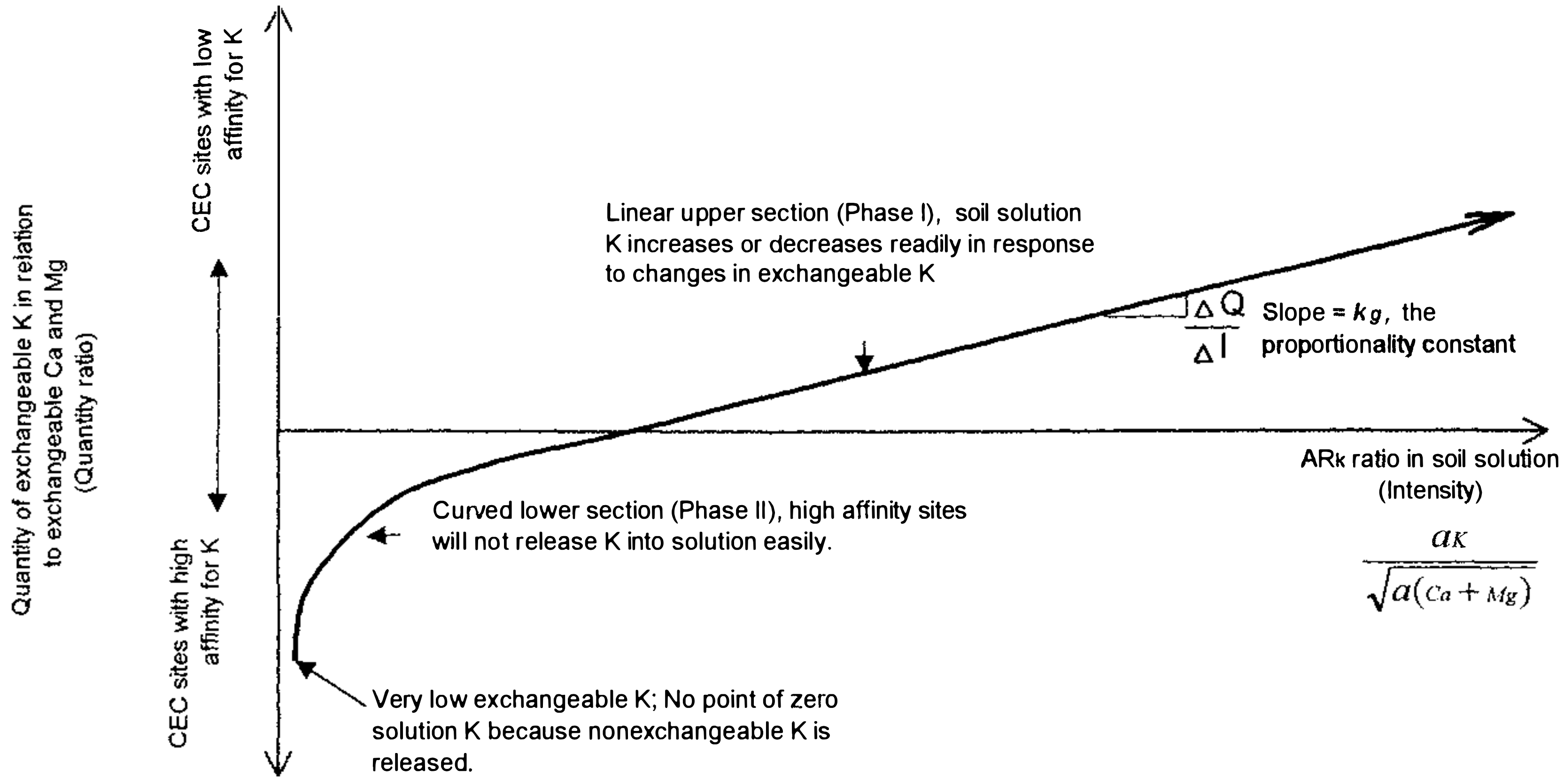


Figure 2.4: Typical quantity intensity curve in a 2:1 layer silicate soil exchangeable system dominated by Ca (after Beckett, 1964 and Evangelou et al., 1994).

vulnerable to exchange by NH_4^+ within the fixed time period, such as K^+ in inaccessible positions or partially hydrated interlayers that will have a greater resistance to diffusion forces. Even the physical size of the 2:1 layer silicates may make sensitivity to concentration gradients slow, because it will K^+ take longer to diffuse into or out of the central parts of an interlayer space, as the area of the 2:1 layer silicates increases (Verburg and Baveye, 1995).

A soil system does not stop supplying K when soil solution K^+ and exchangeable K have been depleted. If the depletion of K continues (as seen in electro-ultrafiltration and resin extraction systems, e.g. Mengel and Uhlenbecker, 1993 and Dobermann et al., 1996), a new typically biphasic release equilibrium is then established with the more soluble fraction of the nonexchangeable K. In this study, the more soluble fraction is estimated as the soil K that is soluble in HNO_3, but is not exchangeable with NH_4 (Step K).

Quantity intensity relationships can be charactered for a particular soil system and can be a useful way to predict how much added fertiliser K might be available to plants, or leached (Beckett and Nafady, 1967a). These principles, in combination with the effects of ionic strength and soil water movement, can also be used to model K^+ movement down a soil profile (e.g Tillman, 1991; Yanai et al., 1996; Vogler, 1997). The quantity intensity relationship will, however, be vulnerable to anything that changes the CEC, or ion, reactivities, such as large changes in pH, complementary anions, competing cations, or temperature (Sparks and Huang, 1985; Evangelou et al., 1994; Sauvé and Hendershot, 1995).

2.2.5 Soil testing for K in New Zealand

In the early stages of the development of agriculture in New Zealand (prior to the 1930's) K was unlikely to be deficient for plant growth, creating an impression that New Zealand soils were naturally high in K, and no K fertiliser was needed (Metson, 1968). In reality, the K reserves in some soils were largely created by the burning of bush and scrub, which formed a reserve of K in the ash (Taylor, 1950). In the 1930's, these reserves began to run out, particularly in the weathered volcanic soils, podsols and peats, which otherwise contain little K. In response to this, significant use of K fertiliser began on some pastures. Further evidence of K shortages appeared in the

1950's, as superphosphate use increased, and the area of pasture was extended to soils with very low levels of natural fertility (Woodcock, 1936; Taylor, 1950; Metson, 1968).

At this time, Hogg (1957) recorded the development of a soil test that distinguished soils responsive to K fertiliser. The test measured the amount of K displaced by NH_4 during a two minute extraction in neutral ammonium acetate and was subsequently adopted for national government soil testing, as the "Quick" test (Mountier et al., 1966). The test appears to have been a reasonably successful indicator of K responsiveness for soils with low mineral reserves of K, particularly soils with volcanic parent materials. Problems were recognised with other soils, particularly the soils in the drier areas of the South Island, which generally have sedimentary parent materials and a high proportion of 2:1 silicates in the clay fraction, like the soils in the present study. In these soils the NH_4-extraction results often had no relation to the observed fertiliser responsiveness. The recommended solution was to test the size of the soil K reserves in these soils, for which a sequential strong acid extraction was adopted. Problems were subsequently also found with this test, with K apparently being reabsorbed from solution and an alternative test using sodium tetraphenylboron (NaTPB) extraction, which precipitates the extracted K out of solution, is now recommended to evaluate soil K reserves (Lee et al., 1978; Williams et al., 1986). Unfortunately, this test has also received criticism, because of misleading disparities between the amount of K extracted from different forms of mica (Dreher and Niederbudde, 1994).

Today, K fertiliser recommendations are still largely based on the standard Quick test, although Campkin (1979) found no relationship between K fertiliser requirements and Quick test K in a national series of trials. Williams et al. (1986) also found no relationship between Quick test K and relative yield, on Recent soils in the South Island, although NH_4-exchangeable K measured by a slower leaching did have a relationship with relative yield. This problem continues to be addressed in this study.

2.3 K in plant and animal systems

Potassium is an essential element for plant growth, and for human and animal health. K is the most abundant cation in plants and the only monovalent cation that is essential to all higher plants. In plants, animals and humans, K is osmotically active and has a principle role in maintaining the electrical potential across cell membranes. Animals and humans can suffer from both insufficient K (hypokalemia) and excessive K (hyperkalemia), affecting the cation balance of Mg, Ca, Na and K, which can have marked effects on muscle and heart function. Excess K also has been associated with reduced levels of Mg in plants and in blood, causing hypomagnesmia (grass staggers, or grass tetany in cattle). Lack of K in plants is associated with reduced rates of photosynthesis, translocation, and transpiration (Huber, 1985; Mengel, 1985; Preston and Lisner, 1985; Serfass and Manatt, 1985).

2.3.1 K in the rhizosphere

In general terms, the amount of K available for plant uptake will be largely dependant on the rate of diffusion of K through the soil, which will in turn mainly depend on the physical surface area of the plant roots and the soil water content (Barber, 1985). Plants create a very strong sink for K, and diffusion alone is expected to account for much of the K depletion from a soil. Under favourable conditions soil solution exchangeable K will typically be deeply depleted for some mm from plant roots (Kuchenbuch, 1987). K uptake by plant roots has some interesting similarities to the processes occurring on silicate surfaces in the soil. Cell membranes generate a negative charge by actively releasing H^+, which creates an area of solution between the cell membrane and the cell wall that has a similar charge relationship to the diffuse double layer chemistry found on negatively charged soil surfaces (section 2.23) (Beckett, 1972). A range of K adsorption sites with different selectivities for K are thought to exist in a cell membrane, providing both active uptake against an electrochemical gradient (e.g. when soil solution concentrations are very low), and passive uptake (which increases as the soil solution K^+ concentration increases). Both the generation of negative charge on the membrane, and the dehydration and transport of K across a cell membrane requires energy inputs by the plant, giving a light-dependant diurnally fluctuating pattern to K uptake (Mengel, 1985).

Plants can deplete NH_4-exchangeable K for some distance from the root surface and deplete nonexchangeable K very close to the root surface (Kuchenbuch, 1987). Barber (1985) suggested that up to 14% of the K taken up by roots could come from nonexchangeable sources, in systems well supplied with K.

The relatively rapid breakdown of 2:1 layer silicates by plant roots, bacteria and fungi on an individual basis in the laboratory has been well documented (Weaver, 1989; Hinsinger and Jaillard, 1993; Paris et al., 1996). In the field, all three are active in the rhizosphere, creating a strong weathering environment for 2:1 layer silicates (Tributh et al., 1987, Robert and Tessier, 1992).

The main weathering mechanism in the rhizosphere is thought to be the very strong diffusion gradient created by the plant root, which is assisted by a drop in pH (often about a unit) as biogenic acids are released in this zone. The breakdown of the 2:1 layer silicates also coincides with the release from the root tip of chelates that attack Al and Fe e.g. oxalic and citric acids. The chelates mainly attack free ions or hydroxy polymers but are also expected to affect the solubility of the 2:1 layer silicates. P shortages and Al toxicity have been shown to trigger greater rhizosphere activity and there is some evidence that K shortages also have this effect (Jones and Darrah, 1994; Jones and Kochian, 1996; Jones et al., 1996; Imas et al., 1997). Soil tests for plant available K based on exchangeable K alone give no acknowledgment to the ability of a plant to modify the soil environment and release nonexchangeable K (Hinsinger, 1998).

2.3.2 K in the plant

Potassium function in plants is a large subject and only a brief overview is given here. The strong control possible over K each time it crosses a cell membrane allows plants to build up concentrations that are 10 to 1000 times greater than those found in the soil solution, and K often becomes the dominant cation in plant sap. This control also allows plants to manipulate K concentrations across membranes between and within cells throughout the plant. Plants use the K concentration gradients in a variety of ways within the plant. The role of K in transpiration has been recognised since early this century. Plants control the rate of transpiration by manipulating the concentration of K in the vacuoles of the stomatal guard cells to cause an influx of water and a build up of osmotic pressure, opening the gaps (stomata) between pairs of guard cells on the leaf surface. Plants use K in numerous similar ways to control the movement of water and many other substances within the plant. Also, small amounts of K are specifically required for enzyme activation, and chloroplast functioning (Läuchli and Pflüger, 1978; Mengel, 1985).

Plants maintain a relatively constant level of K in the circulating sap for all except the end of the growth cycle, when it rises sharply to assist the desiccation of the seeds. Excess K is stored in the vacuoles. The rapid circulation of K tends to keep the concentration of K in the root cortical cells relatively low. In particular, K circulates upwards from the roots as a counter ion for NO_3 that is taken up by the roots. If K levels build up sufficiently to raise K levels at the uptake sites in the roots, then K uptake has been observed to decline. Plants experiencing a K shortage appear to move K to the sites of the more vital enzyme and chloroplast functions first. K required for osmotic and transport processes has less priority and the plant can use other, less efficient cations such as Na, if K is short for these functions (Läuchli and Pflüger, 1978; Leigh and Johnston, 1983; Leigh, 1989).

It is difficult to define at what point a plant becomes deficient in K, because K is re-circulated so readily to areas where it is needed most. Actual total K requirements by plants have been found to be difficult to model (Greenwood and Karpinets, 1997). Leigh (1989) found that there was no unique K concentration in dry matter that characterised a K-sufficient crop, despite the common practice of determining plant availability of soil K in this way. Tissue water concentrations of K were a better indicator of the plant K status. Adequate levels of plant K are associated with faster growth rates (including roots), improved plant and fruit quality, lower water use, better drought, flood and frost survival, and reduced rates of infection. Inadequate K is associated with poor growth rates, poor disease, drought and wind resistance, and poor post harvest quality (Mengel, 1975; Läuchli and Pflüger, 1978; Beringer and Nothdurft, 1985; Mackie-Dawson et al., 1995).

2.3.3 K in grazed pasture

Permanent grazing pastures in New Zealand usually consist of a mixture of clover and grass species. Grasses have dense fibrous root systems, and are very efficient extractors of soil K (Robinson, 1985). Grasses, particularly the rye grasses (*Lolium* sp.), can reduce exchangeable K to very low concentrations, and attack the non-exchangeable fraction, including converting mica to vermiculite (Hinsinger and Jaillard, 1993). Clovers have a small root surface area and do not extract K so efficiently. Consequently, clovers are usually more sensitive to inadequate levels of soil K than grasses, and also require more K than the grasses to reach full potential growth (Duke and Collins, 1985).

Mixed grass and legume pastures are generally held to have adequate K if the dry matter concentration is 2% or more, although, as mentioned above, the dry matter concentrations are dependant on the stage of growth of the plant. This is less of an issue in rotationally grazed pasture, although a large drop in pasture K concentration is observed in late summer if the pasture is allowed to go to seed (McNaught, 1958). As a legume, clovers require adequate K for optimum N fixation. Inadequate K in clovers will limit the amount of N build up in the soil, and thereby restrict grass growth. Specific levels of adequate K in clover have been rather difficult to establish, as the deficiency symptoms do not tend to appear until plant dry matter concentrations of K have dropped below 0.7%. Even then, only older leaves may be visibly affected (McNaught, 1958; Ball et al., 1982; During, 1984).

At 2% K, or more, healthy pasture supplies much more K than is required to the grazing animals. Sheep and cattle require only about 5-8 g K/kg of feed. The excess K is excreted - about 10-30% is lost in faeces and the remainder in the urine. The concentration of K in the urine depends on how much water the stock are drinking, but can be 6-9 g/l of K (Preston and Linsner, 1985; Haynes and Williams, 1993). Much lower values have been found. Sakadevan et al. (1993) reports 1.9 g K/l in sheep urine collected from ewes that were grazing pasture in winter. K forms 60-70% of the cations in the urine, with Cl and HCO_3 as the main counter ions. Most of the N (70% or more) will generally be in the form of urea, the remainder as amino acids and peptides (Haynes and Williams, 1993).

The typical size of a urine patch is about 0.04 m^2 for sheep and 0.16-0.49 m^2 for cattle Excretal patches may cover 30-40% of a pasture surface each year (Haynes and Williams, 1993). Based on the upper estimates of K content in urine, a cattle urine patch can apply 1000 kg N/ha, 900 kg K/ha and 35 kg S/ha. A sheep urine patch is thought to apply about half this quantity of N, K and S, although much lower returns of 146 kg K/ha and 170 kg K/ha per patch have also been estimated (Morton and Baird, 1990; Sakadevan et al., 1993).

Simulated studies of urine movement down a soil profile have found that, after 20 minutes, Br^- from a KBr solution applied in the same volume as a sheep urine patch could be found to a depth of 150 mm (Williams and Haynes, 1994). Similarly, under a simulated cattle urine patch, Br^- penetrated the profile to 400 mm. It is estimated that 15-25% of the cattle urine might normally be lost into the subsoil, below 150 mm (Williams and Haynes, 1994).

In studies of mixtures of K^+ and urea leached though soils with a 2:1 layer silicate mineralogy, K^+ in solution re-equilibrated according to the concentration ratio equations (see Section 2.2.4). Increasing proportions of exchangeable Ca and Mg and decreasing K on the exchange surfaces at greater depths, cause the applied K^+ in soil solution to be successively exchanged for Ca^{2+} and Mg^{2+} so that little K^+ was leached from the deeper profile (Tillman, 1991). Studies of a single application of urine to similar soils found similar effects (Early et al., 1998). In this way Ca^{2+} and Mg^{2+} tend to be the cations leached from under urine patches and relatively little K^+ is lost from the soil profile (Williams, 1988; Sakedevan et al., 1993; Early et al., 1998). (This process is discussed further in Chapter 6.)

In the soil, urea is hydrolysed to NH_4^+ within 24 hrs by the enzyme urease, raising the soil pH by 2.5 – 3.5 units in the top 5 mm, and one unit at 30-40 mm (Haynes and Williams, 1993). NH_4^+ has a size comparable to K^+ and is expected to compete with K^+ for cation exchange sites on the 2:1 layer silicate surfaces, although detailed examinations of K-NH_4-Ca exchange systems have found quite variable effects (Evangelou et al., 1994; Barbayiannis et al., 1996). NH_4^+ and K^+ fixation into the nonexchangeable fraction is often observed. The elevated pH will facilitate fixation into the nonexchangeable fraction (discussed further in chapter 4). NH_4^+ may also be incorporated directly into the organic matter or volatilise as NH_3 (Crush and Evans, 1988; Williams and Haynes, 1994). Both NH_4^+ and K^+ may be taken up by plants (Haynes and Williams, 1993). In studies of the application of urine to pasture, about 20-40% the applied K was recovered in the pasture (Haynes and Williams, 1993; Early et al., 1998).

Over the following 30 – 60 days, the remaining NH_4^+ is oxidised by chemoautotrophic bacteria to NO_2^- (generating H^+ and dropping the pH again) and then to NO_3^-. The speed of this oxidation process is temperature dependent and so is faster in summer conditions, although dry conditions can slow the process, particularly the conversion of NO_2^- to NO_3^- (Haynes and William, 1993). Carran (1988) found that when urine was poured onto wet or dry soils, soil nitrification proceeded rapidly on the wet soil and so did plant growth and uptake of K^+ into the pasture. On a soil at wilting point, nitrification was slow and NH_4^+ remained dominant in the soil solution for an extended period.

Much less K is excreted in the dung, compared to the urine, but the amount is not insubstantial. In comparison, most of the excreted P, Ca and Mg will be in the dung. The K content of dung may typically be 1%, of a similar magnitude to the P and Mg content, applying K at an approximate rate of 50 kg K/ha in a sheep dung patch and 400 kg K/ha in a cattle dung patch (Haynes and Williams, 1993; Sakadevan et al., 1993). Breakdown of the dung tends to be a slow process, dependent on rainfall and macro and micro fauna digesting the high C fibre content. Mg and Ca are often in the form of carbonates, giving the dung a pH of 7-8. Soil exchangeable P, Ca, Mg, organic C and N and soil pH can be elevated for several years under cattle dung patches. Shorter term increases in exchangeable K have also been observed (Haynes and Williams, 1993).

In grazed pastures, K is vulnerable to transfer losses as the stock eat in one place, then move around the paddock, or the farm, before they excrete the ingested K in a different place and on a smaller area than it was grazed from (Weeda, 1979). A natural feature of wild grazing animal communities is a tendency to favour particular pasture areas. This causes an associated transfer of nutrients as the deposition of excreta increases in these areas (Putman, 1986). In captivity, the same process continues, as grazing animals tend to gather at stock "campsites" that are selected by the grazing animals as resting spots. These campsites may be sheltered areas near trees, local high points, or around water and feed troughs, or gateways (Grant et al., 1973; Haynes and Williams, 1993). Stock camping patterns are particularly marked when paddocks are very hilly, as stock avoid the steeper slopes and favour the flatter areas, which tend to be mainly on the ridge-tops in steep country.

2.4 Steepland pasture

The lowland steeplands of New Zealand, popularly called the "hill country", are steep non-arable hills below 1000 m, which cover about 40% of the land surface (Blaschke et al., 1992). Land is defined as moderately steep when the ground slope is between 21° and 25°, steep between 26° and 35°, and very steep when the ground slope is >35° (NZLRI, 1979). Steepland terrain is characterised by rough topography and rapid changes from water shedding (convex) to water collecting (concave) land formations (Figure 2.5). The term steepland also implies that soil catenas or complexes are present, so that several distinct soil profile classes are distributed in either a regular or an undetermined pattern (Tonkin et al., 1982; Blaschke et al., 1992).

In the central North Island of New Zealand the steeplands are often formed on deeply dissected sedimentary parent rock. Volcanic ash and some loess are often mixed into the soil profile, depending on the altitude and slope stability. The original forest typically has been removed some time in the last 130 years. The grazing stock is often a mixture of cattle and sheep, which modify the terrain by the formation of tracks on the small terracettes that run around the contour (Figure 2.6). The animals favour the flatter ground, particularly the tops of the ridges (Figure 2.7) and redistribute ingested N, P and K to these areas (see also previous section).

Steeplands are generally formed by uplift along fault lines and are still eroding, mainly by landslide (slip erosion). The rate of erosion is thought to have increased where the forest cover has been removed. A study of steepland pasture in the Taranaki region found that the losses of soil by erosion were an average of 2 mm /year or 2000 m^3/km, with the most rapid losses from slopes of more than 42°. 40 years after a slip event, the pasture

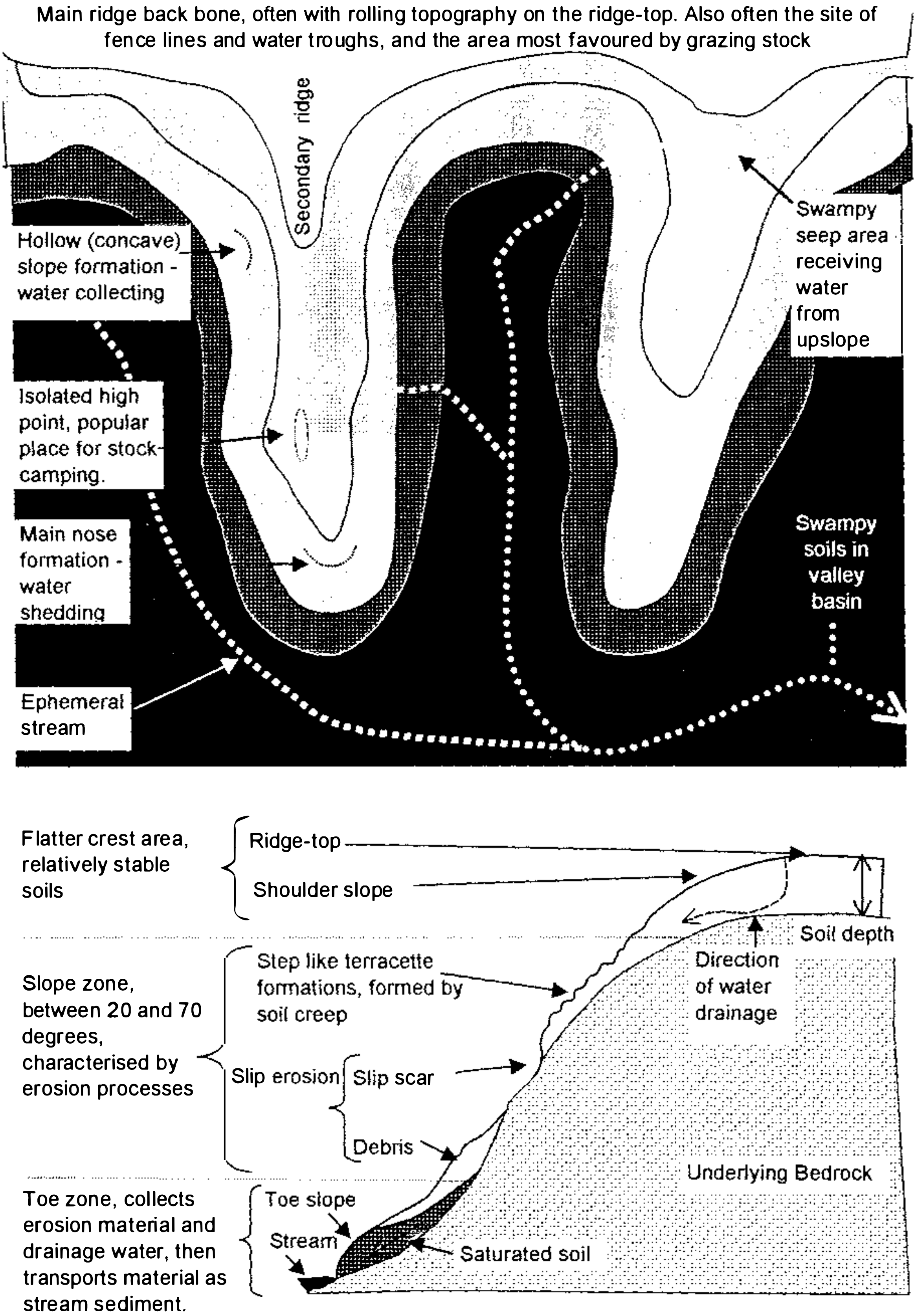


Figure 2.5: Diagram of some typical land formations and terminology associated with steepland terrain. Upper diagram illustrates typical topography from an aerial perspective (lighter shades indicate increasing altitude). The lower diagram illustrates the cross section, or transect, of a typical ridge and valley formation (After Tonkin et al., 1982; Todd, 1986).

Figure 2.6: Terracette formations in steepland pasture. Also shown are the typical greywacke bedrock exposures of the Makara steepland soil at the Tuapaka site.

Figure 2.7: Illustration of the way grazing stock favour flatter ground in hilly pastures, particularly the ridge-tops.

recovery on a slip scar was only 74% of the uneroded level of production (Blaschke et al., 1992; DeRose et al., 1995).

A typical steepland pasture in this area is dominated by low fertility grasses, typically a mixture of browntop (*Agrostis capillaris*) and sweet vernal (*Anthoxanthum odoratum*). The proportion of Yorkshire fog (*Holcus lanatus*) tends to increase in the wetter areas. Many other plants are also usually present, including mosses, rushes and thistles. Regenerating native scrub plants are also common in any areas that are inaccessible to stock. On the campsites the proportions of higher fertility species increase, such as white clover (*Trifolium repens*) and perennial ryegrass (*Lolium perenne*) (Grant and Brock, 1974; DeRose et al., 1995).

The soils on the steep slopes are often shallow and have a reduced water holding capacity resulting in more, and longer, soil moisture deficits (Ledgard et al., 1982, DeRose et al., 1995). Even where soil moisture capacities are similar on sloping and flat areas, the sloping areas will generally be drier in the top layers because of less effective rewetting (Sheath and Boom, 1985). These relationships can be confounded by subsurface water seepage that causes the accumulation of water in a depression at any point in the landscape (Todd, 1986; DeRose et al., 1995). The deeper soils on the concave areas on the slopes also tend to collect and hold more water (Timlin et al., 1998).

Aspect can also have a big effect on the soil moisture status. Surveys of soil moisture in hill and steepland pasture have found that the soils are generally at field capacity from April or June to September or October. As spring becomes summer, large differences in soil moisture tension can develop between the four main aspects. Northerly aspects (which receive the most sun) can be below wilting point for much of the summer and re-wet only slowly in the autumn, compared to southerly aspects that rarely drop to wilting point during the summer and re-wet quickly in the autumn (Gillingham, 1974; Lambert and Roberts, 1976).

Wind can also have an important effect on environmental variability in steepland. Wind run in steepland can be 100% greater than in adjacent lowland (Grant et al., 1973). Lambert and Roberts (1976) reported soil temperatures were warmest on an easterly aspect from September to November (spring), because the prevailing winds were cooling the northerly aspect.

The aspect differences on the slopes may not result in overall differences in pasture growth, because variations in the pasture species present on different aspects can result in different seasonal growth patterns (Gillingham, 1974; Radcliffe et al., 1977). In general, the rate of pasture production on the steeper slopes is expected to be about half the rate of production on the campsite areas (Grant et al., 1973). Pasture production on the campsites can be comparable with intensively farmed flat land on soils similar to those under the campsites (Grant et al., 1973), although Todd (1986) found that overgrazing of campsites, where soils were sandy and relatively dry, could cause the sward to die off in some areas for much of the year.

Estimates of the extent of nutrient transfer onto the animal campsites vary tremendously. The transfer of P has been studied the most, and can vary from 1 kg P/ha/year to 120 kg P/ha/year, transferred from the steeper slopes on to the flatter areas (Saggar et al., 1988). Important factors in this variation are thought to be the amount of P applied as fertiliser and the proportion of flatter areas compared to steeper areas in a paddock. The aspect of the steeper slopes can also influence animal behaviour and subsequent nutrient transfer onto the adjacent ridge-top (Rowarth, 1987; Saggar et al., 1988). Stock tend to favour the warmer, sunnier parts of a paddock, usually slopes with a northerly or easterly aspect, and to avoid the colder areas, particularly the slopes with a southerly aspect (Suckling, 1959).

Gillingham and During (1973) measured the transfer of K, P and N in hilly country, using surveys of the dry matter production and nutrient content of the pasture, and dung distribution. The majority of the rolling to moderately steep slopes were estimated to be losing 22-38 kg K/ha/yr, depending on the pasture composition. The easy slopes were thought to be at equilibrium and small areas that constituted regular sheep camping areas (6% of the area) were estimated to be gaining 222 kg K/ha/yr, and 29 kg P/ha/year. After 30 years of pasture growth and topdressing with P but no K, this transfer had induced growth-limiting deficiencies of K on the slopes, in soils with volcanic parent materials that have relatively low K reserves. No further work appears to have been done on K transfer processes in hilly country, but Gillingham and During (1973) certainly indicated the potential for K deficiencies to develop over time in the soils of all steepland slopes.

Spatial variability of soil K in steepland pasture

Chapter 3

3.1 Introduction

The objective of this study was to examine the relationship between the variability of soil tests for K, and the scales and landform shapes of a typical southern North Island steepland pasture, developed in mainly sedimentary soil parent materials. These steepland pastures were investigated because K fertilisers have not been generally applied to such soils in the past, although a potential for depletion of the soil K by animal transfer has been indicated (Gillingham and During, 1973, Haynes and Williams, 1993), and some responses to K fertiliser have been recorded on these and similar soils (During, 1984; Ledgard et al., 1997). Gillingham and During (1973) found that the transfer of nutrients by grazing stock could result in the depletion of exchangeable K in the slopes and a distinct increase in exchangeable K at points where animals congregate (see Chapter 2.4). Increases in exchangeable K on the ridge-tops, compared to the steeper slopes, have also been reported by Tonkin et al. (1982) and Ledgard et al. (1982). Otherwise, no more detailed study of K fertility patterns in steepland pasture appears to have been made. In particular, no detailed information is available on the spatial variability of K fertility in this landscape, which would enable the mapping of the cumulative effect of the patterns of depletion and gain using regional variable theory.

Beckett and Webster (1971) reviewed a wide range of studies on the variability of common soil properties. They concluded that soil properties could be divided into three classes of variability. Class I consisted of factors that were the most stable in soils under cultivation and were useful to differentiate changes in soil type, such as sand content or total P. Class II consisted of factors that had an intermediate variability and were expected to be somewhat affected by cultivation, such as total N and CEC. Class III consisted of factors that were highly variable and strongly affected by cultivation, such as NH_4-exchangeable Ca, Mg and K. In Class III, the variability of a soil property within a soil type is expected to be as great the variability of the same property between soil types.

Adams and Wilde (1976) examined the variability of a range of soil properties in one New Zealand soil type with a mixture of volcanic and sedimentary parent materials. NH_4-exchangeable K was extremely variable, as was expected based on Beckett and Webster (1971). Total soil K had a low variability within the soil type and was classed by Adams and Wilde into Group I of Beckett and Websters' classification. Wright (1998) also found that exchangeable K values across two paddocks were highly variable and that accurate mapping required a sampling distance of 1 m or less. Evidently, a characterisation of soil K in steepland pasture will require careful attention to the effect of spatial variability at small distances, before the larger scale relationship between soil K and the shape of the landform can be mapped.

3.2 General materials and methods

The general methods section covers the mathematical theory used to interpret the results of two surveys of soil K status, and a detailed description of the two steepland sites utilised throughout the thesis.

3.2.1 Statistical theory

As already indicated in the introduction, the distribution of K in steepland soils is liable to be variable. Therefore, a range of statistical procedures is used in this study to investigate the distribution of K in the landscape. A number of important concepts are introduced below.

3.2.1.1 Frequency and correlation

Frequency distribution

An approximately Normal frequency distribution is an assumption of most probability tests. A Normal distribution is a continuous bell shape and has no skew (i.e., is symmetrical) (Figure 3.1). In this distribution the arithmetic mean, the mode (most common value), the median (middle value if all the values are ranked) all have the same value (Webster and Oliver, 1990). About 68% of the population distribution will lie within one standard deviation, 95% will lie within two standard deviations, and 99.74% will lie within three standard deviations. Skewness is the most frequent departure from normality in data sets based on soil properties (Beckett and Webster, 1971).

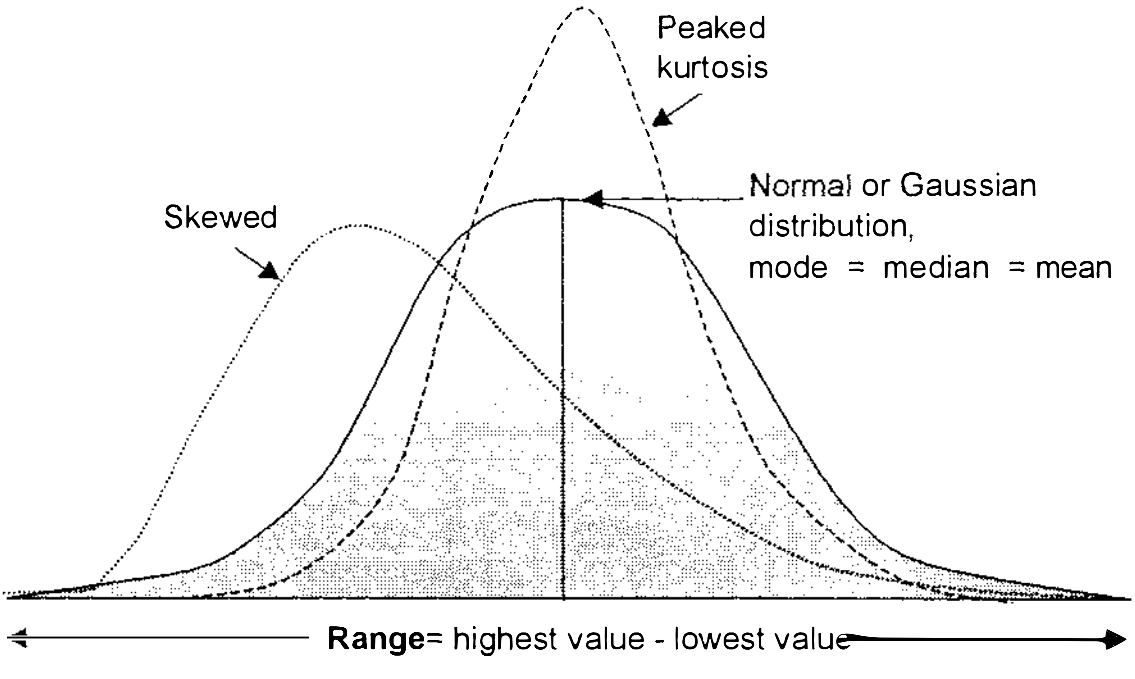


Figure 3.1: An illustration of the Gaussian, or Normal distribution (solid line), which is the standard assumption of univariate statistics, and also some commonly found deviations (broken lines).

Correlation

Linear correlation tests the extent of any linear association between two factors, calculated as a Pearson correlation coefficient (r). If variable x can be expressed exactly as a linear function of variable y, then the correlation is 1 or -1, depending on whether x is positively or negatively related to y. When highly correlated, x and y tend to fall on, or near, a line of fit. A correlation of zero between two variables means that each variable has no linear association with the other and, if the values are normally distributed, that the variables are independent of one another. The probability (p-values) of a null hypothesis that a correlation is zero can be calculated, assuming independent and identically distributed observations from a bivariate normal distribution. Each p-value can be used to assess the significance of the corresponding correlation coefficient. With small p-values (usually less than 0.05), the hypothesis of zero correlation should be rejected.[1]

3.2.1.2 Correspondence analysis

Correspondence analysis is a largely descriptive technique, which identifies the main sources or patterns of variability in a data set. The technique can be used for qualitative data and is frequently used in areas such as ecology and the social sciences to identify the patterns and associations in descriptive information. Dalal-Clayton and Robinson (1993) used the technique to sort groups for reconnaissance soil mapping, and thought that correspondence analysis was a valuable tool for soil science, which has been overlooked.

Correspondence analysis relatively unconcerned with μ, the population mean. Instead, correspondence analysis partitions the populations and identifies the main points of difference between the shapes of the various sub-distributions that have been generated by partitioning the data set. A frequency distribution can be divided into more than one set of classes, based on different variables that might be affecting the distribution. For example, a group of people might be measured in terms of height and weight. If the data set is divided into classes based on two different properties, or variables, and then cross tabulated, with classes for one variable forming the rows (e.g. short, medium and tall heights), and the classes from the other variable forming the columns (e.g light, medium and heavy weights) the table can then be converted into a graph to show the main associations between the rows and columns of the table. In terms of the example, there would probably be a very strong association between increasing height and increasing weight.

---

[1] Help notes, release 6.12, SAS Institute Inc., Cary, NC, USA.

To form the graphical display, the information in the table is treated as set of vector coordinates and the table information used to generate a theoretical multi dimensional plot, or data "cloud". A two dimensional graph is then generated, by identifying a set of axis within the multidimensional plot that describes the strongest patterns within the data cloud. The centre of gravity, located at the origin of the axes, corresponds to the average profiles of both row and column groups. All the points in the data cloud are then projected onto these axes, forming a flat graph, in the same fashion as a contour map. The analysis treats the row and column groups as separate analyses, so physical distances on the graph between members of either the row or column groups have meaning, but the exact distances between members of the row or column groups do not and only general statements can be made about the associations between members of the different groups. In general, proximity indicates association and increasing distance indicates increasing disassociation (Lebart et al., 1984; Greenacre, 1984). A set of quality information is also generated, expressing how much of the total information of the data set is accounted for by each axis, and how well each of original points in the data cloud was represented on the graph. Some of the original points may have been sitting a long way from the axis, in a third dimension, and be poorly represented by their projection onto the graph (Greenacre, 1984).

To ease interpretation of the more complex correspondence analysis presented later in this chapter, a simple example that deals with a readily understandable data set is presented below (drawn from Ganesh 1994).

A survey of drivers was carried out to compare the proportions of people who use seat belts regularly, in various age categories (Figure 3.2). The cross tabulation summarises the results, giving a frequency count of answers found for each category of age and seatbelt use. In the results table (Figure 3.2) it can be see that all age groups were highest in the Sometimes user category, and also that the distributions of the values was very similar in the 21-25 and 36-30 age groups. These classes become the centre of the graph, representing the average situation. The 16-20 age group was different because it had a much higher frequency in the Never category, compared to the other groups.

The >30 row group was different because a much higher proportion of users were in the Always and Regularly categories, and there was a relatively low response to the Sometimes category.

	REGULARITY OF SEAT BELT USAGE			
AGE (years)	**Always**	**Regularly**	**Sometimes**	**Never**
16-20	1	10	70	19
21-25	4	8	80	8
26-30	8	10	77	5
>30	15	30	49	6

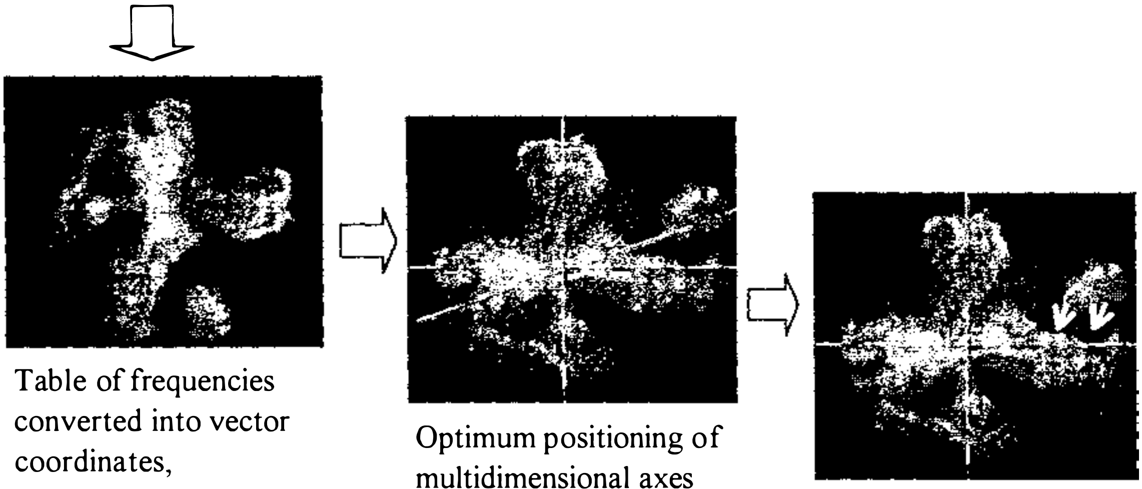


Table of frequencies converted into vector coordinates, generating a data cloud

Optimum positioning of multidimensional axes to capture maximum information in the data set

Projection of all points onto 2 principal axes, some points not projected efficiently

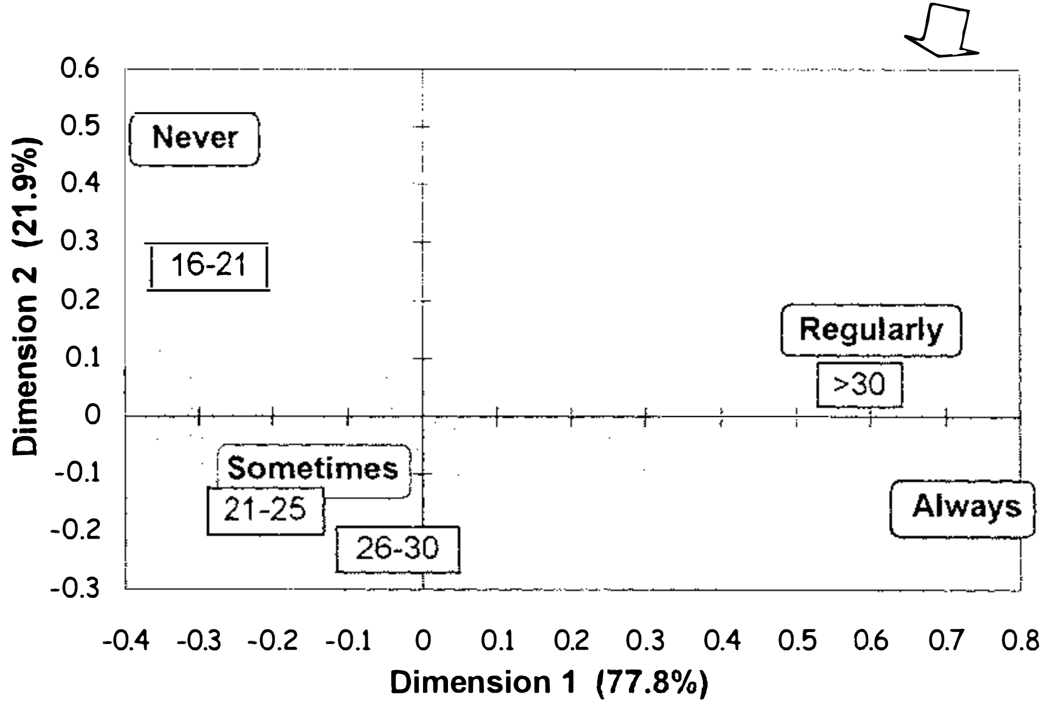


Figure 3.2: Demonstration of the process of correspondence analysis. The example is based on a survey of age and seat belt use (Redrawn from Ganesh, 1994). The data set is crosstabulated into a table of suitable row and column classes, then correspondence analysis turns the table into a multidimensional data cloud, finding two axes that encompass as much of the variability information as possible. All the data points are then projected onto the axes creating a visual summary of the analysis (lower graph).

When the information in the table was converted into a graph (Figure 3.2) the total variation in the information that could be represented was 99.75%, so the graph could be regarded as a very good representation of the correspondence information in the table. The principle axis (Dimension 1) accounted for 77.8% of the total variation, and the secondary axis (Dimension 2) accounted for 21.9% of the total variation. Only 0.3% of the information is not represented graphically.

To interpret the graph, the row and column groups are first considered separately. For the seat belt usage groups (columns) the main axis (dimension 1) may be regarded as a contrast between frequent (always and regular) and rare users of seatbelts (sometimes and never). The secondary axis (dimension 2) is mainly concerned with the Never category, indicating that it is somewhat different from the other categories in the column group.

The plot of the row (in this case, age) groups finds that the younger age categories are grouped together on the negative side of the axis and are contrasted against the >30 age group on the positive side of the axis. The secondary axis information indicates that the 16-21 age group is somewhat different to the other age groups.

Now considering the graph as a whole, the associations between the row and column groups clearly show the association between the age of drivers and their habits of seat belt use. The combined age groups of 21-30 had no distinguishing patterns and represented the data set average, associated with "Sometimes" using seatbelts. In comparison, mature drivers (>30) drivers were more likely to be associated with the Regular or Always classes of users of seatbelts, while the younger drivers showed a tendency to be Rare users of seatbelts.

It must be noted that the analysis sorts out the main points of difference between the various groups, rather than expressing the average situation. For instance, younger and mature drivers still were most likely to be in the Sometimes category, which was not evident from the graph.

3.2.1.3 Distance dependent variability

Regionalised variable methods are designed to characterise the changing values of a property with distance, so that a reasonably accurate prediction of values at unknown points can be made (Oliver and Webster, 1986). These methods have been adopted from the mining industry (e.g. Journel and Huijbregts, 1978), which was mainly interested in estimating the distance to high concentrations of a precious metal, based on the concentrations found at fixed drilling sites. The theory has been extended to the mapping of soil factors, being most useful where there is a continuous, or fairly regular variation in a soil factor, and of little use where soil factors are changing abruptly. (Burrough, 1993).

Characterising the spatial variability of a property, or variable, involves taking many measurements at known distances apart and building up a picture of the average rate of change in the variable with distance. In typical cases, points close together are more likely to have similar values, while points further apart are increasingly likely to have a different value.

In this type of statistical analysis, two different points in the landscape are theoretically represented as points x and x+h, where h is a vector (usually termed the "lag") having both distance and direction. For a given value of h, the squared difference between the value of a property (z) at point x and point x+h is used to calculate the "semivariance" at that lag, according to equation 1;

$$\gamma(h) = \frac{1}{2m(h)} \sum_{i=1}^{n(h)} [z(x_i) - z(x_{i+h})]^2 \qquad (1)$$

where $\gamma(h)$ is the observed semivariance, $z(x_i)$ and $z(x_i+h)$ are the measured values of z at points x_i and x_i+h, and m(h) is the number of paired comparisons (Webster and Oliver, 1992).

By varying the lag (h) in discrete sets, an ordered set of semivariances is obtained. This can be depicted graphically in a "variogram" (Figure 3.3). The variogram often yields a typical pattern of "nugget" and "sill" variances. The nugget variance is the minimum variability in the property (usually at the smallest distance measured). The sill variance is the maximum variability found, which may be at any distance depending on the property, and indicates the limit of distance dependent variability. Beyond the limit of distance dependence, measures of the soil property are regarded as independent. However, between the distances at which the nugget and sill variances are found, the limits of variability are known, and a reasonable estimate of the values of any unknown points between these distances can be made. The method also determines how far apart sampling points need to be for accurate map construction, although Webster (1985) expects that, while all soil factors should exhibit some pattern of spatial variation, there will be no absolute variogram for a soil property, because the variogram obtained from any one study will be very dependent on the scale of that study.

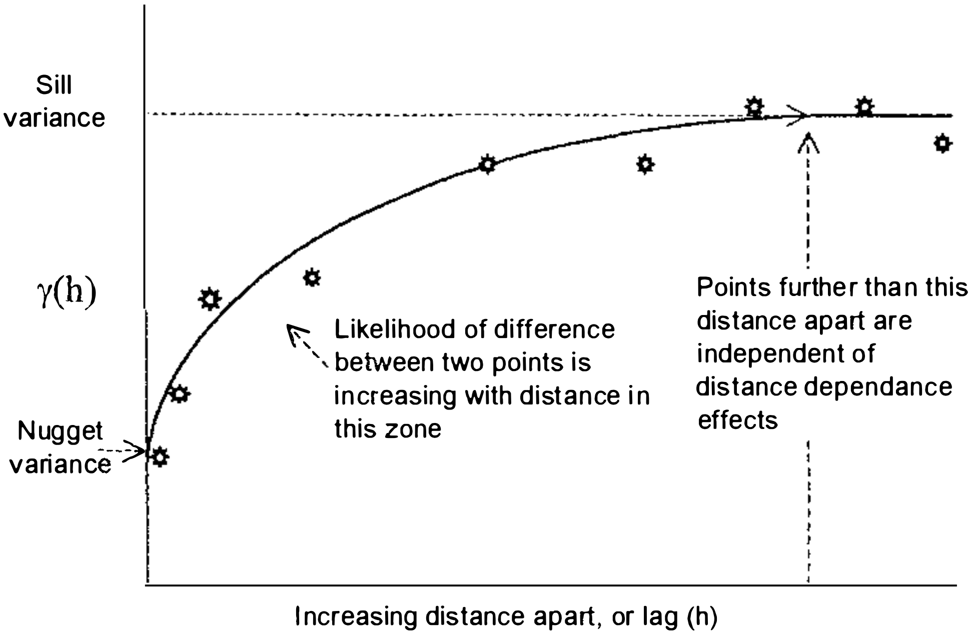


Figure 3.3: Illustration of a typical curve fitting exercise to find the relationship between variability and distance for a soil property (variogram). Between the nugget variance, at zero distance, and the maximum (or sill) variance, there is often a characteristic pattern of increasing variance with increasing distance, to which an equation may be fitted and used to predict unknown values in this zone.

Regionalised variability theory has been successfully used to map soil K fertility trends in the landscape. Mathews et al. (1994) and West et al. (1989) used the technique to map the exchangeable K patterns caused by the animal transfer of K to popular stock gathering points, such as water troughs. Scheinost et al. (1997) used a variation of the technique to map patterns of exchangeable K under different fertiliser regimes. These studies applied regional variable theory to relatively flat, intensively cultivated land. This study will attempt to apply the same technique to steepland pasture.

3.2.2 Site descriptions

This study was carried out at two steepland field sites, both in the greater Manawatu region of the southern North Island of New Zealand.

3.2.2.1 Regional geology

The underlying geology of the Manawatu region is the Wanganui basin, a large uplifted basin of tertiary sediments between Mount Taranaki and the axial ranges of the North Island (Heerdegen, 1982). The axial ranges in the Manawatu are the Tararua and Ruahine ranges, which are mainly formed of Triassic or Jurassic greywacke (a hard sandstone) and argillite (siltstone) (Cowie, 1978) and have a quartz-feldspar-biotite mineral assemblage (Wells and Furkert, 1973). The ranges have eroded relatively quickly, and the ensuing debris has assisted in the formation of extensive terraces to the west of the ranges, that are characterised by banded sandstone, siltstone and greywacke gravels. More recent erosion and eruption events have deposited extensive loess and some volcanic ash over the whole region, the thickness of which depends on altitude and subsequent erosion (Wells and Furkert, 1973; Rijkse, 1977; McLaughlin, 1983).

3.2.2.2 Regional climate

The district is characterised by warm summers, mild winters and a reliable, well-distributed rainfall. Prevailing winds are westerly to north westerly with frequent gales. Frosts are common in the colder months (April to October) (Cowie, 1978). Occasional snow has been noted at the study sites. At Tuapaka farm, the rainfall is estimated to range from 1140-1270 mm/yr from the front to the back of the farm (McLaughlin, 1983) (the study site was near the back of the farm). Rainfall at Bernwood farm was estimated at 1000-1200 mm/yr (D. Scotter, pers. comm.).

3.2.2.3 Vegetation

Previous to the 1850's, the entire region, except for low lying flax swamps, is thought to have been under thick totara and mixed podocarp-hardwood forest, with some localised areas of beech forest. Extensive burning and logging at the end of 19th century cleared the forest, and the region is now largely under pasture or is cropped, and is mainly used for cattle and sheep grazing (Rijkse, 1977; Cowie, 1978). (See Chapter 2.4 for more information.)

3.2.2.4 Experimental sites

3.2.2.4.1 Tuapaka farm

The Tuapaka farm site used in this study was part of a Massey University mixed stock farm located on the north western side of the Tararua Ranges (Figure 3.4). Tuapaka farm is on Aokautere Drive, about 7 km from Aokautere and 5 km from the Manawatu gorge. The study site was paddock S10 (Pollok and McLaughlin, 1986), of roughly 10 ha, located at grid reference: NZMS 260 T24: 425-910. The site ranged from about 240 to 300 m a.s.l, increasing in altitude from the northwest to the southeast part of the site. Greywacke parent rocks are exposed on the steep areas. The site is thought to have received regular aerial topdressings of superphosphate and other fertilisers since the 1950's.

The soils of the flat and rolling areas at the Tuapaka site have previously been described in detail by McLaughlin (1983) and Pollok and McLaughlin (1986). The soils of the steep areas were described by Cowie (1978). The soils in the paddock are mapped (Pollok and McLaughlin, 1986) as a complex of the Korokoro series (norm, complements, and moderately gleyed variant), on the rolling upper slopes. Makara steepland soils are mapped on the steeper side slopes and lower slopes. These soils are Andric Dystrochrepts, Typic Fragiaquepts & Fragiaqualfs respectively in the US taxonomy.

The Korokoro series is defined as forming in loess that is less than a meter thick over greywacke bedrock, with greywacke fragments in the subsurface horizons (Figure 3.5). The Korokoro series was classed as a yellow-brown earth (Cowie, 1978), but is now classed as a Brown Soil in the new New Zealand soil taxonomy (Hewitt, 1992). These soils are moderately leached, contain some volcanic ash, and may have little loess left after erosion, or the topsoil may be thickened by the accumulation of colluvium from further up the slope. The Korokoro Variant soils, on the lower part of the Tuapaka site, are wet, rush-ridden soils with poor drainage.

Figure 3.4: Part of the experimental site on Tuapaka Farm. The photograph was taken looking approximately south, over a cross section of the site. The marker string laid out for vector L is in the foreground (see Figure 3.7).

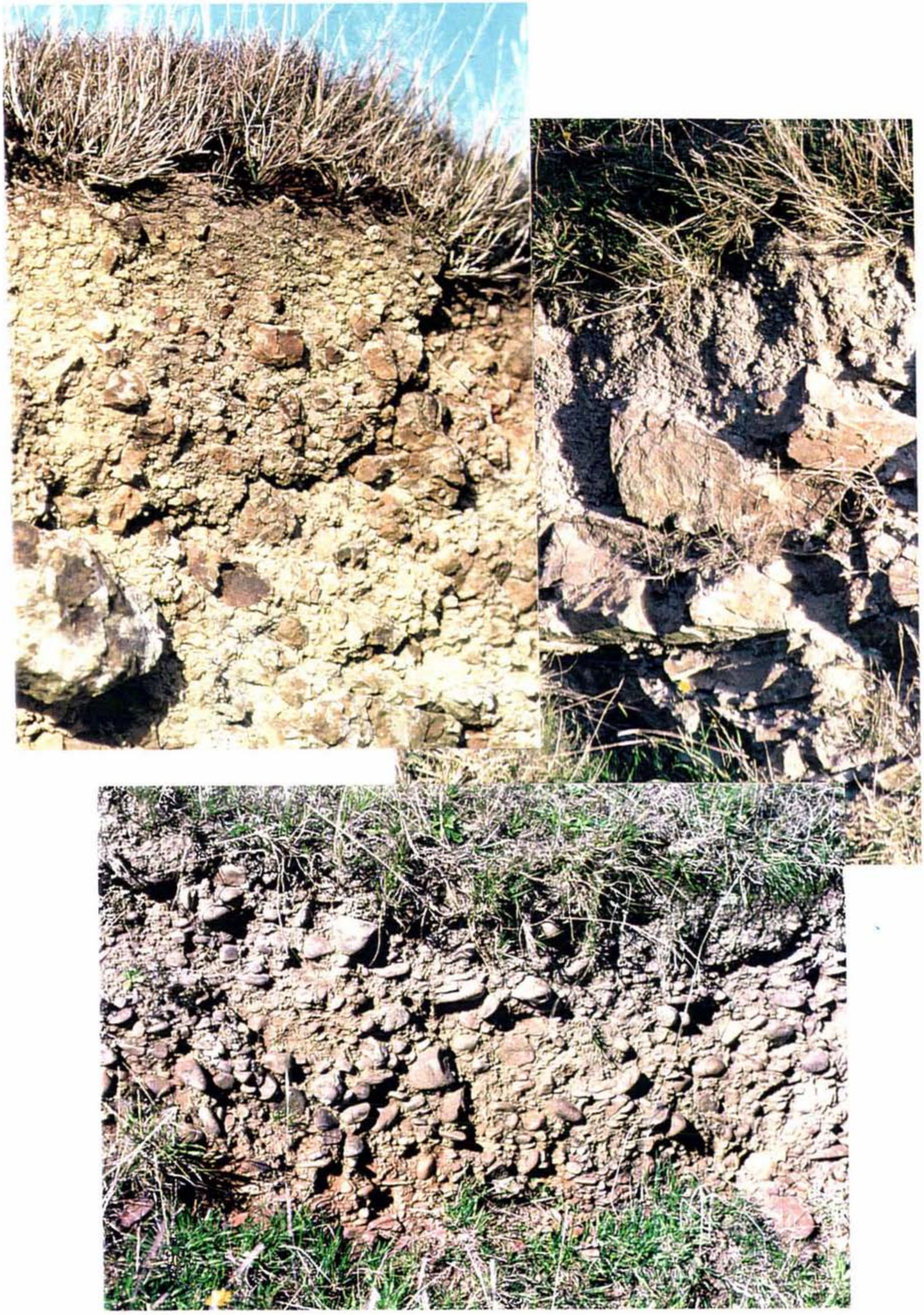


Figure 3.5: Illustration of the range of greywacke parent materials found at both sites. The two upper photographs show soil profiles developed in weathered greywacke colluvium and greywacke bedrock, at the Tuapaka farm site. The lower photograph is of an exposure of the band of loose greywacke conglomerate found in the lower slopes of the Bernwood farm site.

The Makara steepland soils (Pallic Soils, Hewitt (1992) related to yellow-brown earths) are characterised as thin, moderately leached, rather droughty soils developed on slightly weathered greywacke. Slopes ranged between 30° and 46°, indicating some inclusions of the Makara steepland soils, very steep phase, described by Cowie (1978). These soils are classed as relatively stable. The site does have some slip scars on the lower slopes and also some tunnel gully formations, where the soil B horizon has eroded at the bedrock face. Streams run through the main gullys.

The reference soil profiles of the Korokoro series and the Makara steepland soils are very similar. Both have A horizons consisting of dark greyish brown silt loam with a friable moderately developed nut structure, containing some greywacke fragments. Both soil types have a pale yellow, clay loam, mottled, eluvial B horizon with a moderately developed medium nut structure (in the Korokoro soils the B horizon is deeper). Both soil types have a C horizon of weathered greywacke (Cowie, 1978).

3.2.2.4.2 Bernwood Farm

Bernwood farm, is partly bounded by Williamson Road West and Pararorangi Road East, in the Waituna West district, of the Rangitikei region (Figure 3.6). The farm is on the southeastern side of a range of hills bounding the Rangitikei river. The river is about 2 km north of the study site, at 122 m a.s.l. The study site was in the second to last paddock on the left (looking north) before a woolshed, at the end of Pararorangi road. The paddock was roughly 10 ha, located at grid reference: NZMS 1 N144: 0955-100. Altitude in the area examined ranged from about 300 to 350 m a.s.l, increasing from the south to the north end of the site. The site has received regular aerial topdressings of superphosphate and lime since at least the 1970's (T. Clare, pers.com.).

Little information is available about the soils at this site. The local geology appears to be a heavily dissected sandstone layer sitting over a band of loose greywacke conglomerate, deposited between 1 million and 500, 000 years b.p. (A Palmer, pers com.) (Figure 3.5). The site is expected to have been exposed to dustings of loess and volcanic ash, although little might now remain. The average slope is greater than 30°, so the area is classed as steepland.

Figure 3.6: Part of the second site, on Bernwood farm. Photo was taken looking approximately south, along the valley formation that contained peg sites 41 to 60 (see Figure 3.18 for site diagram).

The NZLRI (1979) map of Feilding (N 144) maps the soil type as the Halcombe hill soil (described in Rijkse, 1977 and Cowie, 1978) which is a weakly leached to moderately gleyed yellow-grey earth (Pallic soil) formed on conglomerate with intermixed loess and sandstone (Rijkse, 1977; Hewitt, 1992). A steepland soil classification is thought to be more appropriate for this site.

The property is generally south facing (away from the sun), resulting in rather wet, cold soils. Soil structure and internal drainage is generally poor throughout the landscape and the soil is prone to pugging in basins, and in the saturated lower slopes, during the winter. Slopes where the conglomerate band is exposed are very steep, up to 70°, and often contain regenerating bush, notably golden totara. Slip erosion on the slopes is extensive. There are small ephemeral streams in the valley basins, in which considerable colluvial material appears to have collected.

3.2.2.4.3 Fertiliser recommendations

Fertiliser recommendations for steepland pastures generally expect that the most limiting nutrient will be N, and that the pastures therefore should be fertilised to encourage clover growth. For dominantly greywacke steepland soils, such as found at the study sites, P, S, lime and Mo are usually recommended (Cowie, 1978; Gillingham, 1982). Recommended maintenance dressings range from 125-165 kg/ha/yr of superphosphate depending on the stocking rate, with lime if the pH is less than 5.5. During (1984) reports that adequate pasture growth has been achieved on greywacke derived steepland soils by local farmers using 125 kg/ha /yr of superphosphate, with some Mo and lime applications. During (1984) also reported the results of a 1963 fertiliser trial on a steepland Makara shallow silt loam soil, which found that white clover was highly responsive to lime and superphosphate to very high rates (lime 750 kg/ha/yr, superphosphate 1500 kg/ha/yr @ 9-10% P) but only after 2 years of application. In practise such high rates of fertiliser are unlikely to be used on steepland soils because slope instability and a high frequency of summer droughts tend to limit the production, regardless of the amount of fertiliser applied (see Chapter 2.4). Slight pasture growth responses to potassic fertilisers have apparently been recorded in a few observational trials, but During (1984) advises that K deficiency is "not regarded as being of economic significance at the present stage of development of these soils".

3.3 Survey 1

3.3.1 Introduction

This initial part of this study was carried out at one site only, paddock S10 on Tuapaka farm. The spatial variability relationships of three soil K tests were investigated in the paddock. The tests were; a standard NH_4 extraction for K and other cations (Quick test), a single acid extraction (Acid K), which had been found to be a good indicator of plant availability in a related soil group, and also, the difference between the two tests (Step K), which had been found to be a good indicator of readily plant available K that was not exchangeable with NH_4, in the same soil group (Surapaneni, 1994).

3.3.2 Methods

3.3.2.1 Sampling

On sites where spatial variability relationships are not known, Oliver and Webster (1991) recommended that a preliminary survey using sampling vectors of random direction be undertaken, covering a wide range of the relevant lags, to identify the general ranges of the nugget and sill variances (see Section 3.2.1.3).

The sampling plan in this study was a preliminary survey in the style of the Wye Forest survey (Oliver and Webster, 1986 and 1987). The survey followed a rough 50 m grid sited over the lower 2/3 of the paddock to avoid a vehicle access track and an anomalous area between two streams. Each square was sampled using a 25 m long sampling string, that had one end anchored at the centre point of the square. The string was laid out in a randomly selected direction from the anchor point (Figure 3.7). Along each sampling string samples were taken at: 0 m (centre point), 10 m, 10.25 m, 11 m, 12.5 m, and 25 m. This provided 5 sampling lags of 0.25 m, 1 m, 2.5 m, 10 m, and 25 m and placed the samples taken at short lags in the middle of the string, limiting any unintentional bias involved in choosing the anchor point of the sampling string.

An attempt was made to decrease the effect of variability at very short distances (Beckett, 1987) by bulking samples across the area that one plant might access with its roots. Therefore, each sample consisted of four soil cores (25 mm diameter by 75 mm

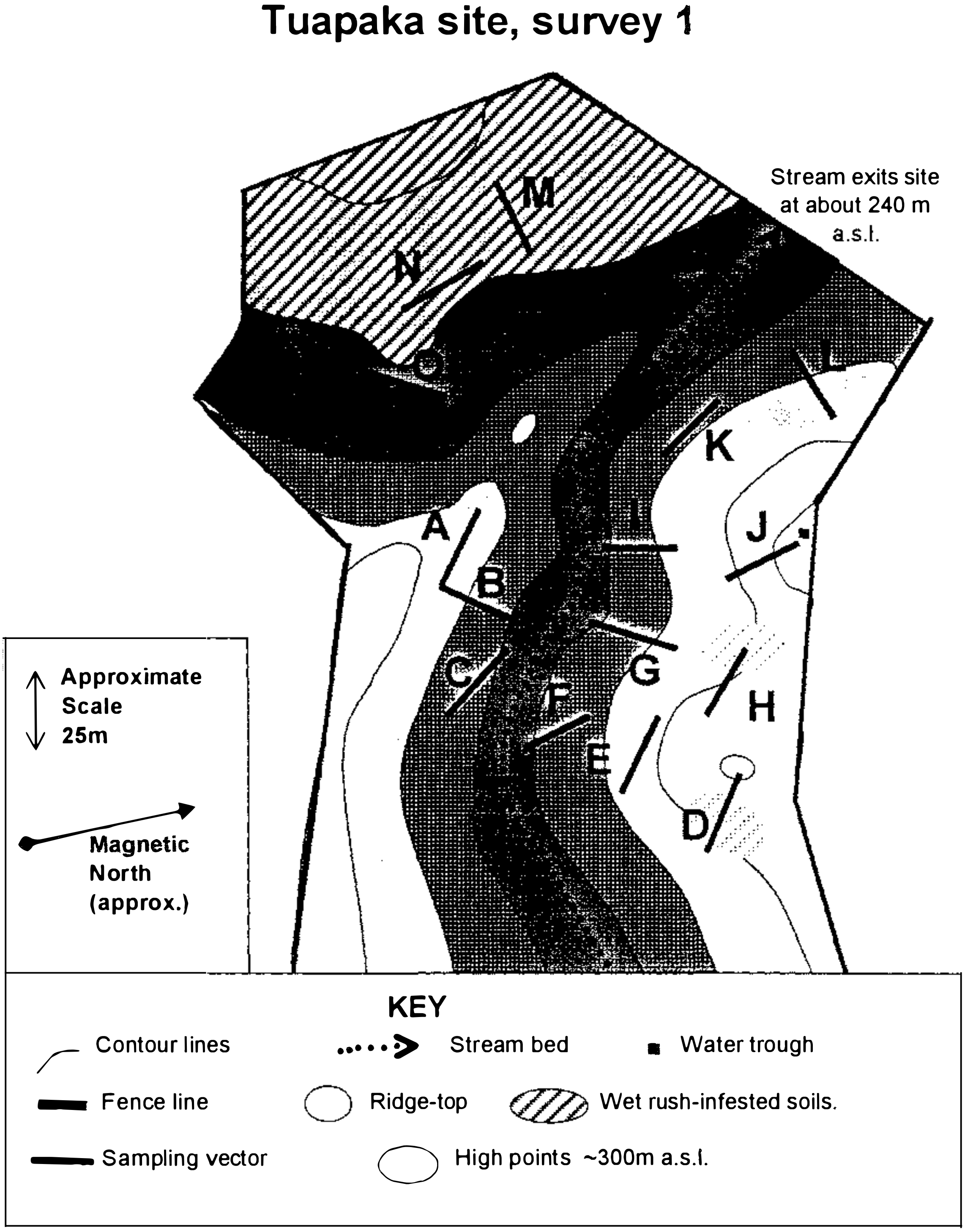


Figure 3.7: Diagram of the Tuapaka site, showing the layout of the sampling strings (vectors) for the first soil K survey (lighter shades indicate increasing altitude). Six bulked samples were taken along each 25 m vector, at 0, 10, 10.25, 11, 12.5, 15, and 25 m. Bulked samples consisted of four 75mm deep cores.

deep) collected from the centre and points of a 100 mm equilateral triangle (Figure 3.8a).

Fifteen vectors (strings) were laid out and sampled in the paddock. Vectors A, B and C were sited on a steep aspect (slopes between 30° and 46°) which was exposed to the north (sunny) (Figure 3.8b). Vectors D to L were sited on the opposite ridge, exposed to the south, with slopes ranging between 21° and 46°. Vectors M, N, and O were on the side of a third ridge, which was at a slightly lower altitude, with more moderate slopes (between 17° and 30^0) and with an easterly aspect.

The site was sampled between 20 May 1993 (early winter) and 3 June 1993. The site was under intermittent light grazing during the sampling period, so the variability of exchangeable K was expected to be at a maximum (Mountier and During, 1967).

3.3.2.2 Landscape description

To support the spatial variability study carried out on soil K, it was desirable to have an indication of the physical size of the landscape features and how rapidly they changed from one shape to another. Combining the descriptive information collected about each sample point with the spatial variability study could do this. Soil sampling was accompanied by detailed observations on the landform at each site (see Figure 3.9 for more definitions of terms). The descriptive information was broken into categories and then graphed against distance, by deciding whether or not there had been a change in each descriptive category between each pair of sampling points. In a sense, a very simplified variogram was constructed for the categories of pasture composition, small and medium scale topography, aspect, and mapped soil type.

Pasture species

Notes were made on the predominant pasture species at each sampling point. The recorded species were: clover, ryegrass, Yorkshire fog, moss, rushes, browntop, dandelion, paspalum, lichen, thistle and butter cup. The degree of utilisation, i.e. whether seed heads were present or the area had been grazed recently, and whether dung was present on the pasture, were also recorded.

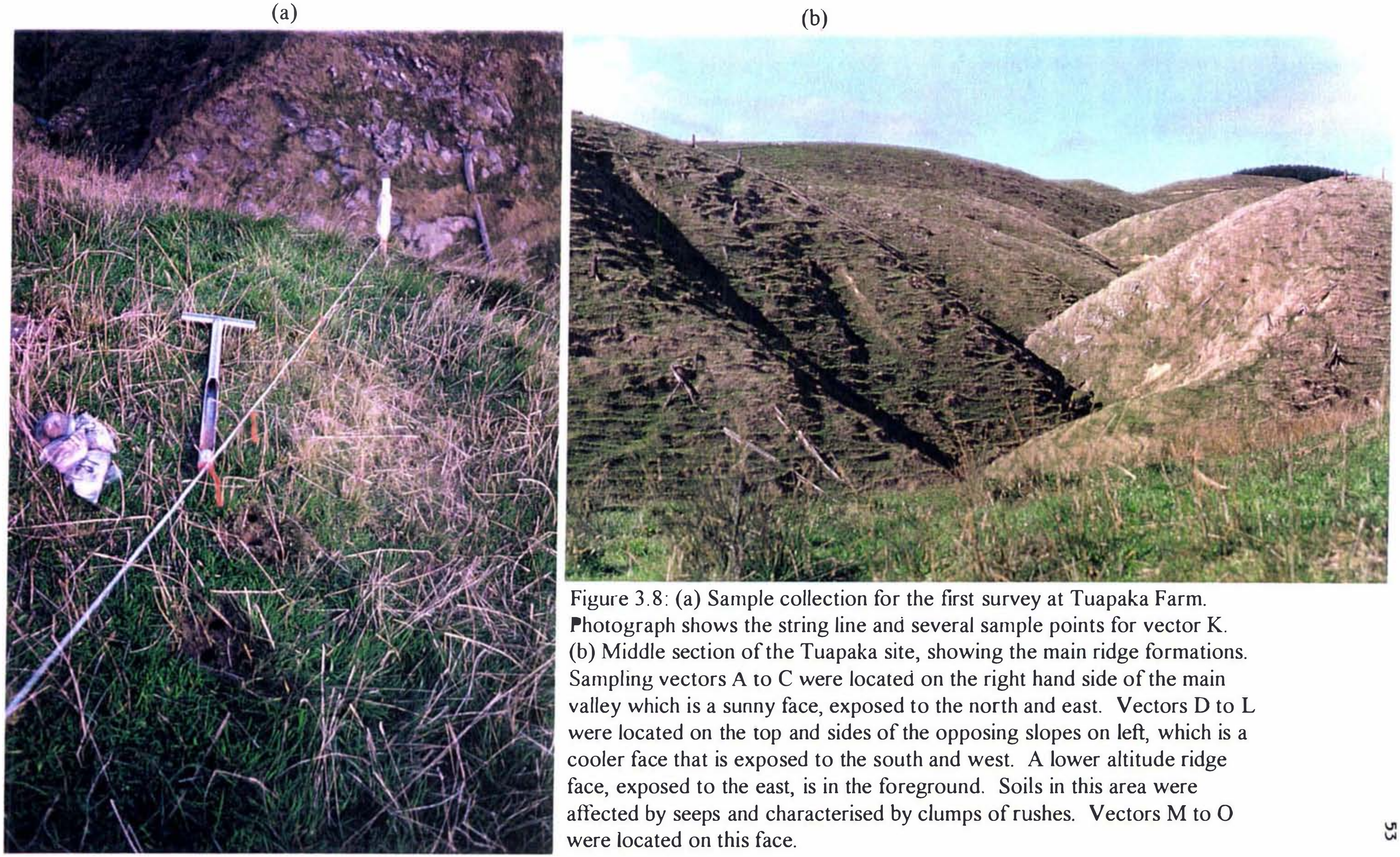
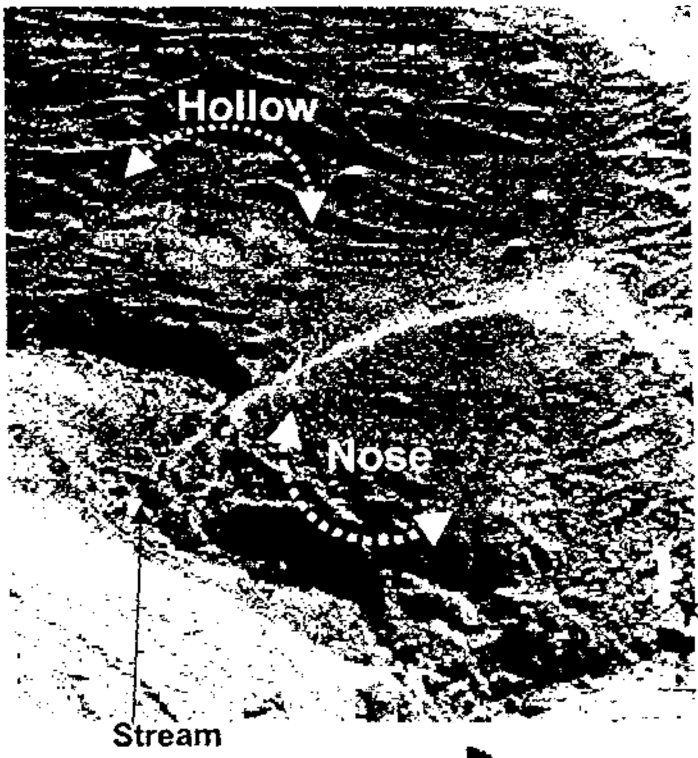


Figure 3.8: (a) Sample collection for the first survey at Tuapaka Farm. Photograph shows the string line and several sample points for vector K. (b) Middle section of the Tuapaka site, showing the main ridge formations. Sampling vectors A to C were located on the right hand side of the main valley which is a sunny face, exposed to the north and east. Vectors D to L were located on the top and sides of the opposing slopes on left, which is a cooler face that is exposed to the south and west. A lower altitude ridge face, exposed to the east, is in the foreground. Soils in this area were affected by seeps and characterised by clumps of rushes. Vectors M to O were located on this face.

Medium scale topography



Ridge and valley alternations form the large scale topographic features in a steepland landscape. Concave convex alternations at the medium scale form the typical nose and hollow topography of the side slopes of the ridges. The concave hollows are water collecting and are often the former, or present, sites of soil slipping, slumping and tunnel gully erosion events. The convex noses are water shedding and are more stable. Noses are commonly associated with the slower soil creep and sheet erosion processes.

Terracette formations

Small scale topography

Concave convex alternations continue down to the relatively small scale in steepland pasture, where soil creep and stock treading form a very uneven soil surface. The most typical small scale shapes are the step-like terracette formations, with alternating treads and risers.

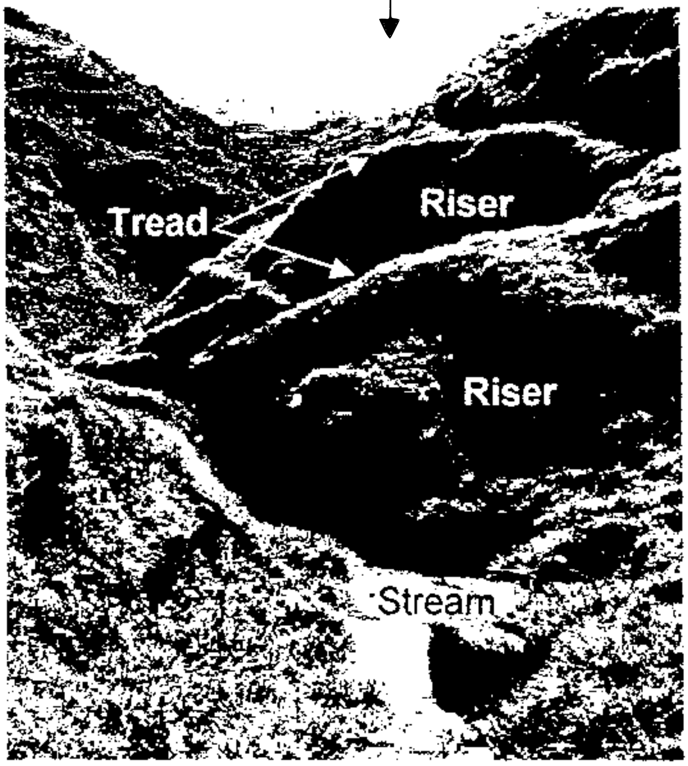


Figure 3.9. Some typical land forms found in steepland pasture, based on Tonkin (1985) and Todd (1986)(see also Figure 2.5). Upper photograph shows the stream that enters the western side of the Tuapaka site (see map Figure 3.7). The lower photograph shows a cross section of the main stream that runs the length of the Tuapaka site.

Small scale topography

The immediate shape of the topography at the sampling point, called the small-scale topography was noted e.g., if the sample was taken from the tread or riser of a terracette.

Medium scale topography

The general or standard shape of the land form that each sampling string covered was described, based on models of steepland and hill country topography (e.g. Tonkin, 1985 and Todd, 1986). These formations were termed the medium-scale topography and the main categories used were; ridge-top, shoulder, nose, hollow, and colluvial toe (see also Figure 2.5).

Aspect

The aspect of the slope was measured at the medium scale, around eight points of the compass (N, NE, E, SE, S, SW, W, NW). For example, a change along the 25 m sampling string from one side to another of a nose formation might results in a change of aspect from NW to NE at the sampling points on either end of the string.

Soil type

Samples were also located and their soil type identified according to Pollok and McLaughlin (1986).

3.3.2.3 Quick test extraction

All the soil samples were analysed using a procedure based on the New Zealand Ministry of Agriculture "Quick test" extraction (see Chapter 2.2.5). This test is expected to extract approximately 80% of the NH_4-exchangeable K that is extracted by the longer more standard analysis (Blakemore et al., 1987; Kirkman et al., 1994). In this study, two replicates of 4 g of air-dried (<2mm) soil were shaken in 20 ml of ammonium acetate (pH 7) for 2 minutes and then centrifuged for 2 minutes at 8000 rpm. The supernatant was then filtered to remove floating material, and the K content measured using emission spectrophotometry. This procedure differed from the standard technique in that the soil samples were measured by weight rather than volume.

Table 3.1: Conversions into various units for standard categories of NH_4-exchangeable K values in New Zealand soils. Based on Metson (1980), Cornforth and Sinclair (1984) and Blakemore et al. (1987).

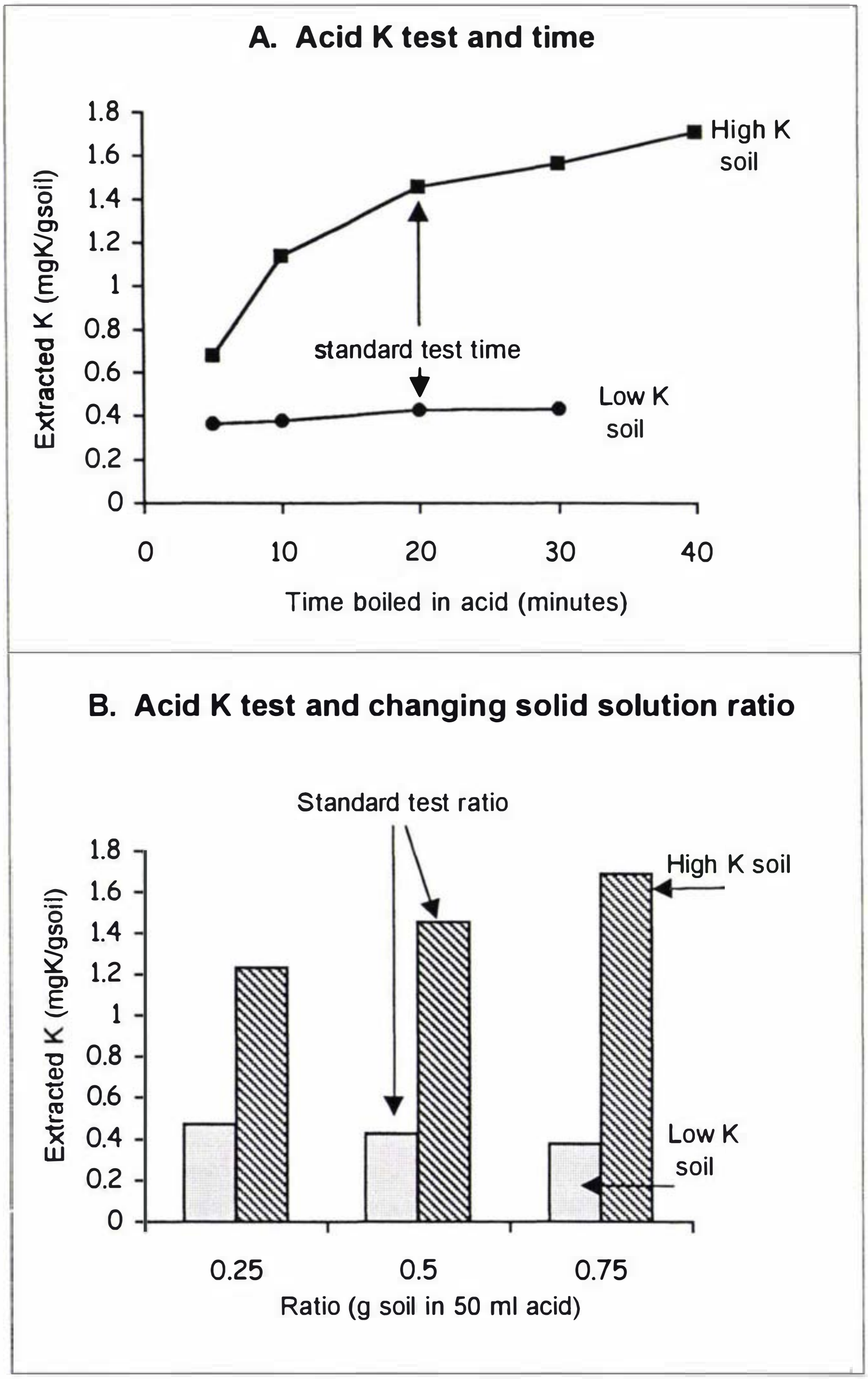
Exchangeable K Rating	cmol K /kg soil	mg K/g soil	Quick test units for K
Very high	> 1.2	> 0.47	>24
High	0.8 - 1.2	0.31 - 0.47	16 – 24
Medium	0.5 - 0.8	0.19 - 0.31	10 – 16
Low	0.3 - 0.5	0.12 - 0.19	6 – 10
Very low	< 0.3	0.12	< 6

In general, New Zealand soils with a medium, or greater, exchangeable K rating (Table 3.1) are expected to supply adequate K for pasture growth, although a disproportionately low NH_4-exchangeable K value is a long recognised characteristic of soils that have developed in sedimentary parent materials. The current standard recommendations indicate that no shortage of K supply to plants is expected in "sedimentary" soils if the Quick test K value is 6 or more, although it is generally recommended that nonexchangeable K be tested as well (Metson, 1980; Williams et al., 1986; Morton et al., 1996).

3.3.2.4 Acid K extraction

A single strong-acid extraction was carried out on all samples. For each soil sample, two replicates of 0.5 g of air dried (<2mm) soil were boiled in 50 ml of 90ml/l HNO_3 solution for 20 minutes. The liquid was filtered and diluted to 100 ml, and the K content measured using atomic emission spectrophotometry. The technique was found to be reasonably stable for typical soils in this study, in terms of variations in time, or solid:solution ratio (Figure 3.10). Haylock (1956b), using similar methods, tested a typical selection of New Zealand topsoils for sensitivity to time, acid strength and solid:solution variations, and also found the method to be reasonably stable under the above conditions.

The above method has been previously found to provide good measure of the plant available K pool in Pallic Soils, extracting both the exchangeable and plant available


A. Acid K test and time

B. Acid K test and changing solid solution ratio

Figure 3.10: Stability with variations in time and solid solution ratio of the strong acid extraction procedure used in this study. Different times and solid solution ratios are compared using two different soils, of either relativity high or low K status.

nonexchangeable K fractions (Surapaneni, 1994). A similar test of acid extractable K has been developed for large scale testing, using 2g soil and 50ml 1M nitric acid which is autoclaved for 30-35 minutes at 120°C (Carey and Metherell, 1997). Like the NH_4-exchangeable test, nitric acid extractions for K have a long history in soil testing (e.g. Bray and DeTurk, 1938) and many variations of the technique have been reported. They have been developed as alternatives to the NH_4-exchangeable test, as tests of the non-NH_4-exchangeable fraction and as tests of the long term reserves of K in the soil (Metson, 1980; Kirkman et al., 1994).

3.3.2.5 Step K extraction

The Step K value was calculated as the difference between the amount of K extracted by the Acid K test and the amount extracted by the Quick test. This particular Step K technique had been found to estimate the readily plant available nonexchangeable K in Pallic Soils (Surapaneni, 1994). This test is a very simplified variation of the Step K extraction that was developed by Haylock (1956b), which consisted of an initial extraction of the soil in N/10 HNO_3 to remove the exchangeable K fraction, followed by five digestions of the same soil sample in boiling N HNO_3 at a 1g:100 ml ratio for 15 minutes. An average of the three final extractions provided an estimate of "constant rate K", very similar to Kc (see Chapter 4.2.1.2). The constant rate K was then subtracted from the total amount of K extracted to provide an estimate of "Step" K, the more readily plant available nonexchangeable K fraction. Haylock (1956a) found that pot trials on a selection of New Zealand soils indicated that soils with a Step K of less than 0.3 K cmol K/kg (0.12 mg K/g soil) could become deficient in K, while soils with Step K of more than 0.5 cmol K/kg (0.2 mg K/g soil) were unlikely to become deficient. Most of the Step K was removed in the first hot acid extraction, and over time the test has been abbreviated to a single boiling acid extraction, less the separately determined NH_4-exchangeable K (Surapaneni, 1994).

3.3.3 Results and discussion

3.3.3.1 Soil type

Soil profiles were examined throughout the paddock and were found to be quite similar in terms of the soil texture, colour and development. The main variable was the soil depth. The soil profiles at the site corresponded well to the published profiles. It has already been noted that the reference profiles of the two soil types previously mapped at this site were similar (the Korokoro soil complex and the Makara steepland soil, see Section 3.2.2.4). A typical soil profile at the site had a 10 cm deep silt loam A horizon. The B horizon was generally rich in clay and contained well-weathered greywacke fragments. Increasing slope generally corresponded to a decreasing profile depth and to the increasing intrusion of weathered greywacke gravels into the B horizon, until, on some steep slopes, the B horizon was more of a gravelly AR horizon, with clay skins on the greywacke fragments.

3.3.3.2 Landscape scale.

Observations of the pasture composition, small and medium-scale topography, aspect, and mapped soil type were made at each sampling point (see Section 3.3.2.2). Combining the observations with the spatial variability study allowed rough estimates to be made of the rates of change within a category, as the distance between two points of comparison increased from 0.25 m to 25 m. Only 15 pairs of points were compared at each distance (lag), so, like the variograms of the soil extraction (Section 3.3.3.4), this was only a preliminary survey to establish the approximate scales.

Changes at 0.25 m sampling distance

At the smallest sampling distance, of 0.25 m, no changes occurred in any of the descriptive categories (Figure 3.11).

Changes at 1 m sampling distance

A comparison of the landscape, between two points 1 m apart, found that the only change recorded was in the small-scale topography (see Section 3.3.2.2 for terms). About half (43%) of the sampling sites were now positioned on a different small-scale topographical formation. This reflected the observation that 1 m was sufficient distance for most samples situated among the terracettes formations to have changed from one terracette (step and riser) to another terracette.

Changes at 2.5 m sampling distance

A comparison of the landscape, between two points 2.5 m apart, found that the small-scale topography and the pasture categories were now both changing with distance. The rate of change in small-scale topography had only increased slightly from the rate

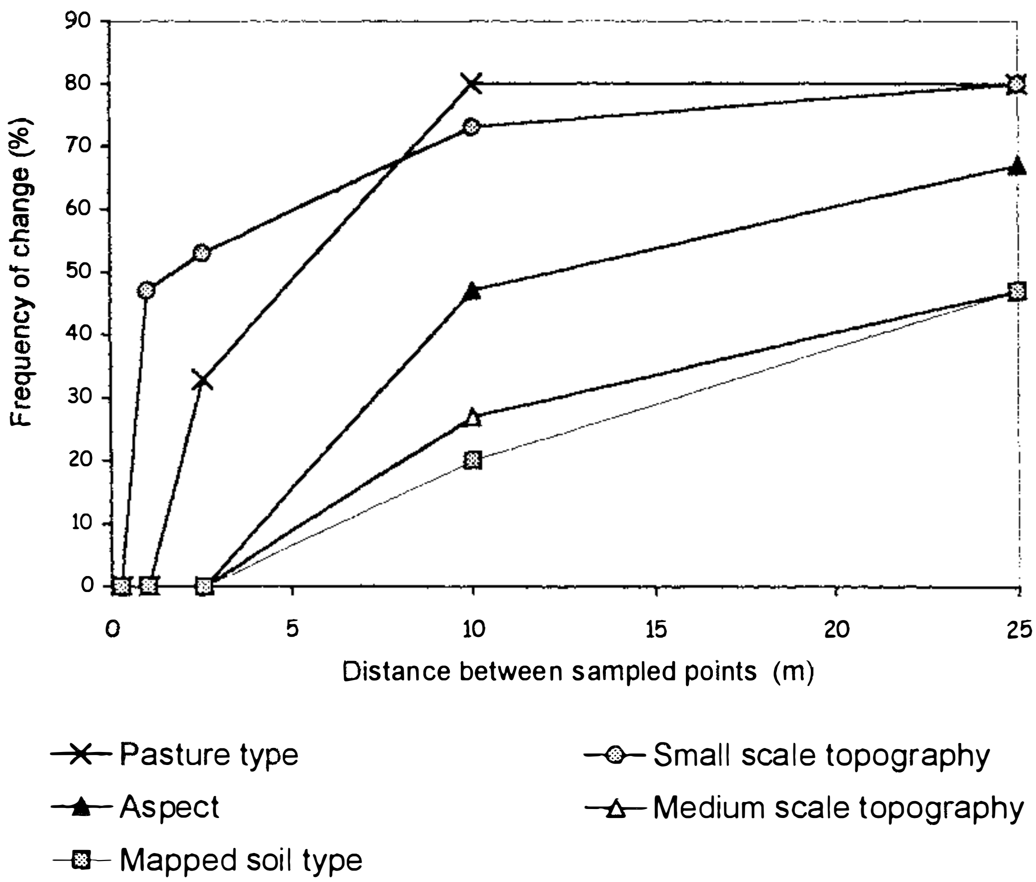


Figure 3.11: Estimation of the rate of change in terrain factors in a steepland pasture. Frequency of change denotes the percentage of times there was a change of category in the property between sampling points. Pasture type indicates change in the dominant species. Aspect indicates a change in aspct at the medium scale, around the main compass points. Mapped soil type was based on Pollok and McLaughlin (1986).

of change found at 1 m. This probably indicated the difference between sampling strings located on the creep slopes (dominated by terracette formations), and the sampling strings located on the remainder of the site, which were on smoother small-scale topography and were not changing much, yet. At 2.5 m apart about 30% of the paired sample sites also had a different pasture composition at each point. For instance, there may have been a change from clover- to Yorkshire fog- dominated pasture. There still was no change in any of the other descriptive categories.

Changes at 10 m sampling distance

At a distance apart of 10 m, all the descriptive categories had at least some degree of change (Figure 3.11). Most of the sample pairs had changed to a different pasture composition. 75% of the pairs changed at 10 m to a different small-scale topographic category, suggesting that this distance encompassed the size of most of the small-scale topography throughout the landscape. A 10 m distance was also sufficient for a change in aspect, in about 50% of the pairs (e.g. from south to southeast). About 25% of the pairs changed from one medium-scale topographic formation to another (e.g. from a shoulder to a ridge-top) and about 20% to another mapped soil type. The method of measuring the aspect in this part of the study was based on the medium-scale topography (e.g. moving around the contour on a nose formation might entail a change from a south east to a south west aspect) so aspect was expected to change more rapidly than the medium-scale landforms, as occurred in this study.

Changes at 25 m sampling distance

The frequency of change information at 25 m sampling distance compared the descriptions made of the sample site located at each end of the sampling string. At 25 m apart, the soil type and medium-scale topography had changed in about half of the sample pairs. At this distance apart, the rates of change of the pasture and the small-scale topography were similar to the rates of change recorded at 10 m. About 75% of the compared points changed aspect from one end of the sample string to the other.

Summary

In summary, pasture composition, small and medium-scale topography, aspect, and mapped soil type were unchanging when compared 0.25 m apart. A size range of less than 1 m and up to 10 m was indicated for the small-scale topography, with a distinct break between the rapidly changing creep slope topography and the rest of the landscape. There was also an 80% chance that sampling sites 10 m apart would have a different pasture composition. The extent of change in the medium-scale topography was low at 10 m spacing and about 50% at the maximum sampling distance of 25m, suggesting a size of at least 25 m across for the medium-scale landscape features. Pasture composition might have been expected to be related to the water relationships of the medium scale aspect and topography (see Chapter 2.4) but appeared to have more of a relationship to the changes in small-scale topography. The implication is that soil moisture and soil depth are changing sufficiently at the smaller scale to significantly affect the survival of different pasture species.

3.3.3.3 Soil test distributions

The raw data from the Quick test K, Acid K and Step K extractions (90 samples from one steepland site) were sorted into divisions of 0.1 mg K/g soil and plotted as frequency distributions (Figure 3.12). The standard comparison is with a Normal distribution (described in Section 3.2.1.1). The frequency distributions of all three extractions were skewed (asymmetrical), with the bulk of the data values lower than the mean and with long tails of much higher values.

The distribution of the results of the Quick test had the largest skew and the largest kurtosis (or, peakedness) (Table 3.2) (Figure 3.12a). The frequency distribution of the Acid K test had a more moderate skew and kurtosis and was quite uneven (Figure 3.12b). The frequency distribution of Step K test (Acid K – Quick test K) had the least skew and kurtosis and would probably be classed as multimodal (Figure 3.12c).

Beckett (1987) observed that soil K distributions could have many forms, and were frequently skewed. Quick test K is expected to be influenced by urine deposition, which is expected to have a skewed distribution, reflecting the uneven distribution of urine within a paddock (Haynes and Williams, 1993). A marked skew, as in this case, is expected to result from the continual animal transfer of dung and urine to the same points in the landscape (Petersen et al., 1956a&b).

Table 3.2: Parameters of the untransformed frequency distributions of Quick test K, Acid K and Step K, from the first survey at the Tuapaka site. In a Normal distribution mean = median, and skew and kurtosis = 0.

	Quick test K	**Acid K test**	**Step K test**
Mean (mgK/gsoil)	0.238	0.805	0.566
Standard Deviation	0.200	0.41	0.31
C.V.	84%	51%	55%
Median (mgK/gsoil)	0.171	0.696	0.509
Range (mgK/gsoil)	0.07 - 1.34	0.12 - 2.43	0.05 - 1.70
Skew (3^{rd} moment)	2.8	1.36	1.1
Kurtosis (4^{th} moment)	10.4	2.48	1.7
Optimum power transformation^2	-0.5	-0.2	0.2

Many statistical analysis techniques require that the data set has a Normal frequency distribution (Figure 3.1). Normalising the Quick test K, Acid K and Step K distributions was found to be difficult. The optimum power transformations (y^x, where y was each value) were calculated to normalise each extraction (Table 3.2) but even

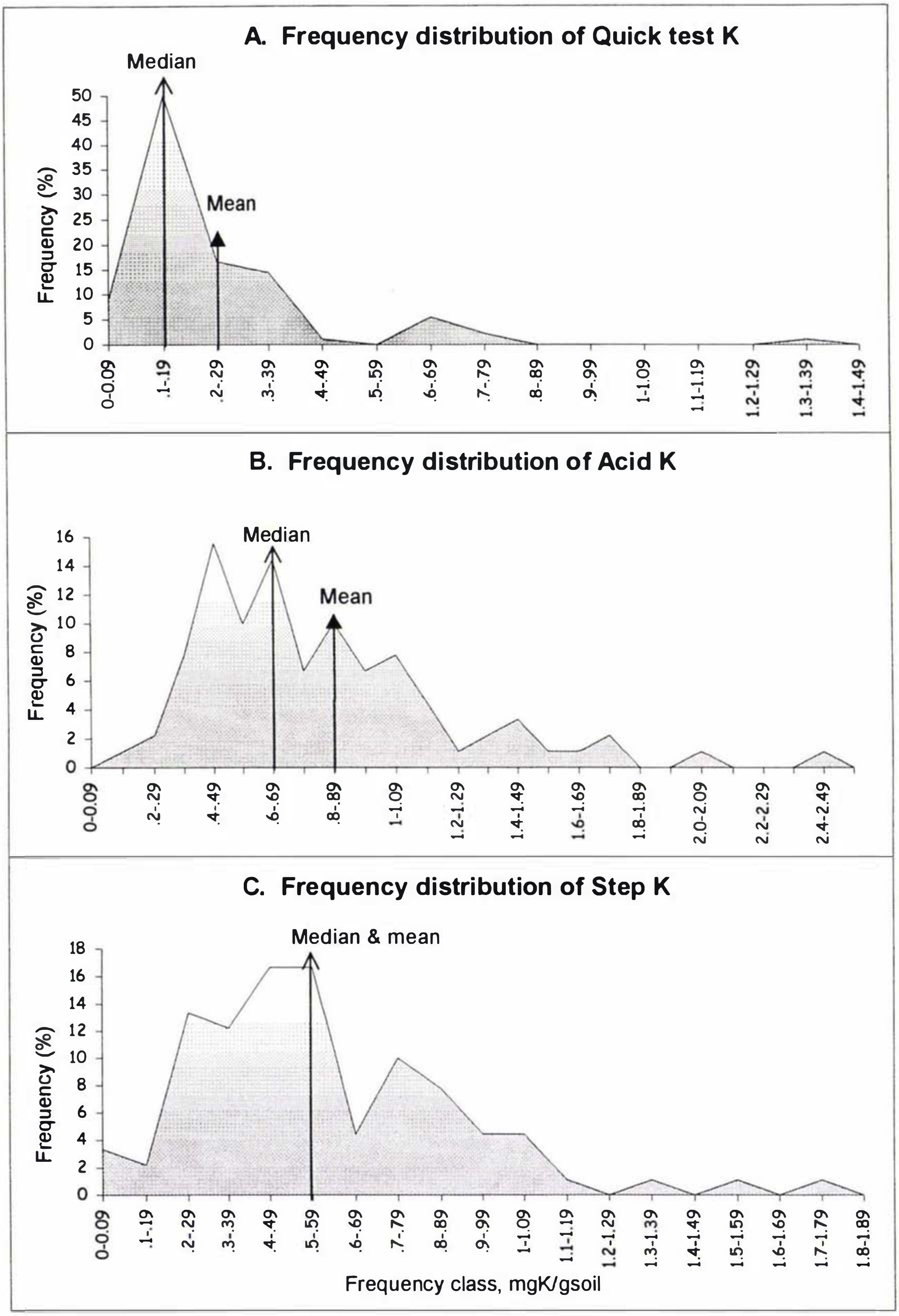


Figure 3.12: Frequency distribution of soil K extractions, from 90 samples collected from the random sampling of one steepland pasture at the Tuapaka site only. The median (50% quartile) and the arithmetic mean are indicated by arrows to illustrate the skew of the distribution.

these transformations still left some skew and kurtosis in the data set, and analysis of the residuals showed that the data set still was not well mixed and had many outliers.[2] Often simply log transforming the data gave the same statistical outcomes, so this transformation was generally preferred, to ease the interpretation of the results of the statistical tests.

The range of Quick test K values found within a paddock in this study, was wider than the range of exchangeable K values found in a survey of the spatial variability of the New Zealand Westmere silt loam (Adams and Wilde, 1976). The range was also wider than the range in NH_4-exchangeable K values found in a survey of the New Zealand central yellow-brown earth soil group (now Brown soils, Hewitt, 1992), of which this site is a steepland associate. Metson (1980) determined that the NH_4-exchangeable K of reference central yellow-brown earth soils ranged from ~0.1 to ~1.5 cmol K/kg soil, which was very low to very high, compared to other New Zealand soils. The lower range of values in this study was similar, but the upper range was more than twice the range found by Metson. Metson apparently used standard Soil Bureau soil samples that were collected from reference sites, so many of the soils would not have been obtained from grazed pastures. The present site was an established grazed pasture, so the wider range of values probably reflected the increase in variability that has previously been found for exchangeable K in grazed pasture soils, compared to ungrazed pasture (During and Mountier, 1967).

The standard deviation and coefficient of variation (c.v.) was calculated for each test. The validity of these parameters is doubtful if the frequency distribution is not symmetrical, especially when the distributions are strongly skewed. However, very little other information for the comparison of the variability of exchangeable K is available.

Beckett and Webster (1971) found that the coefficient of variation (c.v.) of many different studies of the spatial variability of plant available K ranged from 21-142%, with a median of about 70%. At 84%, the c.v. of Quick test K in this study (Table 3.2) was similar to the other studies. Therefore, although the range from the highest to lowest value appeared to be quite wide in this study, the results were probably typical

---

[2] based on a SAS programme (Ganesh, 1994)

for NH_4-exchangeable K in general. No similar information was available for the acid extractions.

The variability of the Acid K and Step K results may also have increased under grazing. The same test techniques were used by Surapaneni (1994) on a range of ungrazed yellow-grey earth (micaceous loess) soils. The range of values found in this study, in one paddock of yellow-brown earth soil (old N.Z. classification), appeared to range considerably lower and considerably higher than results of Surapaneni (1994), for both of the Step K and Acid K tests. The ratio of Quick test K to Step K extracted from each soil sample ranged between approximately 0.1 and 4.4.

If finding the mean is similar to bulking all samples across the paddock, the Quick test mean (0.238 mg K /g soil) put the paddock in the medium, non-responsive category. When considering the results individually, 25% of the values were in the very low category, indicating a possible response to fertiliser in at least some areas of the paddock.

Step K is expected to be an indicator of the plant available nonexchangeable K reserves. If the responsiveness threshold of 0.12 mg K/g soil is applied (Haylock 1956a) then only four samples, all associated with a wet soil variant, would indicate a shortage of nonexchangeable K for plant growth.

3.3.3.4 Correlations

There was no significant correlation between the Step K and Quick test values (r=0.27), indicating that the practise of making an acid extraction and subtracting the independently determined amount of Quick test K had successfully separated two different soil fractions (Figure 3.13a). There was very strong linear relationship between Acid K and Step K value (r=0.88) and there was some linear association between Acid K and Quick test K value (r=0.69), which was still significant after transformation, indicating the common extraction fractions within the Acid K test (Figure 3.13b).

The correlation test is susceptible to outliers, such as the very high values that were found in for the soil tests, so the correlations were also run using transformed data

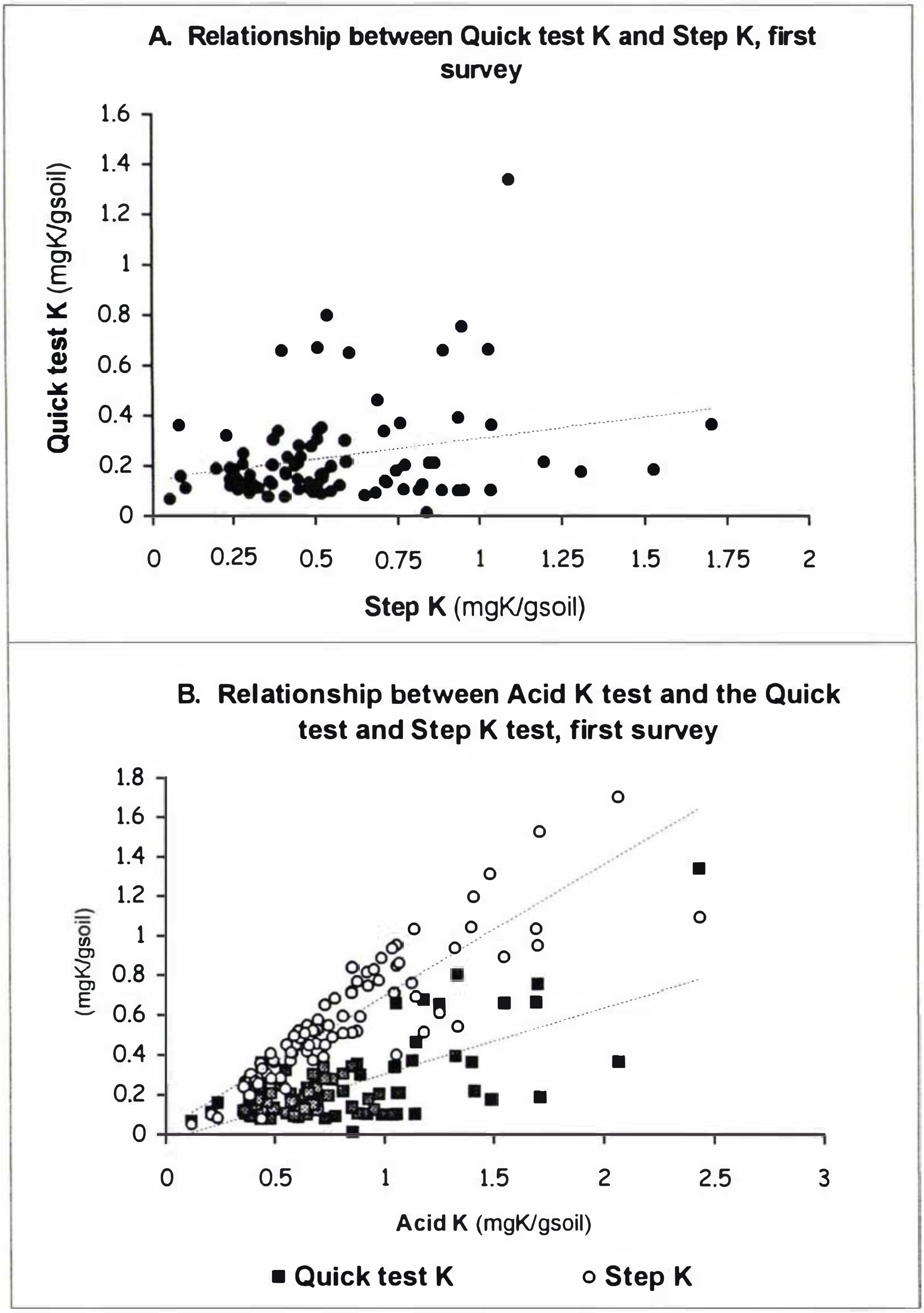


Figure 3.13: Comparison of extent of linear association (correlation) between different extractions of soil K, in randomly sampled steepland pasture (first survey). Relationship between Step K and Quick test K values of the same sample (A). Relationship between Acid K, and the Step K and Quick test K values of the same sample (B). Linear association is indicated by the dashed trend line. Linear fit (correlation) is listed in Table 4, in Appendix 1.

(Appendix 1, Table 4). Similar results were obtained on transformed and untransformed data, indicating that the significant correlations were a real trend.

3.3.3.5 Variograms

Variograms were constructed from the soil test values, to investigate whether any distance dependent variability could be identified between the 0.25 m and 25 m sampling distances for Quick test K, Acid K and Step K (see Section 3.2.1.1 for theory). The theory requires a Normal data distribution, so the calculations were made using log (ln) transformations of the results. The large standard deviations meant that no significant distance dependent spatial variability effects were identified (Figure 3.14). A decrease in the standard deviation for all three tests, at 0.25 m and 1 m sampling distances, may have been an artefact of the sampling technique, which bulked samples up to a 0.1 m lag.

The topography survey (Section 3.3.3.2) found that the landscape was changing very little at 0.25 m distance between points. At larger distances, the small-scale topography and pasture composition were likely to have changed completely at a distance of 10 m and the medium-scale topography, aspect and soil type were liable to be changing at least some of the time at 25 m. It seems that the spatial variability of the soil K tests was not affected by any of the small and medium scale landscape trends, and that all of the K variability was already present at sampling distances of 0.25 m. This is a relatively small scale, but does coincide with the approximate size of a urine patch, which is expected to have a strong influence on the spatial variability of soil K under pasture (Roberts, 1987; Haynes and Williams, 1993). The very high short-range variability indicated that the mapping of K fertility trends at the paddock scale, using regional variable theory, would not be feasible. Alternative methods of dealing with the data were therefore explored.

3.3.3.6 Correspondence analysis

Because no significant distance dependence was found between 0.25 m and 25 m, each of the six samples taken along a sampling vector (25 m) could be regarded as independent representatives of the soil covered by each sampling string. All six samples from each sampling vector could therefore be compared with each group of six samples from the other vectors.

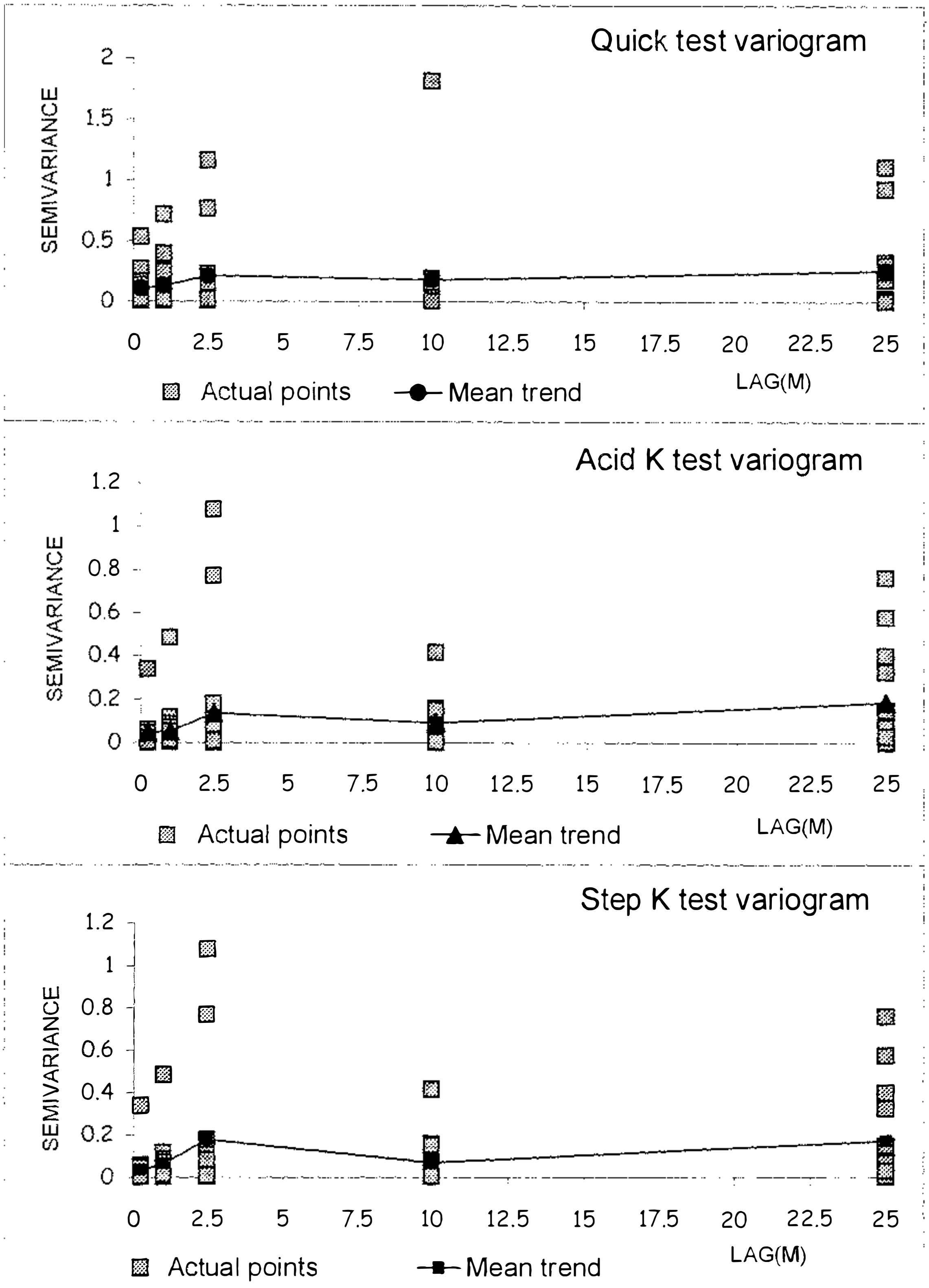


Figure 3.14: Variograms of the log transformed soil K tests of the first survey (solid lines). Actual values at each lag (sampling distance) are included, to show the high variability and hence no significant trends that could be modelled in these results. The increasing variability between 0.25 m and 2.5 m sampling distance (lag) may be an artifact of the short range bulking of the soil samples.

The most suitable method of comparing the vectors was thought to be correspondence analysis (theory and interpretation of the results of this method are explained in Section 3.2.1.2.). This method was particularly useful to examine the information from the soil K extractions, because there is no assumption of a Normal distribution and therefore there was no problem of interpreting a transformed data set.

3.3.3.6.1 Correspondence analysis of the Quick test K data

The results of the Quick test extraction of NH_4-exchangeable K were cross-tabulated using vector as the row variable and the amount of K extracted as the column variable (Appendix 1, Table 1). A plot of the correspondence analysis (Figure 3.15a) formed strong contrasts (or groupings) and accounted for 80% of the total variability (dimension 1 variability plus dimension 2 variability in Figure 3.15a).

The information in the graph could be characterised as one large grouping of vectors that represented the average situation, associated with frequency classes ranging from 0 to 0.39 mg K/g soil (Appendix 1, Table 1). This main group was strongly contrasted with a small group of two vectors (J and E), which were associated with some very high extraction values (0.4-0.79 mg K/g soil). Not all the values from vectors J and E were actually between 0.4-0.79 mg K/g soil. The remainder of the values were in the 0 to 0.4 average range.

Vector D did not fit the general pattern of these two groups. In the plot, vector D is represented as sitting to the side of the main group, close to the highest extraction category (1.2-1.39 mg K/g soil). Five values from this vector were in the main frequency group, except for one value that was extremely high (1.34 mg K/g soil).

All the very high values in vectors J, E and D were associated with relatively well drained soils. The presence of dung patches indicated that the vector sites were popular places for animals to congregate. Vector J was sited on a ridge-top close to a water trough (Figure 3.7). Vector E was sited on a relatively sheltered shoulder formation. The extremely high value from vector D was from a soil on top of a small hillock, while the rest of vector D was on a rather swampy shoulder slope. Stock were frequently observed in all three areas associated with the high values. Other flatter areas of the paddock, such as the areas associated with vector H and the remainder of vector D,

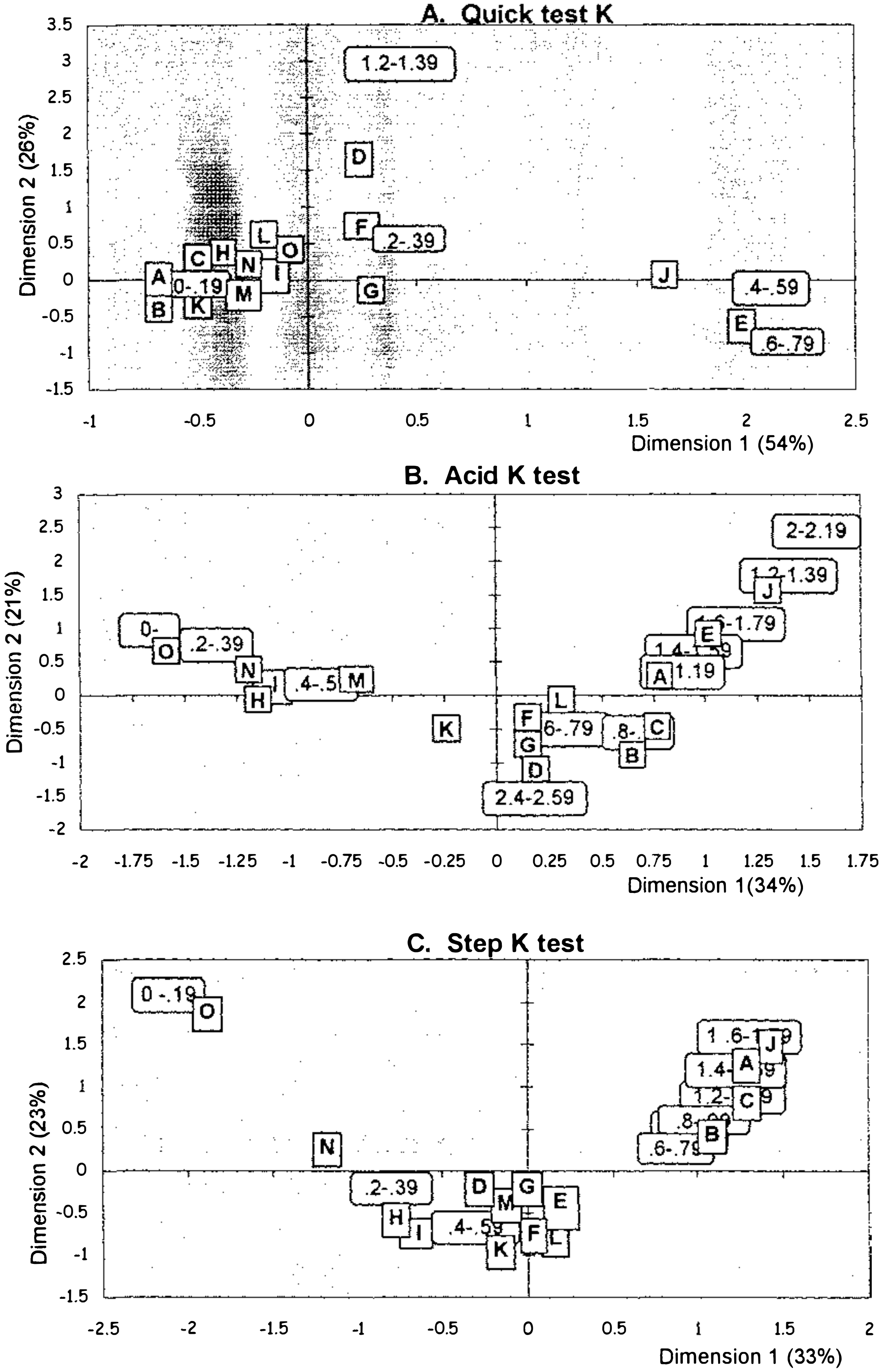


Figure 3.15: Correspondence analysis of results of a survey of three soil K tests in one steepland pasture. 15 vectors (**A** to **O** in each diagram), consisting of six samples each, were sampled in different locations in one paddock. The results found at each vector location were split into categories of 0.2 mg K/ g soil, and sorted into characteristic groupings by the analysis. (For an in-depth explanation of the technique see Section 3.2.1.2.)

were also frequented by stock, but were on wetter soils characterised by surface pugging and rushes.

The differentiation between vectors D, E and J and the main group did not correspond to changes in the mapped soil type, as both groups represented a mixture of the two soil types mapped at this site.

The Quick test K patterns appeared to rather reflect the effect that urine deposition had had on the K chemistry of either a well or a poorly drained soil. In hilly country the grazing stock tend to congregate on the flatter areas and over half the total dung and urine excreted may be concentrated in only 15-30 % of the area (Haynes and Williams, 1993). The effect of urine on soil K may persist for one to two years, particularly on the well drained areas, where a lower soil moisture will slow the breakdown of urine and the subsequent dispersal of urine K in the soil (Carran, 1988; Morton and Baird, 1990). On the well-drained areas where animals congregate, a very high proportion of the soil is expected to be affected by urine patches that have been deposited over the last one or two years. A proportion of the soil will also have been affected more than once during this time (Richards and Wolton, 1976).

In this study, the overlapping of the urine patches in time appears to have caused Quick test K to sometimes increase to extremely high levels in the soils on the well-drained shoulder slopes and ridge-tops. On the poorly drained flatter areas, Quick test K did not increase to the same extent, indicating that urine K was less persistent in the wetter soils (Figure 3.16). Similarly, on the steeper slopes, no extremely high values were obtained. The effective stocking rate will be very low on the steeper slopes and the overlap of excretal deposition is expected to be negligible in these areas (Peterson et al., 1956a). The range of Quick test K values in the soils of the steep slopes, which was still considerable, presumably included soil that had no effect of urine in the profile and soil that had recently been affected by a single urine event. This apparently resulted in the observed range, of very low to high values, but not in the extremely high Quick test K values, which were, apparently, rather the result of multiple applications of urine accumulating under dry conditions.

Figure 3.16: Examples of well drained (A) and poorly drained (B) ridge-top campsites.

3.3.3.6.2 Correspondence analysis of the Acid K data

The results of the Acid K extraction were cross-tabulated using vector as the row variable and the amount of K extracted as the column variable (Appendix 1, Table 3). Then correspondence analysis was used to identify the main patterns in the table.

In the plot obtained from the correspondence analysis (Figure 3.15b) of the Acid K extraction, only 55% of the variability was accounted for, so the patterns were not well defined and some points were rather poorly represented by the graph. This was a poor result compared to the correspondence analysis of the Quick test extraction (above).

The Acid K extraction categories were fairly evenly spread out across the plot of the correspondence analysis (Figure 3.15b), generally progressing from low to high values when moving from left to right across the plot. The vector categories were also fairly evenly spread from left to right. Generally, each vector was closest to the extraction category that represented the mode of the group of six values. Both the vectors that were associated with high values in the Quick test K correspondence analysis (J and E) were also associated with high values in the correspondence analysis of the Acid K results. Vector D and the associated extremely high value category, which was unique in the Quick test correspondence analysis, also broke the trends in this plot, indicating once again that most of the values from sampling vector D were average, except for one very high value. The Acid K extraction values appear to be reflecting quite a lot of the information which was obtained from both the Quick test K extraction and also the Step K extraction (next section), as was also indicated by the correlation analysis (Section 3.3.3.4).

3.3.3.6.3 Correspondence analysis of the Step K data

The Step K results (Acid K minus Quick test K) were cross-tabulated using vector as the row variable and Step K class as the column variable (Appendix 1, Table 2). Then correspondence analysis was used to identify the main patterns in the table.

A correspondence analysis of the Step K results (Figure 3.15c) found three distinct groupings, although only 56% of the total variability was accounted for, so not all points were well represented by the graph. A majority group of 10 vectors (that represented the average situation) was associated with the extract categories of 0.2-0.39 and 0.4-0.59 mg K/g soil. The actual values for these vectors were spread out beyond these categories, so the association only represented four or five of the six values in each vector set (Appendix 1, Table 2). The second grouping consisted of vector O which was associated with the lowest extraction category. The third grouping consisted of vectors A, B, C, and J in a strong association with Step K results categories of more than 0.6 mg K/g soil.

The plot indicated some distinctive associations between paddock location and Step K extraction value. Vectors A, B, and C (Figure 3.7) were all located on the same northeasterly side of a ridge. Most of the soil samples collected from this area had relatively high Step K values. This appeared to be a large-scale effect of aspect, over the whole of the approximately 60 m slope of the ridge face. The soils on a slope of northerly aspect like this one are expected to be warmer and drier and therefore perhaps less weathered, because they are less leached (see also Chapter 2.4). Step K, as a measure of plant available nonexchangeable K, was expected to be higher on less weathered soils with larger mineral reserves of K (explored further in Chapter 4).

Some very low Step K values were associated with vector O, which was sited on a toe slope beside a stream and on the lower slopes of an area of relatively wet Korokoro variant soils. Later testing (Chapter 4) revealed that the soils from beside the stream were formed in an anomalous patch of alluvial material that had low K reserves.

As was found for the correspondence analysis of the Quick test K results, there was no association between the pattern of Step K values and the mapped soil types.

Step K also appeared to be partially affected by animal camping behaviour. High Step K values were obtained for Vector J, which was also identified with some very high Quick test K values. Studies of urine addition to soils have recorded losses of urine K into the nonexchangeable soil fraction (Williams, 1988). So, Step K might be expected to rise on animal campsites, although Vectors D and E, which also had a high score in the Quick test correspondence analysis, had only average Step K values. Vector J was near a trough, so Step K may only be increasing in well drained areas associated with particularly heavy dung and urine deposition. These associations are explored further in the second survey (Section 3.4).

3.3.4 Summary of the first survey

A steepland pasture developed in mainly sedimentary soil parent materials was investigated because K fertilisers are not considered necessary on these soils, although research has indicated a potential for depletion of the soil K in hilly country (Gillingham, 1978), and some responses to K fertiliser have recently been recorded in similar steepland pastures (Ledgard et al., 1997). Three soil tests were investigated. The first test was a standard two minute NH_4-extraction (Quick test), which appears to have been mainly developed for volcanic soils, and is generally regarded as an unreliable indicator of fertiliser responsiveness on micaceous soils. The second test was a single acid extraction (Acid K), which was previously found to be a good indicator of plant availability in a similar soil group. The difference between the two tests (Step K) was the third test, which had been found to be a good indicator of plant available nonexchangeable K in a similar soil group (Surapaneni, 1994).

In this study, soil samples were taken from one paddock that had been under pasture for many years, and was under light grazing at the time of sampling. Maximum variability was expected under these conditions, and the range of NH_4-exchangeable K that Metson (1980) recorded for a related soil group was encompassed in the 90 samples drawn from the random sampling of one paddock. The results of this study were thought to be a classic example of the very high short-range variability that characterises the soil exchangeable chemistry of developed soils.

Distance dependence between the soil samples was investigated at a 0.25 m to 25 m scale. The variability of the soil K tests was very high, even at the smallest sampling distance. Some large but rather erratic increases in soil K fertility were observed at specific ridge-top locations within the paddock. Quick test K and Step K values sometimes increased sharply in soils on well-drained ridge-top areas associated with animal camping. Quick test K values also sometimes increased sharply in soils on well drained shoulder slopes. In contrast, Step K values were consistently high in soils on a steep slope with a warm northeasterly exposure, where the soil parent materials were apparently less weathered. As these effects had abrupt boundaries, instead of gradual changes, and the ridge-top effects were rather inconsistent, these patterns were not picked up by the variograms (Burrough, 1993), however the use of correspondence analysis to uncover the main points of difference was successful. The Quick test K results, representing exchangeable K, and the Step K results, representing plant available nonexchangeable K, were concluded to be varying independently in this landscape. The Acid K test was a good representative of both sets of information. These effects were investigated further in the next survey (Section 3.4).

3.4 Survey 2

3.4.1 Introduction

The second survey was intended to confirm and extend the results of the first survey and was conducted at the original site, and at a new site on a different farm. The sampling layout was designed to maximise the contrast already found between the steeper slopes, and the ridge-top areas that were popular with stock and which tended to have increased levels of exchangeable and nonexchangeable K. Comparisons were also made between the spatial variability trends of the soil K tests, and plant available soil phosphate (Olsen P), soil moisture and pasture growth patterns. Previous studies have examined the process of nutrient transfer onto the ridge-tops in hilly country, but have not examined the effect of this process on the spatial variability of soil fertility.

3.4.2 Methods and materials

3.4.2.1 Sites

Comparisons were made between two established steepland pasture sites. The first site was the same paddock that was previously surveyed (Section 3.3), on Tuapaka farm, in the Tararua ranges. The second site was a steepland paddock on Bernwood farm, in the Waituna West area of the Southern Rangitikei. Some growth problems were previously experienced at this site, which may indicate that a K deficiency is developing on the slopes (G. Smith, pers. com.) (more information about the region and the sites is available in Section 3.2.2).

3.4.2.2 Methods

The second survey was designed to compare and contrast ridge-top campsite soils with the soils on a transect of the adjacent slope. The survey mostly targeted relatively well drained campsites areas, as the wetter areas were previously found to have a K fertility chemistry that was similar to the soil on the slopes. In this survey permanent sampling sites were pegged out at a regular distance of 10 m apart, in transect lines that were generally perpendicular to the main line of the ridge. When the sample line reached the summit of a ridge, or a fenced shoulder, an extra two samples were taken 10 m on either side of the line, along the main line of the ridge (see site diagrams Figures 3.17 and 3.18). About 30 sample points were pegged at each site.

Slope was measured by inclinometer, by sighting from peg to peg using the horizontal as zero. The measurements were so averaged over 10 m, and were not sensitive to shorter range changes like terracette effects.

Aspect was measured by taking a compass reading while standing on the peg line on the slopes, and looking away from the slope.

A secondary purpose of this survey was to identify a subset of possible sites for a future fertiliser trial. To assist in this process, a 0.1 m^2 sampling square was placed alongside each peg and a cut of the pasture regrowth within the square was taken, by trimming with shears to the base of the leaf blades. After about six weeks the regrowth in each clipped area was then assessed, by retrimming the pasture from each square, the paddocks having been essentially ungrazed in the interim. This superficial assessment of pasture growth rates was later used (Chapter 5) to reduce the variability in sites selected to assess the degree of response to K fertiliser addition. However, the data, once available, was also used in the survey reported here.

Soils were sampled after the first pasture cut. Each sample consisted of four samples taken about 100 mm apart within the square used for the pasture cuts (Figure 3.19). The soil samples were 75 mm deep and 25 mm wide cylindrical cores.

Pasture was trimmed and soil samples were collected from the Tuapaka farm site between 23 March 1995 and 31 March 1995 (late summer). The second pasture cut was made on the 9 and 10 May (autumn).

Pasture was trimmed and soil samples were collected from the Bernwood from 4 April to 12 April 1995. The second pasture cut was made on 30 to 31 May.

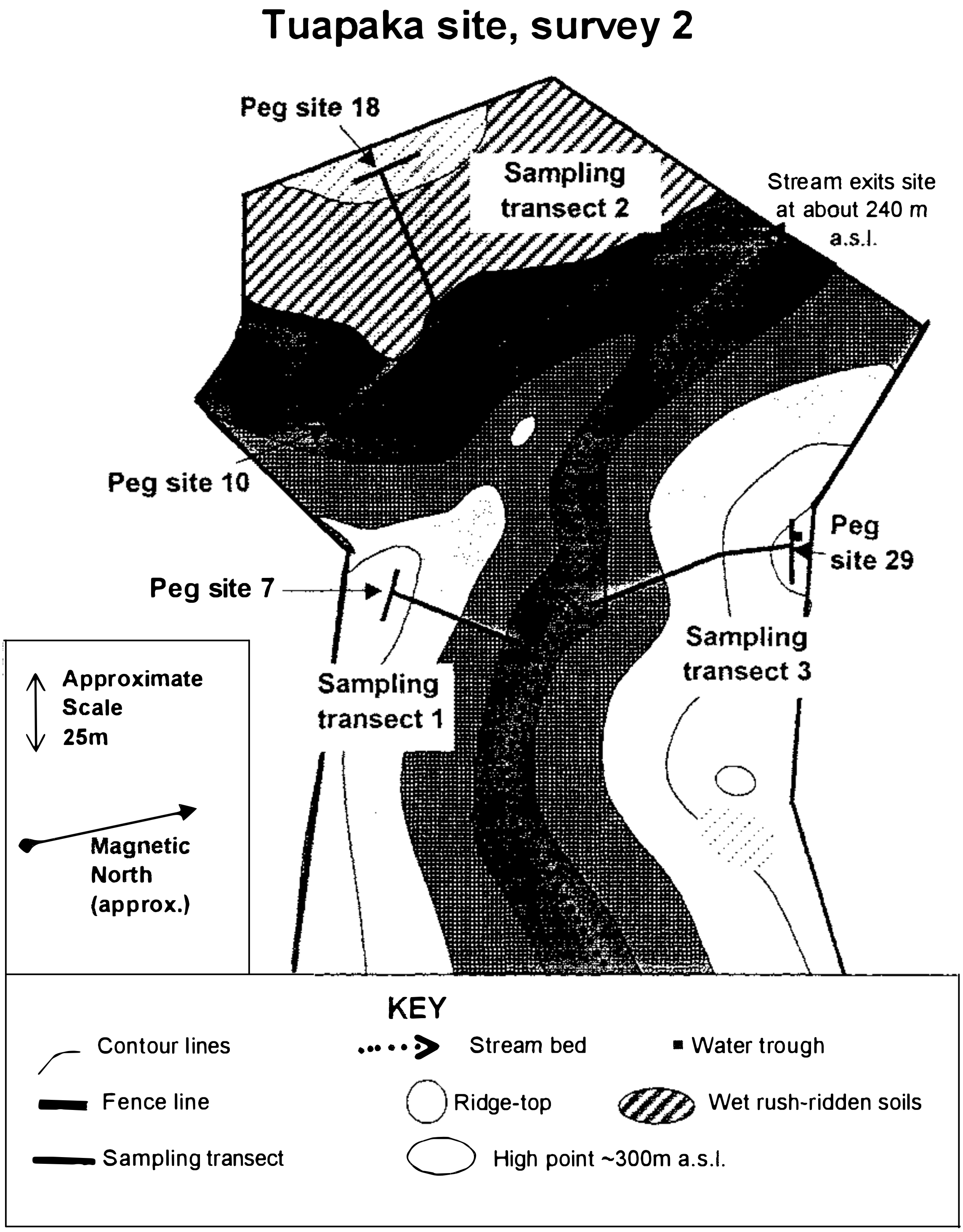
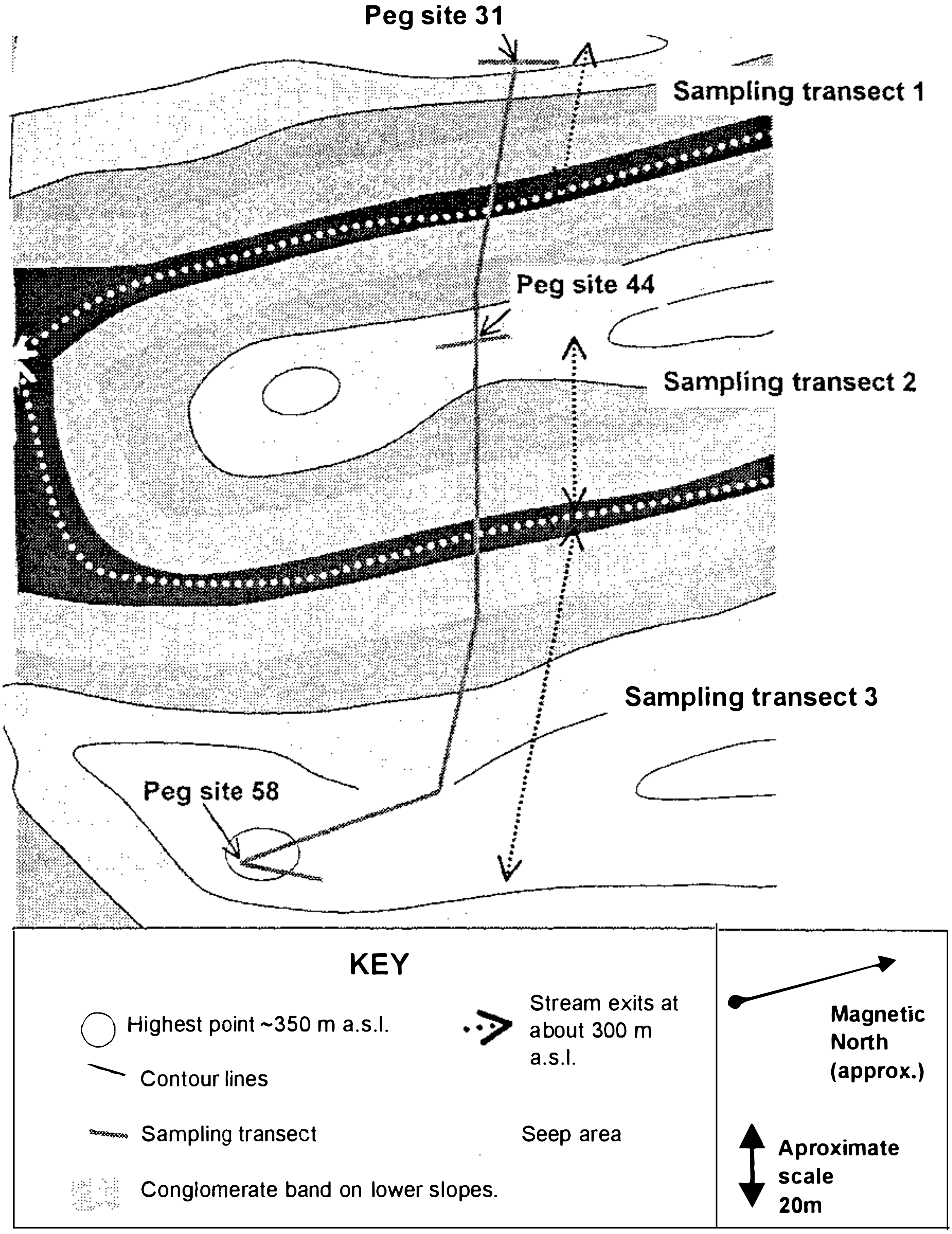


Figure 3.17: Diagram of the Tuapaka site showing the layout of the sampling transects for the second survey. Pegs were laid out every 10m along the strings (lighter shades indicate increasing altitude). Soil and herbage samples were taken alongside each peg.



Bernwood site, survey 2

Figure 3.18: Diagram of the site on Bernwood farm used in the second survey showing the layout of the sampling transects (lighter shades indicate increasing altitude). Pegs were located every 10 m along the sampling transects. Soil and herbage samples were taken alongside each peg. Dotted arrows indicate the extent of each sampling transect.

The herbage was dried overnight at 65°C and weighed.

Soil tests for Quick test K, Acid K and Step K were conducted using the same methods as previously (see Section 3.3.2).

Plant available soil phosphate was measured by the standard Olsen test (Olsen et al., 1954): 1g soil (air dry, sieved <2mm) was shaken in 20 ml 1M $NaHCO_3$ (pH 8.5) for 30 min. The sample was then centrifuged, and the supernatant filtered for colour development of P and analysis by spectrophotometer (Murphy and Riley, 1962).

The soil at each peg site was sampled a second time to measure the soil moisture status. The same sample collection method was used, but the sampling was done much later, on the 26 and 27 October 1996 (spring).

The soil moisture samples (four 75mm deep soil cores from each peg site) were put into plastic bags in the field, weighed in the bags in the laboratory, then laid out in trays and oven dried (100°C) overnight. Soil moisture was calculated as the total water content (weight lost by drying) over the total oven dry mass (%).

Figure 3.19: Soil sample collection method and pasture sampling square used for the second survey.

3.4.3 Results and discussion

The sampling scheme of the second survey was designed to compare results of tests for soil K, Olsen P, soil moisture and pasture regrowth on relatively well drained ridge-top and shoulder areas that were popular with grazing stock (campsites), with results of the same measures on the adjacent steeper slopes. The results of the sampling scheme were suitable for the application of a variety of methods of statistical analysis, including both univariate (anova) and multivariate analysis (correlation and correspondence analysis). The results could also be used to examine distance dependence, at scales from 10 to 70 m.

3.4.3.1 Frequency distribution

The first stage of analysis of the results was to break down the frequency distribution information for the various data sets.

3.4.3.1.1 Comparison between first and second survey at Tuapaka

The frequency distributions of the soil K values from the first survey (Section 3.3), carried out at Tuapaka in early winter of 1993, and the second survey, carried out in late summer and autumn of 1995, were very similar. There was a single skewed peak for Quick test K and a long tail of values to the right of the main group of data in both surveys (comparing Figures 3.13 and 3.20). Step K and Acid K were similarly both skewed with long tails to the to the right. Acid K was again multimodal, while Step K again had a distinct break in the middle of the main group. The data ranges were extensive for the soil K tests in both surveys (Table 3.3). The modes (most common value) and medians (middle value) remained much the same from the first survey to the second survey.

The first survey was based on random sampling and only about 15% of the sites were located on the ridge-top areas. The second survey deliberately targeted well drained ridge-top areas, so that about one third of the samples came from areas that were expected to give some high values. Overall, the effect on the distributions of the results was minimal and the replication between the first and second samplings of soil K was very good.

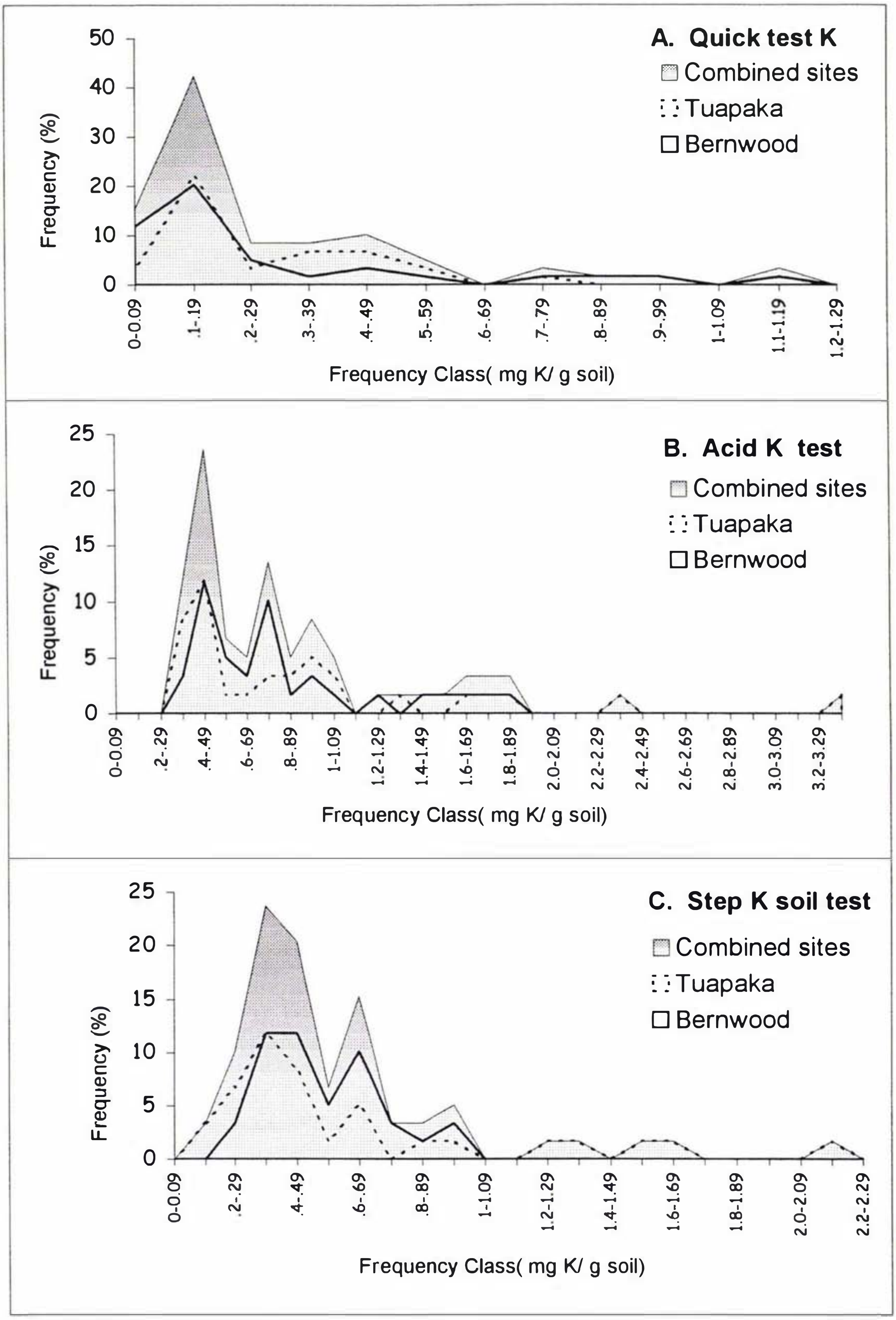


Figure 3.20: Frequency graphs of the soil K tests, from the second survey. The results of the combined sites are presented, as well as separated into the individual sites on Tuapaka or Bernwood farms. Results are presented as the frequency of occurrence (%) over the combined sites (59 samples), and also show the relative contribution of each site.

Table 3.3: Comparison of the untransformed frequency distributions of Quick test K, Acid K and Step K in survey 1 (1993) and survey 2 (1995, **in bold)** in one paddock on Tuapaka farm. Results show tests on, Acid K test and Step K test. N. B. in a Normal distribution mean = median, and skew and kurtosis = 0.

	Quick test K (1)	**Quick test K (2)**	Acid K test (1)	**Acid K test (2)**	Step K test (1)	**Step K test (2)**
Mean (mgK/gsoil)	0.24	**0.29**	0.81	**0.92**	0.57	**0.63**
Standard Deviation	0.20	**0.24**	0.41	**0.68**	0.31	**0.49**
Median (mgK/gsoil)	0.17	**0.19**	0.7	**0.77**	0.51	**0.43**
Range (mgK/gsoil)	0.07 - 1.34	**0.09-1.18**	0.12 – 2.43	**0.3-3.32**	0.05 - 1.70	**0.19-2.1**
Skew	2.8	**2.13**	1.36	**1.97**	1.1	**1.68**
Kurtosis	10.4	**5.6**	2.48	**4.5**	1.7	**2.3**

The population distributions appeared to be relatively stable with time, which was rather in contrast to the work of Roberts (1987), on volcanic soils, who found that biweekly bulked soil samples tested for Quick test K exhibited both high temporal variability and some distinct grazing effects. Volcanic soils, rich in allophane, will have a limited capacity to adsorb urine K, so the time since grazing and rainfall is expected to have a large effect on the amount of exchangeable K remaining in the topsoil. In contrast, the soils in this study have a large capacity to absorb urine K, and the effect of the urine patches is expected to be more durable. A population of recently and not so recently urine affected soils may develop in micaceous soil under pasture, that is essentially stable over time, although the actual values may change from point to point with time.

It is also noteworthy that, if the main effect of grazing is an increasing incidence of very high NH_4-exchangeable K and nonexchangeable K values, then the average values of bulked samples will be disproportionately increased in grazed compared to ungrazed soils. Bulking samples from frequency distributions like the ones in this study would also give highly variable results depending on which samples in the high ranges did or did not happen to be included (Reynolds, 1975). Even if the soil test value of a bulked sample does happen to accurately reflect the arithmetic mean of the soil population, the relevance of a single number remains highly debatable as an adequate representation of such a wide ranging population. Collecting individual samples and analysing them separately for a full description of the range, median and skew of the population is thought to be a more appropriate way of describing these distributions.

3.4.3.1.2 Distribution of results from the two sites

In this section, the frequency distributions of the results of soil K and P tests, soil moisture and pasture regrowth were compared at the Tuapaka and Bernwood sites. In general, the sets of results obtained from the two sites were very similar (Table 3.4).

Table 3.4: Arithmetic means of soil and pasture measurements at each site in the second survey.

	TUAPAKA	BERNWOOD
Acid K (mg K/g soil)	0.94	0.82
Step K (mg K/g soil)	0.64	0.54
Quick test K (mg K/g soil)	0.29	0.29
Olsen P (ug P/g soil)	28.7	28.2
Pasture (kgDM/ha)	1460**	1060
Soil Moisture (g/g%)	53.7	48.0

.**Tuapaka significantly different from Bernwood.

Soil K and Olsen P tests.

The frequency distributions of the soil K extraction results from the Bernwood site were quite similar to the distributions found at the Tuapaka site (Figure 3.20) (which were described in Sections 3.3.3.3 and the previous section).

The frequency distribution of the Olsen P results were also similar at both sites (Figure 3.21a). The distribution of the combined results for Olsen P (Table 3.5) had a skew and kurtosis that were similar to the soil K tests. Olsen P also had a similar extensive range, compared to the soil K tests. The combined Olsen P values ranged from soils with values of less than 10 ug P/g soil to one site that had over 100 ug P/g soil. The low end of this range represented values for which pasture would have a high probability of responding to phosphate fertiliser, especially from late summer to early spring. In contrast, soils with an Olsen of 30 – 40, (closer to the mean in the study) are unlikely to have a pasture response to fertiliser and are likely to maintain maximum production for several years without P fertiliser (During, 1984; Saunders et al., 1987). 12% of the Olsen P values in this study were greater than 40, and the high end of the range (101) is off most published scales for Olsen tests (e.g. Cornforth and Sinclair, 1984).

The standard deviation and coefficient of variation (c.v.) was calculated for each test, although the validity of these parameters is doubtful. However, very little other information for a comparison of the variability of exchangeable K and P is available. Beckett and Webster (1971) classed measures of plant available K and P together in a

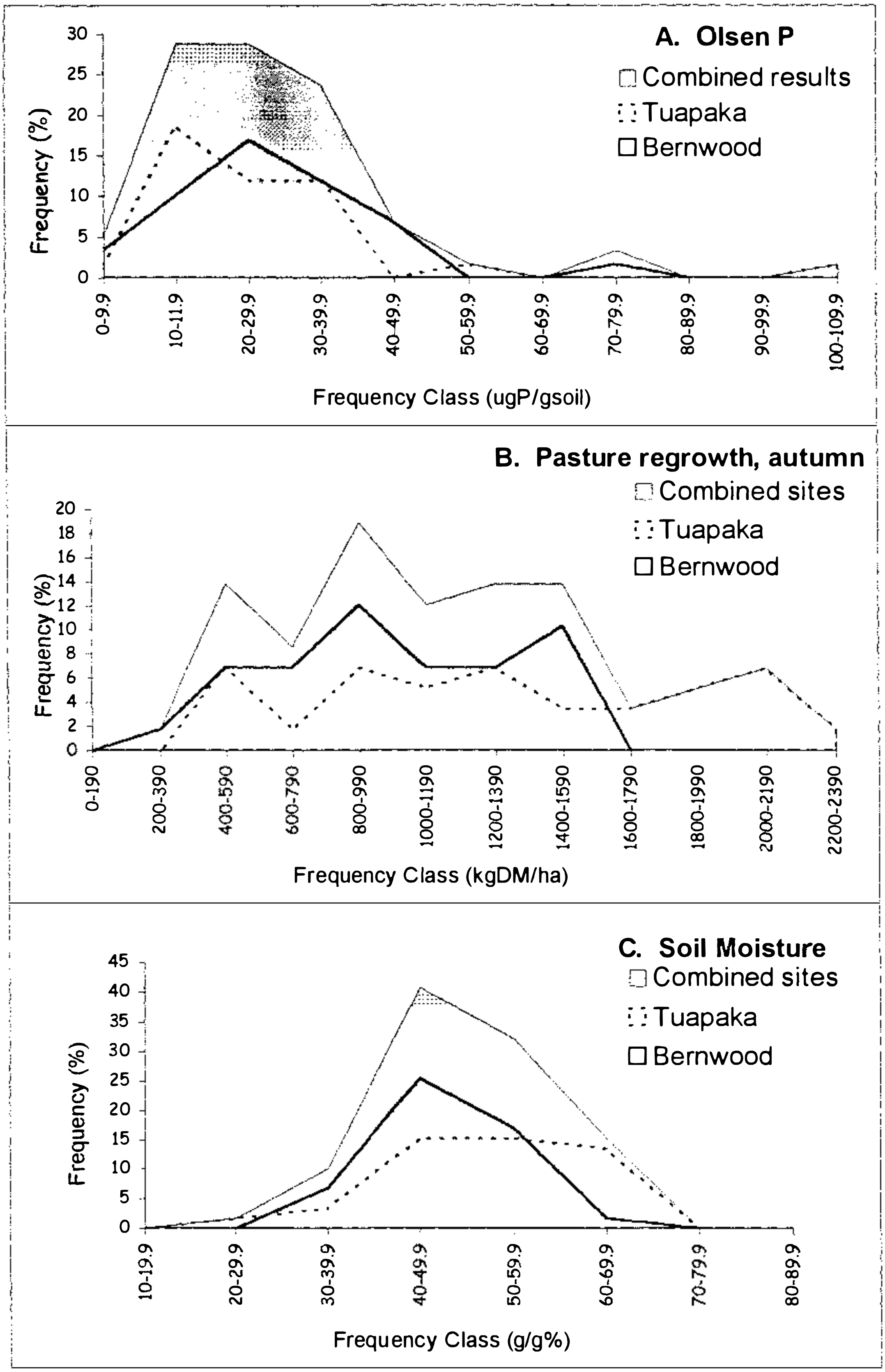


Figure 3.21: Frequency graphs of the combined results of the second survey at two sites (Tuapaka and Bernwood), and the separate results for each site for; Olsen P soil test (A), pasture regrowth, cut in early May 1995 at Tuapaka and late May at Bernwood (B), gravimetric soil moisture, sampled in spring, 1996 (C). Results are presented as the frequency of occurrence (%) in each class from a total of 59 samples.

maximum variability class. The c.v. of the soil K tests was similar to the results of the first survey (Table 3.5 compared with Table 3.2) and therefore typical of the results of other studies. For plant available P in topsoils, the range in c.v.s reported by Beckett and Webster (1971) was 11-131%, with a median of 45%. Boyer et al. (1996) found that soil P extracted in dilute acid-fluoride had a c.v. of 99% in a steepland pasture. Adams and Wilde (1976) found that the c.v. of 0.5M H_2SO_4-extractable P in a New Zealand soil with mixed sedimentary and volcanic soil parent materials was 67%. In this study, the c.v. of the Olsen P test was 60% (Table 3.5), so again, the results of this study appeared to be entirely typical of other studies.

Table 3.5: Tests on the frequency distribution of the data sets from the second survey (untransformed). Results are from 59 sampling sites, combining the Tuapaka and Bernwood farm sites. N.B. in a Normal distribution; mean = median, and skew and kurtosis = 0.

	Quick test K mgK/gsoil	**Acid K test** mgK/gsoil	**Step K test** mgK/gsoil	**Olsen P** ugP/gsoil	**Pasture regowth** kgDM/ha	**Soil Moisture** g/g%
Mean	0.289	0.872	0.582	28.2	1158	50.5
Std.dev.	0.26	0.57	0.37	17.0	490	9.9
C.V.	91%	65%	64%	60%	42%	20%
Median	0.168	0.727	0.478	24.3	1120	49.8
Range	0.06-1.18	0.3-3.3	0.19-2.1	6.2-101	290-2230	23.4-69.6
Skew	1.82	1.95	2.13	2.04	0.297	-0.056
Kurtosis	2.95	4.95	5.37	5.95	-0.68	-0.004

Pasture regrowth

The pasture production ranges in this study were typical of autumn pasture growth in improved steepland pasture in this region (Suckling, 1959). The distribution of the results of the regrowth were approximately Normal, but were multimodal (Figure 3.21b). Tuapaka farm had significantly more pasture regrowth (also examined in Section 3.4.3.4) compared to the results for Bernwood farm. The differences probably indicated both the earlier time of the cuts at Tuapaka and the aspect differences between the largely north facing Tuapaka site and the largely south facing Bernwood site. The owner of the Bernwood property has noted that overall production on his property was less than production on his brother's property, which is on the opposite side of the same dissected terrace formation and so has a largely northerly aspect (T. Clare, pers. com.). Suckling (1959), working in the same district, found that paddocks on northerly exposures (sunny faces) had consistently better pasture growth and stock performance than paddocks with a southerly exposure (shady faces).

Soil Moisture

The soil moisture results were similar between the sites, and the distribution of the results was close to a classical Normal distribution (Figure 3.21c). The mean and the median matched quite well, and the standard deviation was 20%, instead of nearly 100% for Quick test K. A survey of central yellow brown earths previously found a similar range in field capacity from 74.6% to 32% in the top 50 to 70 mm, with a wilting point of 12.8-40% and a typical available water capacity of about 20 % (Gradwell, 1974). Similar ranges of field capacities have also been found in other reports of soil moisture in steepland pasture soils (Gillingham, 1974; Rowarth, 1987). Previous surveys of soil moisture in hill and steepland pasture have found that soils are generally at field capacity from April or June to September or October (see literature review Section 2.4). This survey was carried out in spring (late October) after a wet winter, and the bulk density of the soil on the slopes was close to one (Table 6.1), so the gravimetric soil moisture values from the slopes were thought to be approximately indicating field capacity. Soil bulk density was lower in the soils on the ridge-top areas, so the soil moisture values obtained overestimated the field capacity by approximately 10%.

Summary of the frequency distributions

Replication of the soil K surveys in time and between the two sites was excellent. The Olsen P and soil moisture results were also very similar between the two sites. Only pasture regrowth differed between the two sites. Results ranges were extensive for all the factors examined, but comparisons with published information suggested that the patterns of variability were typical of steepland pasture, and probably developed land in general.

3.4.3.2 Correlation

Correlation tests the extent of linear association between two factors (see Section 3.2.1.1). The test can be influenced by outliers, such as in the long tails that were found in the soil test results, so the correlations were also run using transformed data, as a check.

Soil tests

In the first survey (Section 3.3) Quick test K and Step K had no linear association. In the second survey a significant degree of linear association was found between the two tests ($r=0.61$, Table 5, Appendix 1), which was also robust after transformation (Figure 3.22a). The change indicated that, although the frequency distributions of the soil K tests that were picked up by the two different survey techniques were very similar, changing from a random sampling technique to a targeted comparison of the ridge-tops and slopes did change the relationship between Step K and Quick test K. There was now a likelihood that a soil that had a high Quick test K value would also have a high Step K value.

All three soil K tests also had strong positive linear association with Olsen P (Figure 3.22b), that was robust after transformation, so Olsen P was also increasing in samples when Quick test K and Step K were increasing.

Step K was the only factor to have a reasonable correlation to the spring soil moisture status, which was thought to be mainly indicating field capacity (Figure 3.22c). The relationship improved slightly when Step K was log transformed (Table 5, Appendix 1).

Pasture regrowth

Pasture regrowth also had some linear relationship to Quick test K, which may indicate a K responsive situation (Table 5, Appendix 1) or may have been an artefact of both factors increasing with slope (next section). (The relationship between the soil tests and pasture yield are explored in more detail in Chapter 5.)

Slope

All the factors examined had a negative correlation to increasing slope, although the relationship was weak for some of the tests. An increase, with decreasing slope, in exchangeable P and K and pasture yield, caused by stock camping, has previously been well documented (e.g. Gillingham and During, 1973; Gillingham, 1978; Ledgard et al., 1982; Rowarth, 1987; Saggar et al., 1988). Plotting the more significant correlations against slope showed that the actual relationships were not linear, except for pasture regrowth (Figure 3.23). There was little trend in the soil test results between about 20° and 50° of slope. Between 0° and 20° of slope there was a marked increase in the range of values obtained, particularly a big increase in the highest value obtained. This

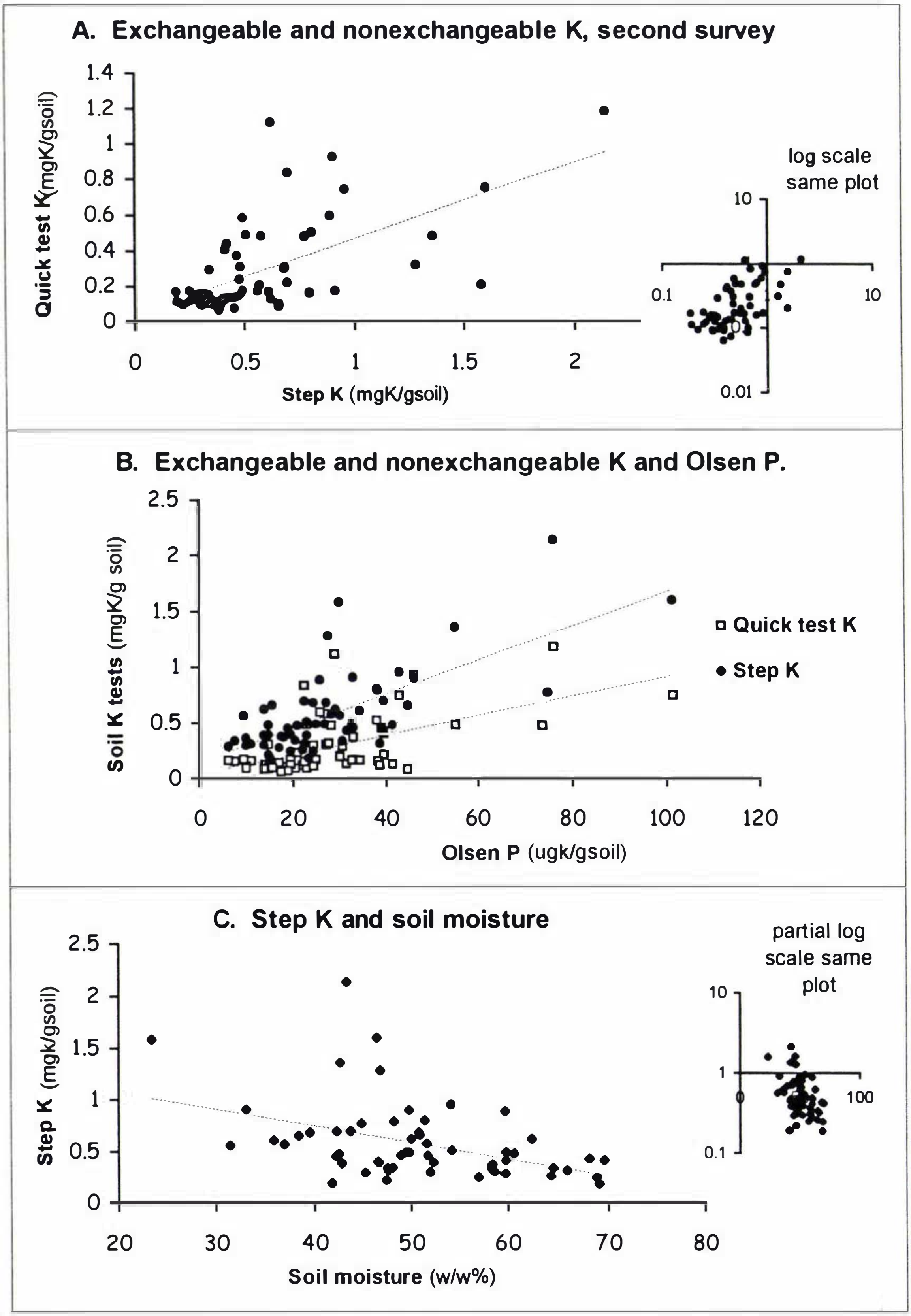


Figure 3.22: Relationship between Quick test K and Step K values, second survey (A). Relationship between the soil K tests (Quick test K, Step K) and Olsen P (B). Relationship between spring soil moisture status and Step K values of the soil samples of the second survey (C). Insets (where present) show the same graph replotted on a log scale. Linear association is indicated by the dashed trend line.

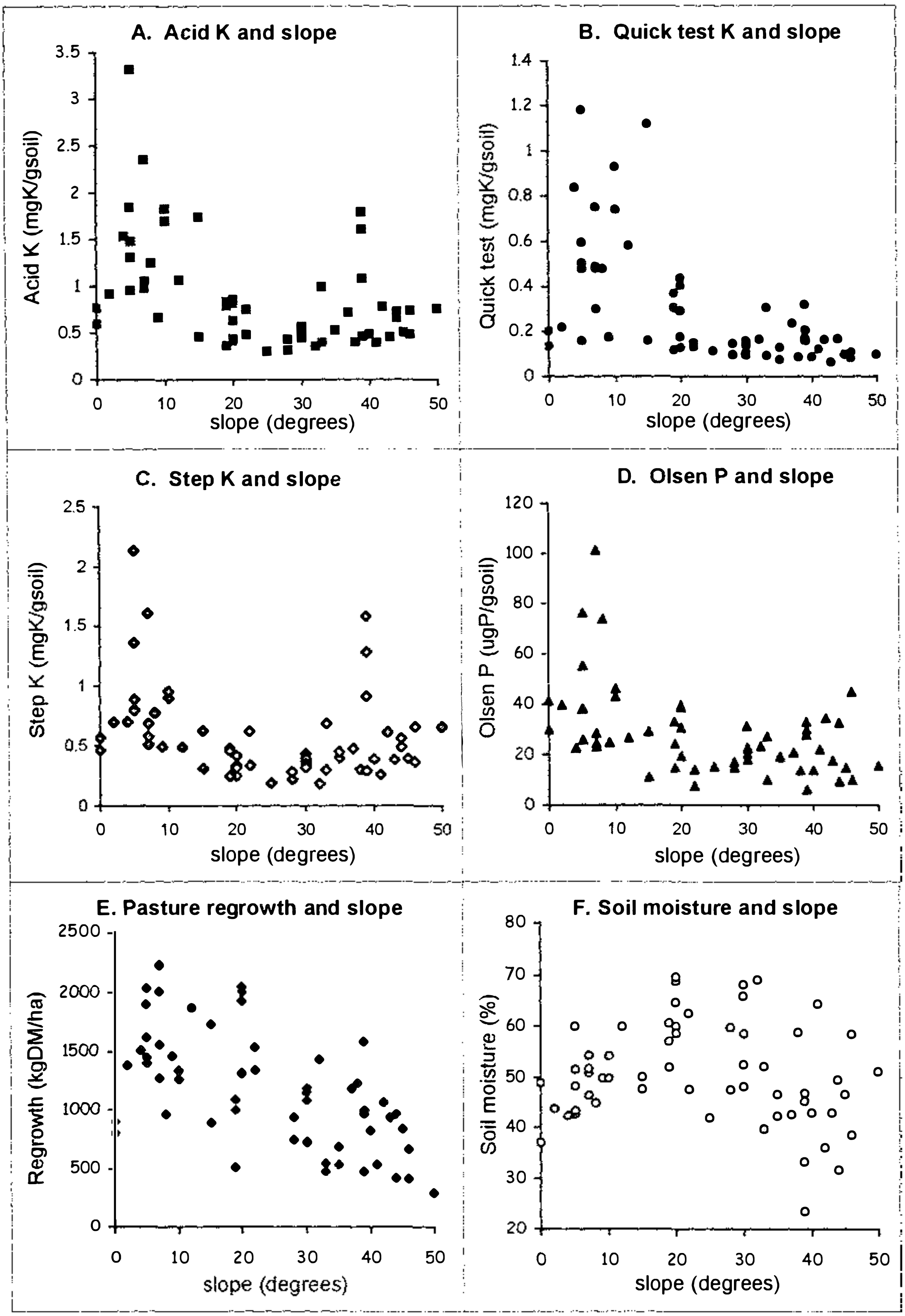


Figure 3.23: Association between the ground slope that a soil sample was collected from and; Acid K test value (A) Quick test K values (B) Step K test value (C) Olsen P value (D), pasture regrowth (E) and spring soil moisture (F). The two points of zero slope were valley bottoms at the Bernwood site.

pattern was very marked for Quick test K, and also Olsen P, but was less obvious for Acid K and Step K because of some high results at about 40° of slope.

The pattern of soil moisture with slope was rather different. The soils tended to be wetter in areas of moderate slope and drier on the flatter and very steep areas. Drier soils are generally expected in the shallow profiles of the very steep slopes (see Chapter 2.4), although in this study the soil moisture pattern was also strongly associated with aspect and with the location of water seeps (explored further in Chapter 3.4.3.4.2). The trend to drier soils on the flatter areas was thought to be an artefact of deliberately targeting these areas in the second survey.

Slope classes

To further explore interaction between animal camping effects and slope, the soil test results were split at 20°, corresponding to the change from the flat and rolling topography of the ridge-tops and shoulder slopes, to the steep topography of the slopes. The frequency distributions were plotted for each variable for classes of ≤ 20 and > 20 degrees of slope (Figure 3.24 and 3.25). A sharp change in distribution was particularly marked for Quick test K (Figure 3.24a), with a change from a fairly compact but skewed distribution (mean 0.14 mg K/g soil, skew of 1.6 and kurtosis of 2.6) on slopes of >20°, to a very spread out distribution on slopes ≤ 20° (mean 0.45 mg K/g soil, skew of 0.9 and a kurtosis of 0.3). The differences were not so evident for the other soil tests.

Correlations were re-calculated for the factors after splitting the data set into the two slope classes (Table 6, Appendix 1).

Within the >20° steep slope class, there were no significant correlations, except among the soil K tests. Acid K and Step K had a nearly perfect correlation (r=0.99) in soils on the steeper slopes, and Step K no longer had a significant correlation to Quick test K (r=0.56). This pattern resembled the pattern of correlations found in the first survey (Tables 4 and 6, Appendix 1). Olsen P had no significant correlations to the K tests. Dung and urine, which are expected to have a strong influence on the variability of exchangeable K and P, will be deposited on the slopes but will probably be scattered. (Access tracks, which tend to form campsites on the slopes, were avoided in this study). So, the lack of relationship between Quick test K and Olsen P on the steep slopes was

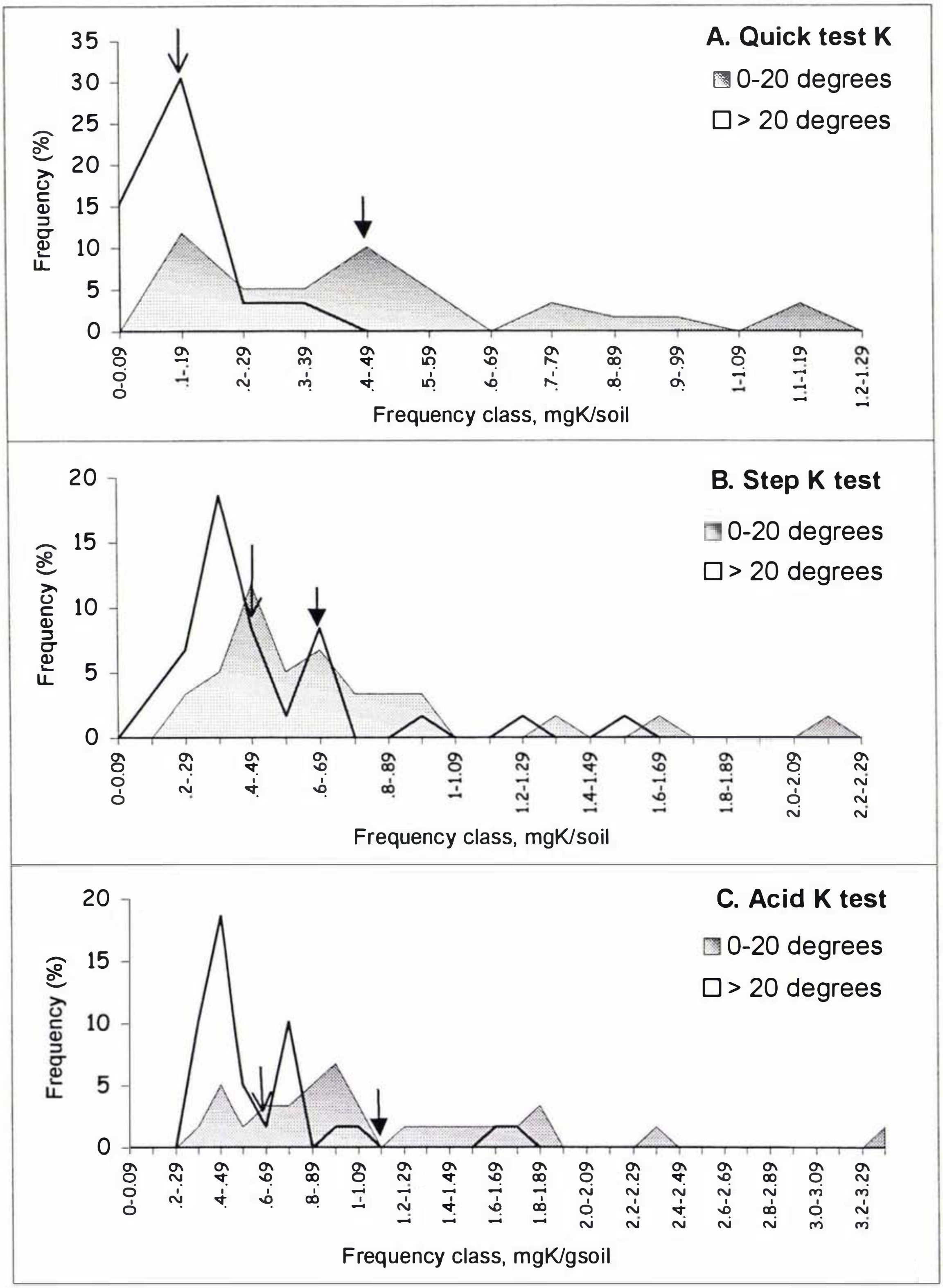


Figure 3.24: Frequency diagrams for three soil K tests from the second survey split into two slope classes, of 0-20 degrees (shaded) and >20 degrees of slope (no fill). The mean of each distribution is indicated by an arrow (solid for 0-20 degrees and line for >20 degrees).

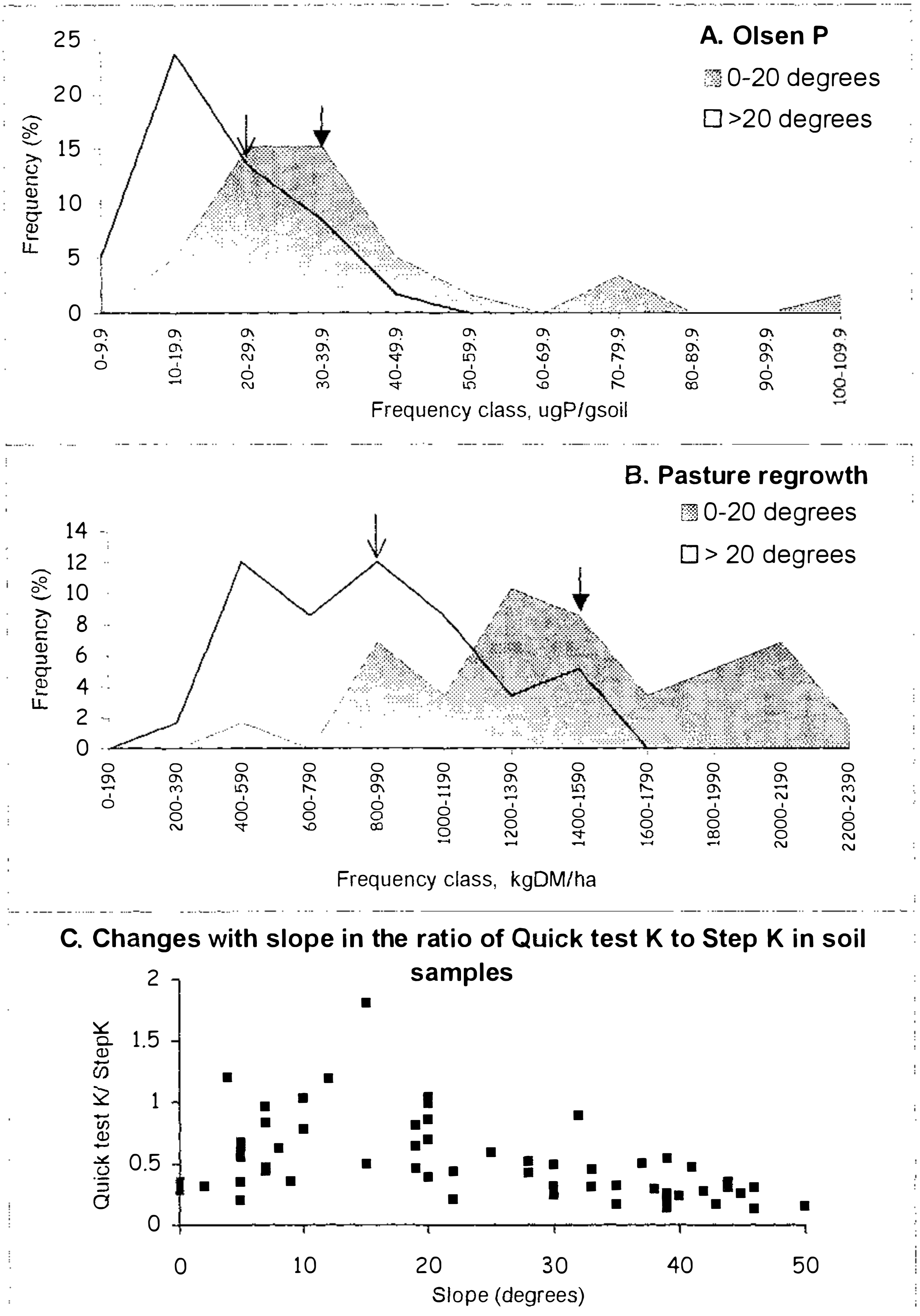


Figure 3.25: Frequency diagrams for Olsen P (A) and pasture regowth (B) from the second survey, split into two slope classes, of 0-20 degrees and greater than 20 degrees of slope. The means of the distributions are indicated by arrows (solid for 0-20 degrees and line for >20 degrees). The changes with slope in the ratio of Quick test K to Step K, are also shown (C).

predictable. Step K only appeared to be affected by the deposition of urine under the animal campsites on the ridge-tops. On the steeper slopes, if Quick test K reflects the distribution of the urine patches and Step K reflects the pattern of the clay mineralogy, then these factors would not be expected to be correlated, as was observed.

Within the ≤ 20° slope class (flat to rolling topography), Step K now had some correlation to Quick test K (r=0.66). Step K and Acid K were strongly correlated to Olsen P, but Quick test K was not significantly correlated to Olsen P (Appendix 1, Table 6). These effects reflected the relationship between slope and the soil tests, where Olsen P and Step K, and to a lesser extent Acid K, had few high values until the slope was less than 10° (Figure 3.23). In contrast, Quick test K had some high values on sites where the ground slope was between 10 and 20° of slope, as well as ≤ 10°, so was not so well correlated to the other factors in the ≤20° slope zone.

The slope zone effects could be further illustrated by breaking the results into three slope classes and calculating the average and the coefficient of variation (c.v.) of each factor in each class. Statistically, this approach was less than ideal, but it did provide a widely understood way of summarising the results. The slope classes were; relatively flat areas of ≤ 10° of slope, shoulder slopes of 11° to 20°, and steep slopes of greater than 20°. The average Quick test K value increased steadily as the slope decreased, with a very large c.v. on the shoulder slopes (Table 3.6). The Step K pattern was different. The average Step K results were similar on the steep slopes and the shoulder slopes, then increasing sharply on the flat areas, with the lowest c.v. associated with the shoulder slopes. The difference was further illustrated by the ratio of Quick test over Step K, which was lowest on the steep slopes and highest on the shoulder slopes (Figure 3.25c). The difference between Quick test K and Step K was foreshadowed in the first survey, when Quick test K but not Step K gave some very high results on well drained shoulder slopes, and both Quick test K and Step K gave some very high results on well drained ridge-top campsites.

The average Olsen P result increased with decreasing slope, with a small increase from the steep slopes to the shoulder slopes, and a sharp increase in both the mean and the c.v. on the flat areas (Table 3.6). In comparison to the soil tests, the average pasture regrowth was low but more variable on the slopes, increasing sharply on the shoulder slopes and then remained similar to the shoulder slopes on the flatter areas.

Table 3.6: Average and c.v.(%) of the soil test results and pasture regrowth within three slope zones in two steepland pastures. These statistics can only be regarded as rough estimates because the distributions of most of the factors tested were skewed.

	21-50°		11-20°		0-10°	
	MEAN	C.V.	MEAN	C.V.	MEAN	C.V.
Quick test K (mgK/g soil)	0.14	44%	0.37	78%	0.51	59%
Step K (mgK/g soil)	0.49	62%	0.4	29%	0.88	50%
Acid K (mgK/g soil)	0.63	54%	0.77	51%	1.38	49%
Olsen P (ugP/g soil)	20	44%	28	35%	43	52%
Pasture (kgDM/ha)	880	40%	1430	37%	1480	27%
Quick test K / Step K	0.34	48%	0.85	48%	0.59	48%
Number of values	31		11		17	

A similar trend, for Quick test K and Olsen P with slope, was found by Gillingham and During (1973), where Quick test K, and K in the herbage, appeared to increase faster with decreasing slope than Olsen P. Gillingham and During also noted that sheep tended to have permanent campsites on the flat areas, while cattle tended to be more mobile and also to use different parts of the shoulder slopes as camps. Williams and Haynes (1994) found that the greater volume of cattle urine patches, compared to sheep urine patches, affected a larger volume of soil with higher solution concentrations. If cattle are likely to congregate on the shoulder slopes, then the occasional sharp increases in Quick test K observed in this zone could be describing the effect of recent cattle urine patches, possibly where they have overlapped. Much less P than K is deposited in excreta (see Chapter 2.3.3), and evidently not enough P is deposited in this zone to much increase Olsen P, compared to the large increase in Quick test K. In contrast, the large increase in Olsen P on the flatter areas (≤ 10° in slope) indicated a high rate of excreta deposition by the grazing stock. Quick test K and Step K also increased, presumably reflecting the now very high incidence of more recently deposited and overlapping urine and dung patches from sheep and cattle.

The difference between spatial variability patterns of Quick test K and Olsen P does have an implication for soil sampling procedures. The current recommended procedure is to avoid obvious animal campsites on the ridge-tops, based on the presence of dung (Cornforth and Sinclair, 1984). This study confirmed that Olsen P increases markedly in these areas and that they should be avoided if an accurate estimate of the P status of the rest of the paddock is to be made. However, this study also found that an unbiased estimate of Quick test K would require avoiding the shoulder slopes as well the ridge-top areas. Inclusion of the shoulder slopes, particularly the well drained areas, could cause overestimates in the Quick test K status of the remaining paddock and underestimates in the fertiliser requirements (Kachanoski and Fairchild, 1996). The simplest practise for accurate Quick test K sampling would probably be to walk around tracks on the mid slope and sample the terracette risers above the track, thus avoiding most of the urine deposition effects. Step K is not routinely tested, but any regular sampling for Step K would probably require the opposite sampling technique. The most stable Step K results were found on the shoulder slopes, where Step K was influenced neither by the sharp increases found under the well drained ridge-top campsites, nor by the variability in Step K found as the soil parent materials and aspect changed on the steeper slopes.

Summary of correlation analysis

On the steep slopes there was no relationship between the patterns of NH_4-exchangeable K (Quick test K), plant available nonexchangeable K (Step K), plant available P (Olsen P) and autumn pasture regrowth.

The expected animal campsite effects in steepland pasture were found. Quick test K, Olsen P and pasture regrowth all tended to increase as slope decreased, although the different factors had different patterns. Both the mean and the range of the Quick test K values increased markedly on well drained slopes of ≤ 20°. In contrast, the mean and the range of the Olsen P results did not increase markedly until the slopes were ≤ 10°. Step K was more variable. High Step K values, related to low soil moisture, were found on both the steeper slopes and the flatter areas. The pattern of Step K values was similar to the Olsen P pattern on the well drained ridge-tops, and contrasted with the Quick test K pattern. It was speculated that Quick test K increases on the shoulder slopes marked the position of more recent overlapping cattle urine patches, while Olsen P and Step K only increased in zones of very high dung and urine deposition on flatter areas.

3.4.3.3 Distance dependence

All points of sampling were 10 m apart in this study, and laid in straight lines down the slopes and across the ridge-tops, so the information was suitable for building variograms (see Section 2.2). Variograms were constructed using log transformed data and lags of 10 m to 70 m (compared to a range of 0.25 to 25 m in the previous study). No significant distance dependent spatial variability effects were observed for any factor, at either site, at this scale, further confirming the results of the first survey (Section 3.3.3.5).

3.4.3.4 Anova comparison.

The data collected in the second survey could also be examined using a nested anova design with fixed effects. Location in the landscape was used as the treatment effect in the model. The three nest levels of the anova model were (1) farm (comparing the Tuapaka and Bernwood sites), (2) transect (comparing three slope and three adjacent ridge-top samples with similar sets of results from other parts of the same site), and (3) slope (comparing samples from the mid-steep slopes with those collected from the adjacent ridge-top). Treatments effects were examined using a Least-Squares-Means test, reporting the p-value of the t-test between pairs of means. In order to balance the anova design with three replicates in each mid-slope class, all samples from the transitional shoulder zones and some samples from the lowest steep slopes were excluded, so the anova tested observations from 38 of the total of 59 sites.

Based on the frequency distributions (Section 3.4.3.1.2) the data from the soil K and Olsen P tests required transformation to meet the normality assumption of an anova test. The overall fit of the data to the nested anova model was good if the soil test data sets were log transformed. More specific individual transformations for each test did not improve the fit or change the anova outcomes.

Log transformation tends to compare the medians in a statistical test, rather than the arithmetic mean (Parkin et al., 1987), so the results are less sensitive to the tails of the skewed distributions, which was thought to be a good outcome for these wide ranging and highly skewed data sets. In this study, the results of an anova test on log transformed data were reported in the tables and figures after a simple antilog transformation, to convert the anova results back to meaningful units.

3.4.3.4.1 Comparison of the two sites

The only significant difference between the overall results from the two sites was the amount of pasture regrowth (p-value=0.0002). There was more pasture regrowth at Tuapaka, confirming the difference noted between the pasture frequency distributions (Section 3.4.3.1.2). No significant differences were found between results from the two farms for any of the other tests, confirming the use of these two steepland sites as replicates.

3.4.3.4.2 Comparison of whole sampling transects within the sites.

Significant differences between the amalgamated results of whole transects were found for the Acid K and Step K soil tests and the spring soil moisture status (Table 3.7). Step K and soil moisture had a similar pattern of significance, confirming the correlation result that linked Step K and soil moisture, regardless of slope (Section 3.4.3.2).

Table 3.7: Anova test results of Step K, Acid K (mgK/g soil) and gravimetric soil moisture patterns (g/g%) at each site, by transect. The K test values are back transformed from the anova of log transformed data. Soil moisture values are the arithmetic means. Transect numbers refer to Figures 3.17 and 3.18.

FARM, TRANSECT		GENERAL ASPECT	ACID K TEST	STEP K TEST	SOIL MOISTURE
TUAPAKA	**1**	70 (Northeast)	1.57 a*	1.15 a	38.9 a
	2	135 (East & South)	0.61 b	0.38 b	59.8 b
	3	180 (South)	0.76 b	0.45 b	60.3 b
BERNWOOD	**1**	90 (East)	0.80 b	0.59 a b	42.3 a
	2	70 (East)	0.71 b	0.51 b	48.8 a b
	3	250 (West)	0.83 b	0.49 b	53.5 b

*a and b denote no significant difference between values with the same letter, based on l. s. means test, p-value<0.0005.

The most marked association between soil moisture and Step K was found in transect one at Tuapaka. This transect was also the site of vectors A, B, and C in the first survey. It was noted that the entire ridge face, ranging from northerly to easterly exposures had generally dry soils, and consistently high Step K values were obtained from all soil samples taken from the face, as well as the ridge-top.

These results contrasted strongly with the relatively low Step K values and higher soil moistures taken from the opposite ridge face, which had a southerly aspect (vectors D to L in the first survey and transect two in the second survey).

The association between aspect and Step K was confounded at the Tuapaka site by transect three. The sampling sites were on both easterly and southerly aspects (Figure 3.18), although the Step K and soil moisture values were similar to soil on the southerly aspect. This third transect at Tuapaka was associated with the wet Korokoro variant soils, which were poorly drained and apparently affected by water seepage.

Soil moisture in this study was expected to approximately reflect the field capacity. The results were consistent with Gillingham (1974) who found that soil on northerly aspects had a lower field capacity than soils on the southerly aspect. This effect appeared to extend throughout the lower slopes and the adjacent ridge-top, so that an entire ridge face tended to have a similar field capacity and Step K status, unless confounded by water seeps. In the soils on the slopes the relationship between field capacity and Step K reflected a soil mineral weathering effect (explored further in Chapter 4), so more weathering of the mica minerals occurred in wetter soils, resulting in less Step K. On the ridge-tops this pattern was confounded by animal campsite effects.

At the Bernwood site there was no northerly exposure available for comparison with the Tuapaka results. The contrasts between the easterly and westerly aspects were not strong, and the significant differences were thought to have been generated by a seep zone on the upper slopes of the westerly aspect (transect 3) that was associated with higher soil moisture values and relatively low Step K values. Any strong associations between soil moisture and Step K at Bernwood were also confounded by the banded nature of the soil parent materials at this site (Section 3.2.2.4.2). The soils in the lower slopes were formed in a layer of loose conglomerate while the soils in the upper slopes were formed in a consolidated sandstone layer, which capped the conglomerate layer. When the Step K values of soils collected from the valley bottom and 10 m up either slope were compared with the Step K values of soil collected from further up the slope, there was significantly more Step K ($p=0.0001$) in the soil from the lower slopes (mean=0.59 mg K/g soil) compared to soils from the upper slopes (mean=0.37 mg K/g soil). Subsequent mineralogical analysis (Chapter 4) found that the clay minerals in the topsoil associated with the conglomerate band were relatively rich in K. The very loose rubbly nature of the conglomerate band was vulnerable to slipping and stock treading, which seemed to be constantly exposing fresh, relatively unweathered, soil parent material to the soil surface.

3.4.3.4.3 Comparison between ridge-tops and the adjacent slope

Comparisons between the two sites, and between transects within the two sites have been reported in the previous sections. The third nest level of the anova compared each ridge-top with an adjacent steep slope (>20°), within each transect. Significant differences (p-value=0.0001) between sites on a steep slope and an adjacent ridge-top were found for the Acid K, Quick test, and Olsen P soil tests, and for pasture regrowth (Figures 3.26 & 3.27). A significant model fit (p-value=0.0007) was provided by the Step K test. No significant model fit was found for soil moisture at this nest level.

Significant differences between the ridge-top and slope pairs were generally only declared when results from the slopes were particularly low, although the values of all factors usually increased on the ridge-tops compared to the slopes. This reflected the problem of the increased variability of the results on ridge-tops, compared to the slopes (Section 3.4.3.2).

For the soil K tests, most of the significant ridge-top/slope differences were associated with the third transect at both the Tuapaka and the Bernwood sites (Figure 3.26). Both of these areas had relatively wet slopes and well defined campsites on the ridge-tops, generating strong differences in soil K status.

Olsen P had quite a different pattern of significant differences compared to soil K, with significant differences between slopes and ridge-tops found for transect two at Tuapaka and transect one at Bernwood. Interestingly, Quick test K and Step K were both low in the wet seep affected ridge-top area of transect two at Tuapaka (Korokoro wet variant soil complex), but Olsen P was comparable to other ridge-top areas at Tuapaka. This may indicate a better persistence of P from dung, compared to the K from urine, in wetter ridge-top soils.

Although the general trend was for more pasture regrowth on the ridge-tops and less on the slopes, only two significant differences were recognised, in transects one and three at Tuapaka (Figure 3.27a). On the slopes the strongest rate of pasture regrowth was in the relatively wet soils associated with transect two. Both Quick test K and Olsen P were relatively low in the steeper slopes of transect two at Tuapaka, perhaps indicating a greater loss of nutrients by transfer due to the relatively high pasture growth rates

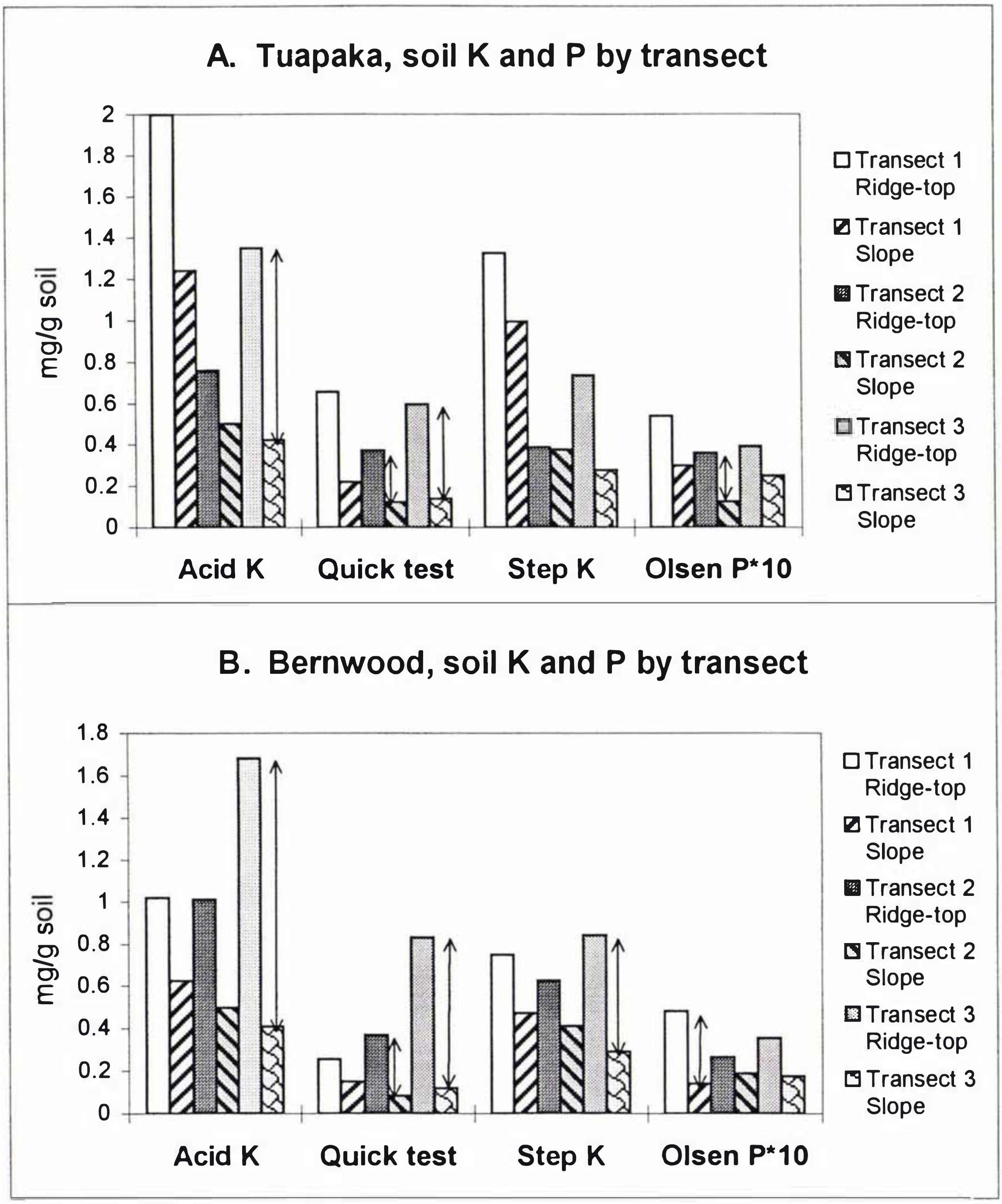


Figure 3.26: Comparison of Acid K, Quick test K, Step K and Olsen P values in samples from ridge-tops and adjacent slopes at the Tuapaka (A) and Bernwood (B) sites. N.B. results for the Olsen P test are *10, for visual clarity. Groups of bars show the results for each test in order of transect (see maps 3.17 & 3.18), split into ridge-tops (solid) and adjacent slopes (pattern fill). A significant difference (p-values of t-test between least-squares-means<0.0005) between each ridge top and adjacent slope pair is indicated by an arrow. All data distributions were skewed and the values in these charts are the back transformed treatment means from the anova test.

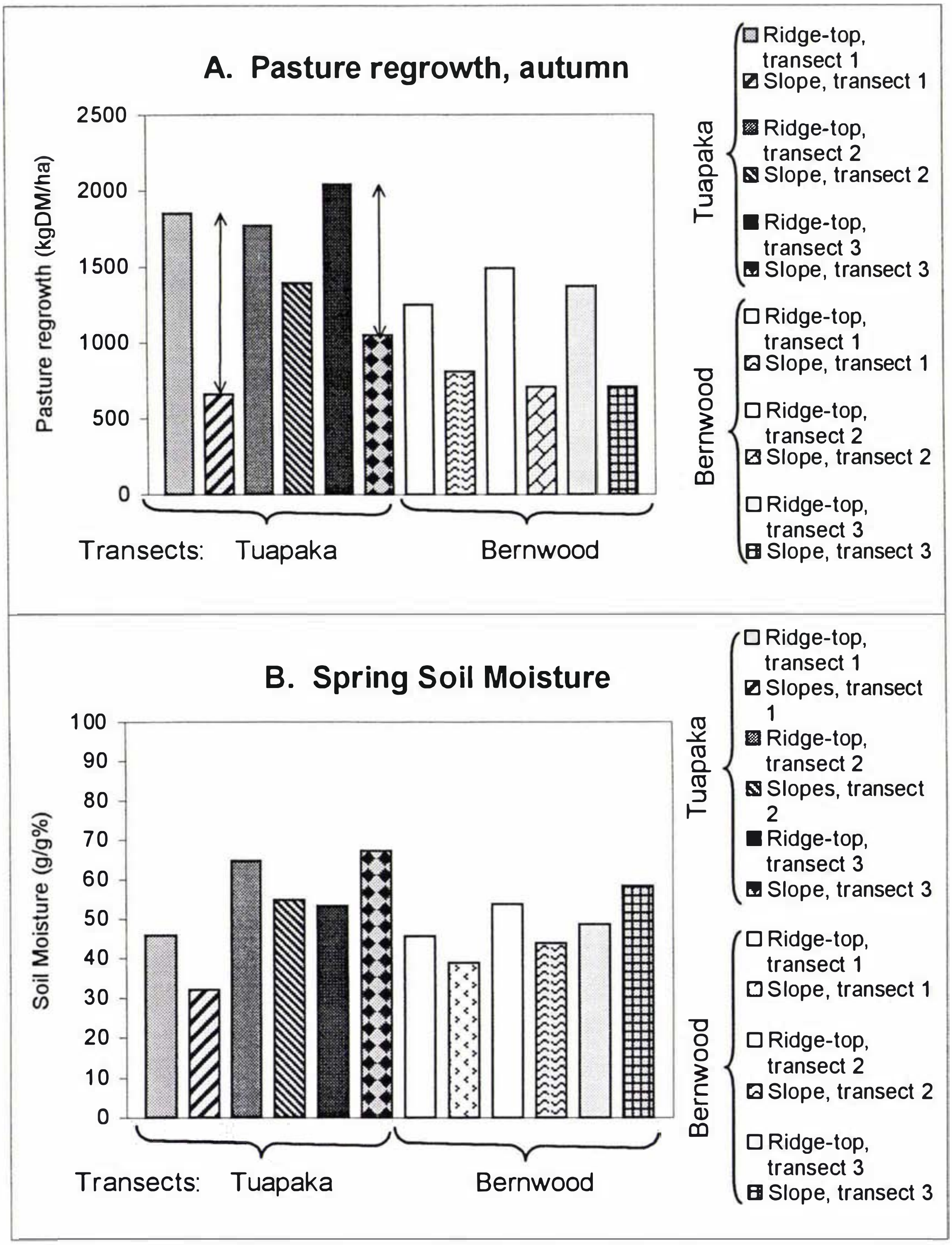


Figure 3.27: Mean levels of pasture regrowth in Autumn (A) and soil moisture in spring (B) at the Tuapaka and Bernwood sites. Bars show the mean values in order of transect (see maps 3.17 and 3.18), split into ridge top (solid) and slope (pattern fill). A significant difference (p-values of t-test between least-squares-means<0.0005) between the ridge top and the adjacent slope is indicated by an arrow. Data distributions were approximately Normal and the data sets were not transformed.

recorded on the slopes of this sheltered area with wet soils (Figure 3.26a). Evidently, the reduced K and P fertility was not growth limiting. A more in-depth study of the pasture growth patterns was subsequently carried out (Chapter 5).

As indicated by the lack of a significant model fit, there were no clear pattern to the gravimetric soil moisture values at this scale (Figure 3.27b). Ridge-tops tended to have a higher gravimetric soil moisture content compared to soils on the adjacent steep slopes, reflecting the increased organic matter and decreased bulk density of the soil on the ridge-tops. This trend was not very consistent and, as expected from the anova results, there was a stronger difference between whole transects.

3.4.3.4.3 Summary of the anova results

The anova results were not particularly strong, as would be expected from the high variability, but all the significant differences that were found supported the information previously derived from the frequency distributions and the correlations.

Between the two sites, results for Acid K, Step K, Quick test K, Olsen P and soil moisture were very similar. The only overall difference between the two sites was that Tuapaka had a greater autumn regrowth rate, probably reflecting the warmer, sunnier orientation of this site.

Step K was had a negative correlation to the soil moisture status, whether the soil moisture was determined by aspect or by water seeping from further upslope, except where the pattern was confounded by marked changes in the nature of the soil parent materials.

Comparisons between each ridge-top and slope pairs found that Quick test K, Acid K, Step K, Olsen P and pasture regrowth were all consistently higher on the ridge-tops compared to the adjacent slopes, but the results were so variable that few significant differences were declared.

3.4.4 Summary of second survey

The first survey of K fertility in a steepland pasture identified the main effects that influence the spatial variability of Quick test K (NH_4-exchangeable) and Step K (single acid extraction, nonexchangeable K). The second survey targeted these effects for an in-depth investigation using a variety of statistical techniques. Slope and ridge-top transects were laid out at two sites, on Tuapaka farm (same site as the first survey) and at a second steepland pasture site on Bernwood farm.

The distributions of the soil K tests results between 1993 and 1995 at Tuapaka and between the Tuapaka and Bernwood farm sites in 1995 were very similar, with the same heavily skewed distributions and wide ranges that were previously identified. The distribution of the Olsen P results was similar to the soil K distributions. Soil moisture and pasture regrowth had relatively Normal distributions. More autumn pasture regrowth was obtained at the Tuapaka site, which had a warm generally northerly exposure, compared to the colder southerly exposure of the Bernwood site. All the available comparisons of the results with other studies continued to suggest that the results obtained were very typical of other New Zealand steepland pastures developed in mainly sedimentary soil parent materials.

On the steep slopes (>20°) Step K, Quick test K, Olsen P, spring soil moisture and autumn pasture regrowth had no correlation to each other, except that Step K had a negative correlation to the soil moisture status. Only soil moisture and Step K had an identifiable relationship to the topography of the steep slopes. At the Tuapaka site, the principle trend in the Step K values on the steep slopes was an increase in value on dry soils associated with a northeasterly exposure, as was found in the first survey. On the steep slopes at the Bernwood site, the Step K value had some relationship to soil moisture but the principle trend was an increase in Step K value in soils formed in a rapidly eroding band of loose conglomerate in the lower slopes.

The expected campsite effect of increasing soil exchangeable P and K, and pasture production, with decreasing slope was identified, although the exact relationship with slope was different for each factor. Quick test K sometimes increased sharply on both the well drained shoulder slopes (10-20°) and ridge-top campsite areas (0-10°). In contrast, the spatial variability of the Olsen P and Step K results were relatively low on the shoulder slopes and then increased on the well drained ridge-tops, where some very high values were obtained. Step K did not always increase under the ridge-top campsites. The correlation between Step K and soil moisture remained on the ridge-tops, and high values of Step K were not obtained in some ridge-top areas associated with wetter soils where Olsen P increased.

The relationship of pasture production with slope was quite different. The amount of pasture regrowth in an autumn cut increased steadily from the steepest slopes to the ridge-tops, with no change in the variability of the results with slope.

3.5 Conclusions

1. **A wide degree of variation was found for tests of Quick test K (NH_4-exchangeable) and Step K (nonexchangeable K).** The hallmark of steepland pasture is variability. The landscapes in this study were characterised by concave/convex alternations at every scale, associated with large variations in localised aspect and pasture composition. A high degree of variation was found for measures of plant available K in the soils, even at the smallest sampling distance apart, of 0.25 m. In one steepland paddock with mainly sedimentary soil parent materials, the values of Quick test K (a two minute extraction in neutral ammonium acetate) ranged from 0.07 to 1.34 mg K/g soil, which were very low to extremely high values compared to other New Zealand soils. The range of variability may even have been underestimated, as the soil samples were bulked over an area of about 100 mm^2. However, comparisons with other studies suggested that such results were in fact typical of the spatial variability of tests of plant available soil K, but the effect is normally disguised by the practice of bulking soil samples.

   Step K (the difference between Quick test K and an HNO_3 extraction) appeared to have a similar extensive range although few other studies were available for comparison.

   The extensive ranges of results were similar when the tests were repeated in time and at a second site.

   A less extensive survey of Olsen P found values ranging from 7 to 101 ugP/g soil in one paddock, suggesting similar trends for plant available P.

The wide ranges of the distributions indicated, at the two steepland sites tested, that a wide range of soil fertility conditions existed, from fertiliser responsive soils to soils with excessive K and/or P. At present, the soil K status of a paddock is usually evaluated using a single bulked sample. The wide ranges of values indicated that inadequate sampling to create a bulked sample could result in very wide error margins. Even if the test result of the bulked sample does happen to accurately reflect the arithmetic mean of the soil population, the relevance of a single number remains highly debatable as an adequate representative of such a wide ranging population. A better practise for tests of plant available K may be to analyse a number of separate samples so that the distribution can be characterised, rather than bulking the samples together. If the distributions, once characterised, are stable in time, as indicated in this study, and are also similar between farms, as found in this study and as indicated to be likely by Beckett and Webster (1971), then an accurate characterisation may only need to be done occasionally to characterise large areas of pasture soils with similar soil parent materials.

2. **The frequency distributions of tests of Quick test K and Step K were skewed, so that the mode, median and mean were different.** In two steepland pastures the distribution of soil K test results were skewed, so that the arithmetic mean of Quick test K and Step K for the paddocks was higher than 60-70% of the values. Olsen P results were likewise skewed.

   Again, the pattern of soil K distribution raises problems with the common practise of bulking soil samples. The bulking of soil samples disguises skew which, where present, will inflate the impression of the K status of the bulk of the soil in the paddock. In terms of soil sampling, and the transfer of the results of K fertiliser response experiments from one site to another, the skew of the population needs to be characterised at each site.

3. **The spatial variability of the soil tests increased markedly in conjunction with animal campsites.** The spatial variability of Quick test K increased markedly, as the slope decreased to less than 20°, on the relatively well drained ridge-tops associated with animal campsites and the adjacent shoulder slopes. This change was marked by a large increase in the range of values, caused by a small increase in the very lowest values which were obtained, and a very large increase in the highest values which

were obtained. The spatial variability of Step K increased similarly on the flatter areas, but only as the slope decreased to less than 10°, on the well drained ridge-top campsites, in association with increased Olsen P. The marked increases in Quick test K and Step K on the flatter areas appeared to be associated with the sustained exposure of a soil to multiple urine events. Dry conditions would slow the breakdown and dispersal of urine and increase the likelihood of a soil being re-affected by urine before the effect of a previous event had gone from the profile. These effects constituted the main evidence that the process of K transfer, from the steep slopes to the animal campsites, by the grazing stock, was occurring in this landscape. There was only very limited evidence that this process had reduced the K fertility on the steep slopes.

The current recommended practise for soil sampling in hilly country is to avoid obviously dung affected areas on the ridge-tops, targeting the soils that are more likely to be nutrient deficient. The results of this study suggested that sampling for soil K would require the exclusion zone to be extended to the shoulder slopes. Only the steep slopes should be sampled if the soil samples are to be bulked together. However, separate sampling and characterisation of the distribution will still be desirable on the steep slopes, because the range of K fertility would still be extensive and the skew significant.

4. **Step K was linked in a complex way to position in the landscape.** In this study, the Step K test was the difference between NH_4-extractable K (Quick test K) and single HNO_3-extraction (the Acid K test). This test was not the older Step K test that is based on a sequential acid extraction.

   The Step K patterns in the landscapes in this study were found to be largely independent of the pattern of the Quick test K results. On the steeper slopes (>20°), the Quick test K value of a soil had no relationship to the other factors that were measured. The Quick test K distribution in these areas was presumed to be reflecting the range in K status of soil that had never been affected by urine, to soil that had recently been affected by a single urine event. In contrast, the Step K value of a soil on the steeper slopes was strongly related to the position of the soil in the landscape, and was particularly influenced by the soil moisture pattern and the pattern of the soil parent materials. At the Tuapaka site, the principal trend in Step

K value was an increase in value on dry soils associated with the northeasterly exposure of a ridge face. On the steeper slopes at the Bernwood site, the Step K value had some relationship to soil moisture but the principal trend was an increase in Step K value in soils formed in a rapidly eroding band of loose conglomerate in the lower slopes. These variations in Step K on the steep slopes were subsequently found (Chapter 4) to be associated with variations in the K content of the clay fraction of the topsoil.

On the flatter areas of both sites (≤20°), Step K appeared to be mainly influenced by an interaction between animal camping patterns and soil moisture. In conjunction with increases in the Olsen P value in soils under campsites, the Step K value sometimes increased to levels that were as high or higher than those found on the relatively unweathered parts of the steep slopes. The increases in Step K value in the flatter areas appeared to be reflecting an interaction between soil moisture, heavy urine and dung deposition, and the 2:1 layer silicate chemistry of the topsoil. The effect on the 2:1 layer silicate fraction was rather mixed and is discussed further in Chapter 4. Quick test K also increased on these areas but with a different pattern. Olsen P was not always linked to Step K, as, unlike Step K, some large increases in Olsen P were found in areas where animal campsites were associated with relatively wet soils.

Over all, soil exchangeable K and plant available nonexchangeable K were largely independent factors, in these steepland landscapes with mainly sedimentary soil parent materials. If an evaluation of both factors is required for the assessment of the soil plant available K, then the Acid K test was a good indicator of the combined status of both factors in these soils.

Topsoil mineralogy in steepland pasture

Chapter 4

4.1 Introduction

This study examines the mineralogy of two steepland pastures, developed in mainly sedimentary parent materials, on Tuapaka and Bernwood farms, southern North Island, New Zealand (see Chapter 3.2.2 for more information on the sites). The general mineralogy of 2:1 layer silicates, the associated soil K chemistry, weathering processes and definitions of mineral terms, were reviewed in Chapter 2.2.

Previous studies (Chapter 3) have established the relationship between the soil extractable K chemistry and a steepland pasture landscape. On the steeper slopes, distinct patterns were found in the NH_4-exchangeable and acid-extractable K chemistry that were related to the patterns of soil moisture, aspect, and the erodability of the soil parent materials. On the flatter areas, there was a distinctive effect of animal camping (see Chapter 2.4) in some relatively well-drained ridge-top soils. Soil NH_4-exchangeable K, Olsen P, acid-extractable K and pasture production sometimes increased markedly in these areas. The effect was rather erratic, apparently corresponding to animal campsites where drier soil conditions had slowed the breakdown and dispersal of urine. A longer residence time would increase the likelihood of soil being re-affected by urine before the effects of a previous urine event had gone from the soil profile.

In this study, the mineralogy of a subset of the same soils was examined, including the campsites. The effect of animal campsites on the mineralogy of soils rich in 2:1 layer silicates does not appear to have been previously investigated.

McLaughlin (1983) examined the mineralogy of two soil profiles at sites adjacent to the Tuapaka site in this study. One profile was at the highest altitude of the present paddock, on an ancient partially loess covered (with some volcanic ash) uplifted greywacke surface. The second profile was in a paddock adjacent to the lower end of the present site, developed in loess and volcanic ash deposited over greywacke gravels. The clay mineralogy of the A and B horizons of both profiles was dominated by vermiculite, interlayered to various degrees by hydroxy polymers. The soils of the present Tuapaka study site have developed at altitudes that were between these two profiles.

The Tuapaka study area was characterised by deeply dissected valleys, with many exposures of greywacke bedrock on the steeper slopes. Much of the loess and ash has been stripped away from the flatter areas and the soil profile depths were relatively shallow, with weathered greywacke present in the profile at about 50 cm depth on the flatter areas and as little as 6 cm depth on the steeper slopes. The soils on the slopes are relatively stable, with occasional tunnel gullies and slip scars (Cowie, 1978; Pollok and McLaughlin, 1986).

No such detailed previous study was available for the second site, on Bernwood farm. The soils of this site have formed on an uplifted band of sandstone capping a layer of loose conglomerate. The site is expected to have been exposed to loess and some volcanic ash, although little might now remain. The soil parent materials are evidently highly susceptible to erosion, with extensive slip scars on the slopes. Blaschke et al. (1992) found that hilly pasture soils formed in weathered sandstone had lost soil, since deforestation, at a rate of 2 mm/year and that the average ground surface age was about 450 years. (More information about the sites is available in Chapter 3.2.2).

4.1 Materials and methods

4.2.1 Soil Sampling and testing.

Two separate sets of topsoil samples were examined in this study. The first set of 32 samples was a subsample of the 90 topsoil samples taken from Tuapaka in the first survey (Chapter 3.3). The set included; all six samples lifted for vectors B, G and J (25 m strings laid out on adjacent ridge faces with northeasterly and southerly aspects and a ridge-top), the samples taken at 10 m along each of the remaining 12 sampling vectors, and also three samples from vector O, which had shown rather different K chemistry. Subsequently, the mineralogy of a second set of 16 topsoil samples was examined from samples lifted for the second survey, consisting of four more samples from the Tuapaka site and 12 samples from the Bernwood site (Figures 4.1 and 4.2). Quick test K, Step K, Olsen P, soil moisture and slope information was cross-referenced for these samples from the previous soil surveys (Chapter 3).

All the soil samples were obtained from the top 75 mm of the soil profile by standard soil corer, as described in Chapter 3. Only green pasture and loose litter was removed from the soil surface prior to sampling. After the soil cores had been air dried, the soil was sieved (<2 mm).

4.2.1.1 Soil pH

Soil pH tests were conducted on all samples used in the mineralogy study. 10g of soil (air dry, <2mm) was mixed well in 25 ml of distilled water and left to stand overnight. The following day the pH of the supernatant solution was measured by KCl electrode. (Blakemore et al., 1987)

4.2.1.2 Kc extraction

The Kc extractions were conducted on the 32 samples that were also used for the first mineralogy study set, from the Tuapaka site only. The Kc test consisted of first boiling the soil at a 1:100 ratio in 1M HNO_3 (2g in 200ml) for 20 mins, using a 'cold finger" condenser to prevent the loss of water. This first extract was then washed into a centrifuge tube and the supernatant discarded after centrifuging (the discarded portion

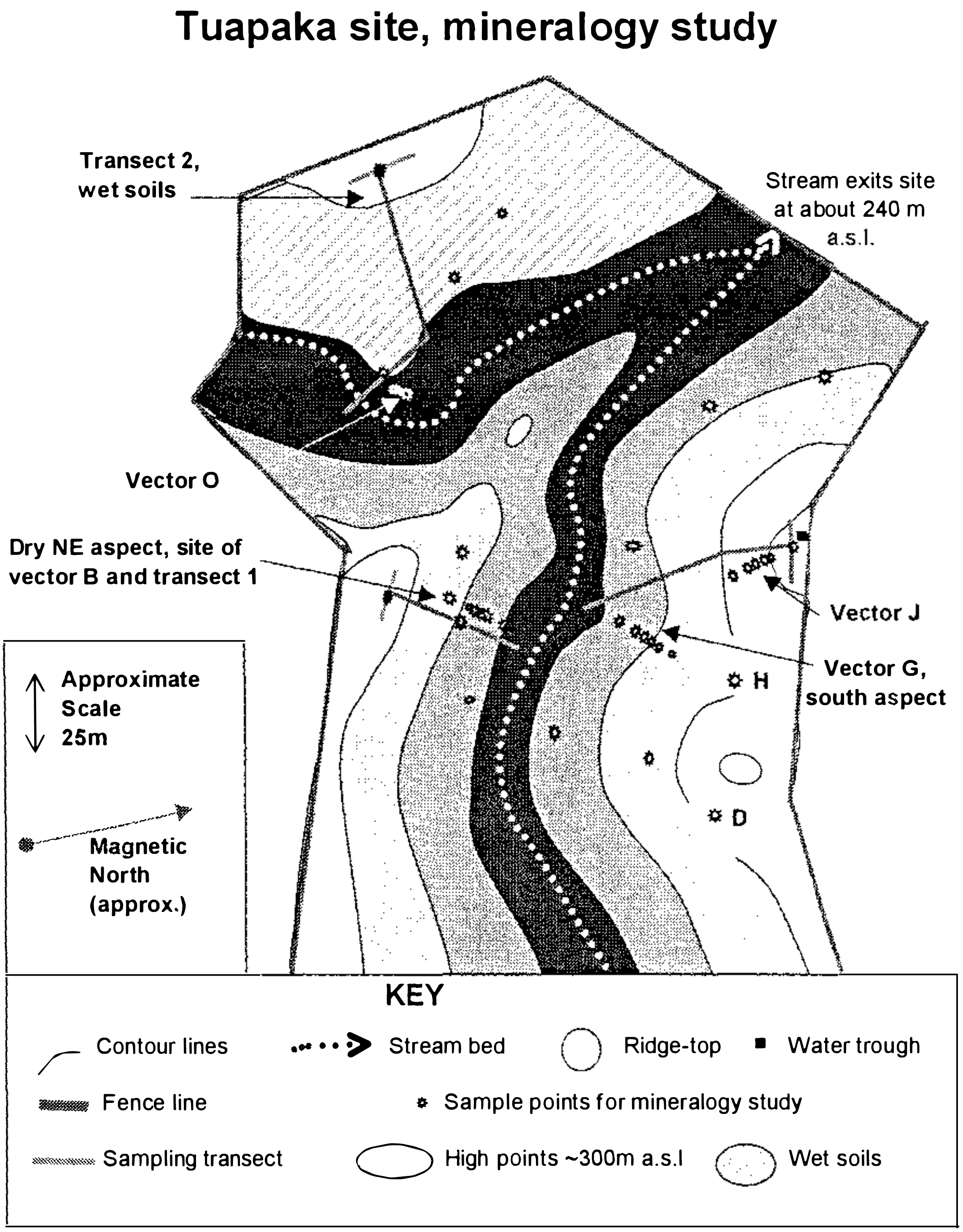


Figure 4.1: Diagram of the Tuapaka site showing the approximate location of the topsoils sampled for the mineralogy study in relation to layout of the sampling transects used in the second survey (Chapter 3.4) (lighter shades indicate increasing altitude).

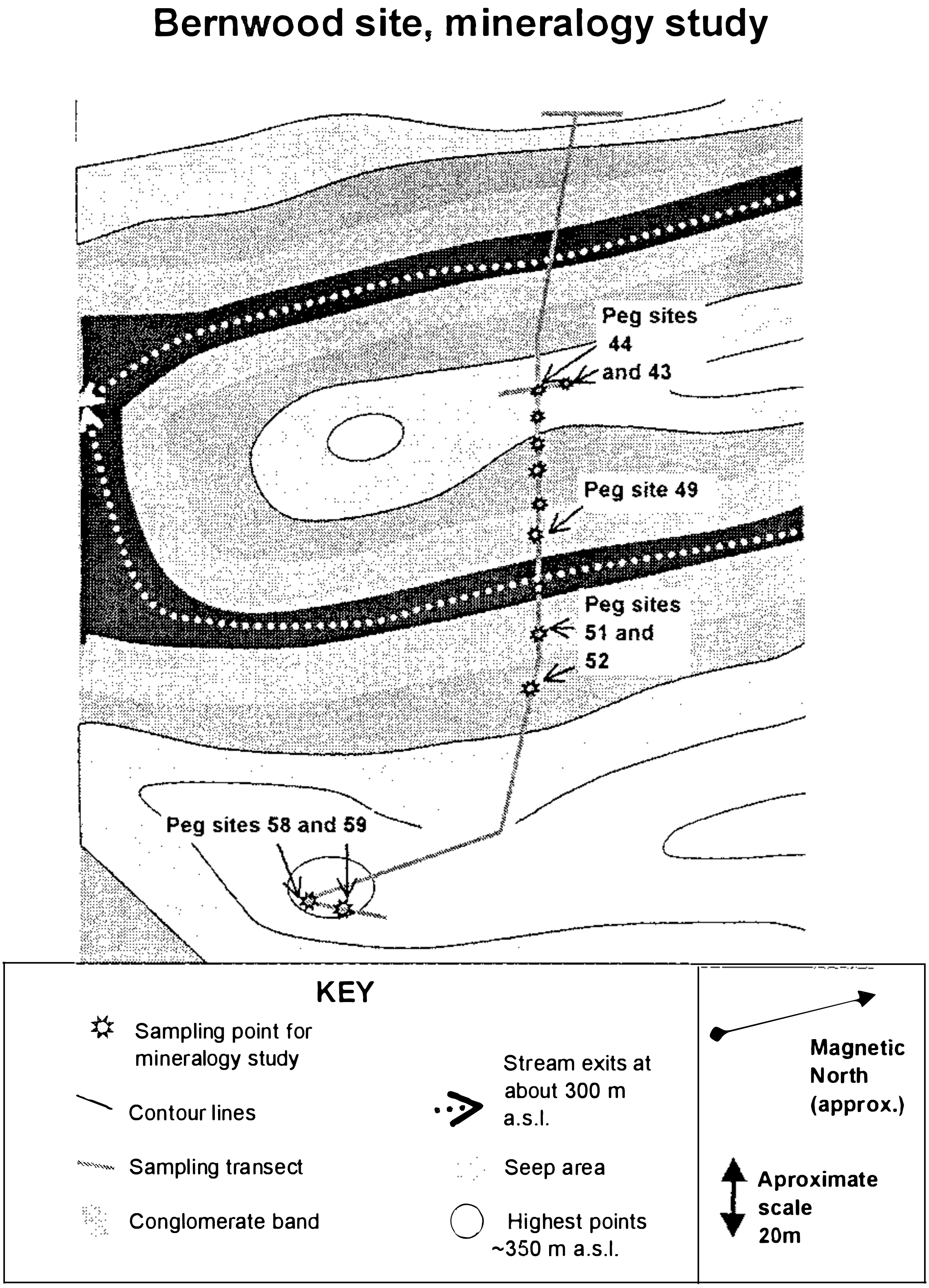


Figure 4.2: Diagram of the site on Bernwood farm, showing the approximate location of the soils sampled for the mineralogy study, in relation to layout of the sampling transects used in the second survey (Chapter 3.4) (lighter shades indicate increasing altitude).

was analogous to the Acid K test in this study). Three more extractions were then made on the substrate at a 1:12.5 ratio, boiling for 10 minutes in 25 ml of 1M HNO_3, and removing the supernatant by washing and centrifuging. The K content of each supernatant solution of the 1:12.5 extractions was then determined by atomic emission spectrophotometry, and an average found, to provide the Kc value (Blakemore et al., 1987).[1]

The Kc test was developed by Metson et al. (1956) as a measure of the rate of release of K from very slowly plant available nonexchangeable K sources in the soil, which supply K to the more rapidly plant available nonexchangeable K fraction (Step K). Metson et al. (1956) suggested that for soils to be deficient in K, both the Kc and Step K values would need to be below 0.3 cmol K/kg soil (0.12 mg K/g soil). Although Kc was developed as a rate of supply test, it has also been found to be related to the extent of K depletion in soils (Metson, 1980). Consequently, the test has come to be regarded as a general measure of the plant available K reserves. The average Kc values of the reference soils of the major soil groups have been incorporated into a K fertiliser requirements model for New Zealand soils (Cornforth and Sinclair, 1984; Campkin, 1985).

4.2.2 Mineralogical analysis

A mineralogical analysis was carried out using the standard analysis methods of Whitton and Churchman (1987), summarised as follows.[2]

Following the removal of calcium carbonate with 1:1 HCl, the organic matter was removed from approximately 10g of soil, using 10 ml of "100 volume" H_2O_2. Samples were stood for several days in the peroxide, then heated on a water-bath, diluted and centrifuged. Iron and aluminium oxides and oxyhydroxides were then removed using successive digestions with citrate dithionate solution.

The clay fractions (0.002 μm) were separated out using timed centrifuging, and ultrasonic separation. Silt and sand mixtures were redispersed and separated by successive timed gravity settling. 1-2 ml aliquots of the silt fraction were laid out on

---

[1] The Kc extractions were carried out by Dr A. Surapaneni.

[2] The mineralogical analysis was carried out with the supervision and assistance of Mr J.S. Whitton.

slides and left to air dry. Heavy minerals and volcanic glasses were separated from the sand fraction by suspension and centrifuging in two densities of sodium polytungstate (2.9 and 2.45 g/cm respectively). These samples were then filtered, washed and dried, and examined optically, and the heavy mineral fraction was examined by x-ray diffraction. Slides of the sand fraction were prepared by grinding a sample in a mortar and pestle, and then mounting the sample on a slide in acetone.

Various treatments were applied to the separated clay fractions. The bulk of a suspended clay fraction was saturated with $MgCl_2$ to open all expansible interlayers, then reflocculated, washed, laid out on slides in 1-2ml aliquots and allowed to air dry. A small amount of each clay fraction was saturated with KCl, to shut down all expansible interlayers, then reflocculated, washed, and mounted on slides in the same way.

50 mg of the Mg-saturated clays were also finely ground and packed into a furnace cup for differential thermal analysis (DTA). This process measured the amount of kandite (kaolinite plus halloysite) and gibbsite in the sample based on the endothermic and exothermic patterns as the sample was heated or cooled.

All slides were examined by x-ray diffraction. Drying the clay minerals on the slide causes them to form orientated stacks with consistent distances between the layers, depending on the cation with which the clays have been saturated. The slide is then scanned with x-rays at a range of angles of incidence and the various interlayer spacings diffract the x-rays in characteristic patterns. Some of the diffraction patterns of the clay minerals overlap, so various treatments are applied to open and shut the interlayers and generate characteristic changes in the diffraction pattern.

The prepared slides were first x-rayed in air. Then the Mg-saturated clays were sprayed with 10% glycerol to fully expand the smectite interlayers and x-rayed again. These slides were then heated to 550°C to collapse any hydroxide material in the interlayer spaces and then re-x-rayed. K-treated clay slides were also heated in sequences of 100°C rising to 550°C and x-rayed at each stage. This procedure successively collapsed any hydroxide polymer material in the interlayer spaces.

The relative amount of each mineral present was then apportioned based on the relative area under each principal diffraction peak. The expected methodological error was 10 to 20% of the quantitative estimate, if the particular mineral constituted 20% or more of the whole clay fraction. Quantitative estimates of interstratified clay minerals and also estimates for clay minerals that constitute less than 20% of the clay fraction are subject to higher expected error, up to 50% of the estimated quantity.

4.2.3 Major oxides

A selected range of the topsoil samples were analysed for the major oxides; SiO_2, Al_2O_3, Fe_2O_3, Na_2O, CaO, K_2O, MgO, TiO_2, P_2O_5, MnO by X-ray fluorescence (XRF) analysis. Also included were two soil cores of 100 * 100 * 100 mm, split into 25 mm depths, lifted from peg sites 52 and 58 (Figure 4.2).[3]

4.3 Results and discussion

4.3.1 Kc

The distribution of the Kc values had a wide range, encompassing the very low (<0.04 mg K/g soil) to very high classes (>0.2 mg K/g soil) proposed by Metson (1980) (Table 4.1). The Kc values had a Normal distribution (see Chapter 3.2.1.1), so the median was similar to the mean. The wide range of Kc values in this study supported the conclusion of Surapaneni (1994) who found that both Step K and Kc were quite variable within one soil group and should be measured at each site if they were to be used to model K fertiliser requirements.

Table 4.1: Distribution of Kc values (mg K/g soil) and correlation to other soil K tests. Results for Kc were obtained from 32 topsoil samples from the Tuapaka site.

	Distribution				Correlation	
	Mean	C.V.	Median	Range	Quick test K	Step K
Kc	0.14	36%	0.16	0.02-0.26	0.05 (p=0.79)	0.75 (p=0.0001)

The Kc method extracted approximately a quarter of the amount of K extracted from a soil by the Step K test (method Chapter 3.3.2.5). Although the two tests measured different nonexchangeable K fractions, and had different population distributions, they

---

[3] The XRF analysis was carried out by SpectraChem Analytical Ltd., after Kennedy et al. (1983).

had a reasonable correlation at this site (Table 4.1). Removal of one outlier, from a ridge-top animal campsite with a very high Step K value and a disproportionately low Kc value, further improved the correlation between the two tests (r=0.88). No relationship was found between the Quick test K value and the Kc value of a soil.

4.3.2 Soil pH

The distribution of the pH values was Normal (see Chapter 3.2.1.1), so the mean (pH=5.5) matched the median (Table 4.2). The pH ranged from 5.1 to 6.0 at Tuapaka (strongly acid to slightly acid) and 5.3 to 5.8 at Bernwood (moderately acid) (Blakemore et al., 1987). The average pH at each property was the same (5.5). The low statistical variability was an artefact of the pH log scale (Boyer et al., 1996).

Table 4.2: Distribution of the pH (water) results, and correlation to other soil K tests. Results for pH are from 47 samples from the Tuapaka and Bernwood sites.

	Distribution				**Correlations**	
	Mean	**C.v.**	**Median**	**Range**	**Quick test K**	**Step K**
PH	5.5	4%	5.5	5.07-6.0	0.19 (p=0.21)	0.09 (p=0.05)

There was no significant linear association between soil pH and any other factor that was tested. Two ridge-top areas that were associated with marked increases in Quick test K, Step K and Olsen P were also associated with an increased average soil pH of 5.7. Rowarth (1987) also found a significantly higher soil pH in animal campsites compared to the steeper slopes.

4.3.3 Mineralogy of sand and silts

The sand fraction of the topsoils at the two sites mainly consisted of quartz (average content, 68%), with approximately 15-25% feldspar. The sand fractions also contained 2-7% heavy minerals, 2-14% volcanic glass and occasional trace amounts of mica.

An exception to these trends was found in three samples obtained from a foot slope next to a stream at the Tuapaka site (vector O). These samples contained smaller proportions of quartz with much more feldspar (30-35%) and heavy minerals (10-12%). Subsequent analysis of the major oxides (Section 4.3.5) indicated that these soils had probably formed in a mixture of basaltic and greywacke parent materials that were atypical for the site.

The heavy minerals in the sand fraction of the topsoils at the two sites were from a mixture of volcanic ash (magnetite, hypersthene, augite and hornblende) and greywacke (epidote) origins. There was a fairly even mixture of the various heavy minerals in the Tuapaka soils, except for the three vector O samples, which were dominated by epidote. The samples from the Bernwood site were also dominated by epidote.

The silt fractions of the topsoil samples at both sites contained quartz (average 43%), with feldspars ranging from approximately 20-30% and plant opal ranging from 20-35%. The silt fractions of the Tuapaka soils generally contained only trace amounts of mica, while the Bernwood soils generally contained about 10% of a combination of mica, interlayered mica-vermiculite (MV) and interlayered mica-smectite (MS). Trace amounts of chlorite were also recorded in some silt fractions at both sites.

Some samples from the Bernwood site formed an exception to the trends of the silt fraction. These samples were obtained from topsoils associated with exposures of a loose conglomerate in the lower slopes of the Bernwood site. These soils contained relatively low quantities of plant opal (8%), and relatively high quantities of mica, MS and MV (about 30%) of the silt fraction. These samples appeared to be formed in relatively unweathered parent materials. The conglomerate parent material was very loose and susceptible to stock trampling that would continually push topsoil material down-slope and expose new, relatively unweathered parent materials to the surface. A soil sampled beside a stream directly below the sites in the conglomerate material also had similar properties, consistent with the colluvial accumulation of the finer material from between the gravels.

The greywacke derived parent materials at these sites was expected to consist of quartz, feldspar and also biotite, a trioctahedral mica that is highly susceptible to weathering (Wells and Furkert, 1973). The lack of mica in the sand and silt fractions of the topsoils, in all but two samples, suggested that any biotite or other mica that may have been present in the sand and silt fractions of the original parent materials has now weathered to form clay sized mica, probably dioctahedral illite. Topsoil under pasture is expected to be a strongly weathering environment for biotites (Chapter 2.3.1).

4.3.4 Clay mineralogy

The clay fraction of the topsoils was examined using XRD and DTA analysis.

4.3.4.1 XRD traces

The XRD traces of the first mineralogy set had strong peaks with low background. The traces of Mg-saturated clay sprayed with glycerol had well defined peaks, representing 7.2 A°, 10 A°, 14 A° and 28 A° interlayer spacings, with a reasonably distinct shoulder on the 14 A° peak representing 12 A° spacings (Figure 4.3, top two traces). The traces were not as well defined for the second set of samples. A red tinge in the clays of the second set indicated that the citrate dithionate pretreatment may not have removed the oxide and hydroxide material as thoroughly as for the first set.

Some particular samples in both sets were characterised by a very poorly defined 14 A° peak (Vector J, Figure 4.3, bottom trace). The poor peak definition indicated the presence of poorly formed, irregularly interstratified mixtures of expanded 2:1 layer silicate material. The samples with the irregularly interstratified material in the first set of samples were all from well-drained ridge-top campsite topsoils. The same effect was also apparent in the second mineralogy set, despite the less distinct traces, and again all of these samples were from well drained animal campsites on ridge-tops. The reasons for the effect are explored further in Section 4.3.4.2. The assignment of MS and MV classes in the clay fraction, which imply regular interstratification, was not particularly appropriate for these samples, although the classes were carried through for convenience.

4.3.4.2 Assigned mineral proportions and variability

The method of Whitton and Churchman (1987) was used to assign the proportion of the various minerals in the clay fraction identified in the XRD traces.

Approximately 35-45% of each clay fraction was a combination of quartz, feldspar, and kandites (Table 4.3). The variability (c.v.) of these minerals was relatively low, compared to the 2:1 layer silicates.

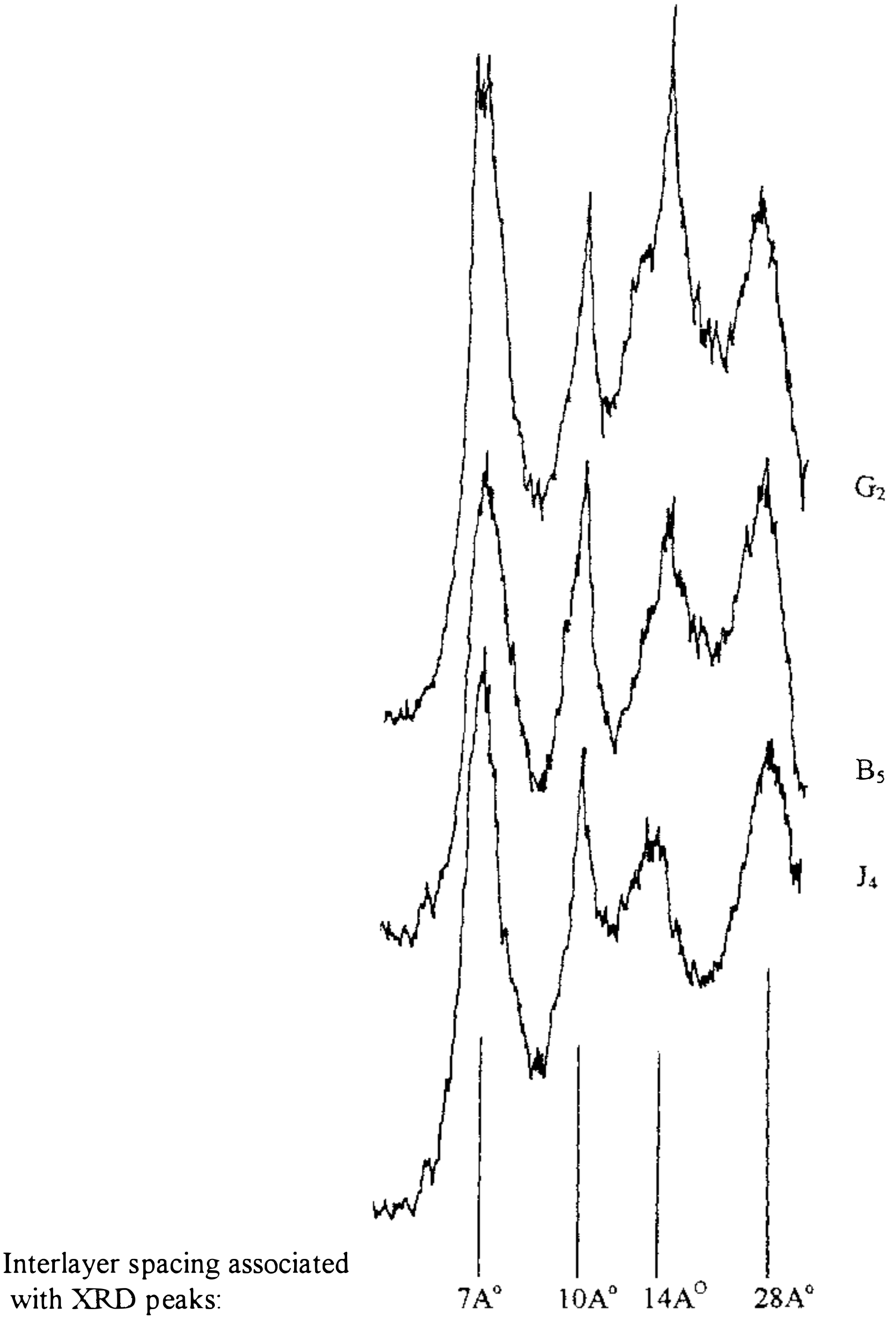


Figure 4.3: XRD traces of Mg-saturated steepland topsoil clay fractions, sprayed with glycerol. The top trace (G2) was from a soil on a typical steep slope. The middle trace (B5) was from topsoil on a steep slope with a dry northeasterly exposure. The bottom trace (J_4) was from a ridge-top soil associated with a water trough and high exchangeable K and P levels, indicating an animal campsite. There is a characteristic lack of definition in the part of the trace associated with 12 and 14 A°, indicating irregular interstratification of the expanded phases.

Approximately 55-65% of each clay fraction was a variable mixture of 2:1 layer silicate clays. Many of the clay fractions of the topsoils contained interlayered mica-smectite (MS) as well as 'pure' mica. Small amounts of smectite, chlorite and interlayered mica-vermiculite (MV) were also found in some clay fractions (Table 4.3).

Table 4.3: Mineralogy of the clay fraction of topsoils (75 mm depth) from two steepland pasture sites. Results are presented as averages, with the coefficient of variation in brackets. The distribution of the mineral components was relatively normal, so that the skew and kurtosis of the mineral distributions were less than one and the median value was similar to the mean.

		Minerals in clay fraction (%)								
	N	**Quartz**	**Feldspar**	**Kandites**	**Mica**	**MS**	**MV**	**Chlorite**	**HIV + Vermiculite**	**Smectite**
Tuapaka site	36	11 (27%)	4.5 (33%)	32 (19%)	13 (65%)	13 (47%)	3 (89%)	3 (85%)	19 (67%)	0.4 (450%)
Bernwood site	12	4.5 (20%)	5 (30%)	25 (13%)	16 (60%)	9 (67%)	7 (69%)	3 (64%)	27 (36%)	3 (117%)
Both sites	48	9 (41%)	5 (32%)	31 (21%)	14 (64%)	12 (52%)	4 (94%)	3 (80%)	21 (59%)	1 (300%)

All the samples contained some vermiculite or hydroxy interlayered vermiculite (HIV). Vermiculite is a catch-all term for 2:1 layer silicates with a layer charge between mica and smectite (See Chapter 2.2). In temperate soils, vermiculite is often interlayered with the smaller sized Al-hydroxy polymers. The citrate dithionate treatment will remove some interlayer hydroxy polymer material, but not all, so the assignment of vermiculite or HIV is rather dependent on the thoroughness of the pretreatments (Bautista-Tulin and Inoue, 1997). As indicated in the previous section, this treatment did not appear to be consistent between the sets examined, and the proportion of vermiculite to HIV was different between different laboratory analysis sets for samples obtained from similar field sites. To prevent this effect from causing bias in the analysis of the results, the assigned proportions of vermiculite and HIV for each clay sample were henceforth usually combined and referred to in the plural as “vermiculites”.

4.3.4.3 Correspondence analysis of the clay fraction

To elucidate any patterns of association between the mineral factors or with site the clay fraction information was examined by correspondence analysis. The method and interpretation of this statistical technique have been previously explained (Chapter 3.2). Because the clay fraction results were in the form of percentages the data could be analysed directly by correspondence analysis. The smectite content of the clay fraction was not included in this test, because the extreme variability of this minor factor would have dominated the results.

Correspondence analysis could account for 75% of the total variability in the clay fraction results. Most of the information (59% in the first dimension) could be described as a contrast of mica and MS against the vermiculites (vermiculite plus HIV), with a smaller contribution from chlorite, which was associated with the vermiculites (Figure 4.4a).

A second, relatively minor, relationship (second dimension) accounted for a further 16% of the variability and mainly expressed the differences between the results from the two sites. Results from the Tuapaka site were largely sorted onto the lower half of the plot, in association with quartz and MS, indicating the higher proportion of quartz and MS in some Tuapaka samples, compared to the Bernwood site. The Bernwood results were largely sorted onto the upper half of the plot and associated with mica and MV, indicating the higher proportions of mica and MV in some Bernwood samples.

The correspondence analysis indicated that much of the information in the data set could be accounted for by adding together the mica and MS fractions, and comparing this with the vermiculites (vermiculite + HIV). A very strong antagonistic relationship was found between the combined factors (correlation $r=-0.83$, $p=0.0001$) (Figure 4.4b). The clay fractions ranged from 48% mica plus MS with 7% vermiculites in one sample, to 52% vermiculites in the clay fraction with no mica present in another sample. A good way of expressing this relationship was thought to be the ratio of mica + MS to vermiculites (vermiculite + HIV) in a topsoil, termed the mica:vermiculite ratio in this study.

Compared to the dominating continuum between the micas and the vermiculites in these topsoil samples, other trends in the mineralogy of the two sites were relatively minor. The small amounts of chlorite (and smectite) were generally associated with the presence of the vermiculites, while MV appeared to be rather indeterminate intermediate product, with no particular associations. The lack of association between the kandites and the

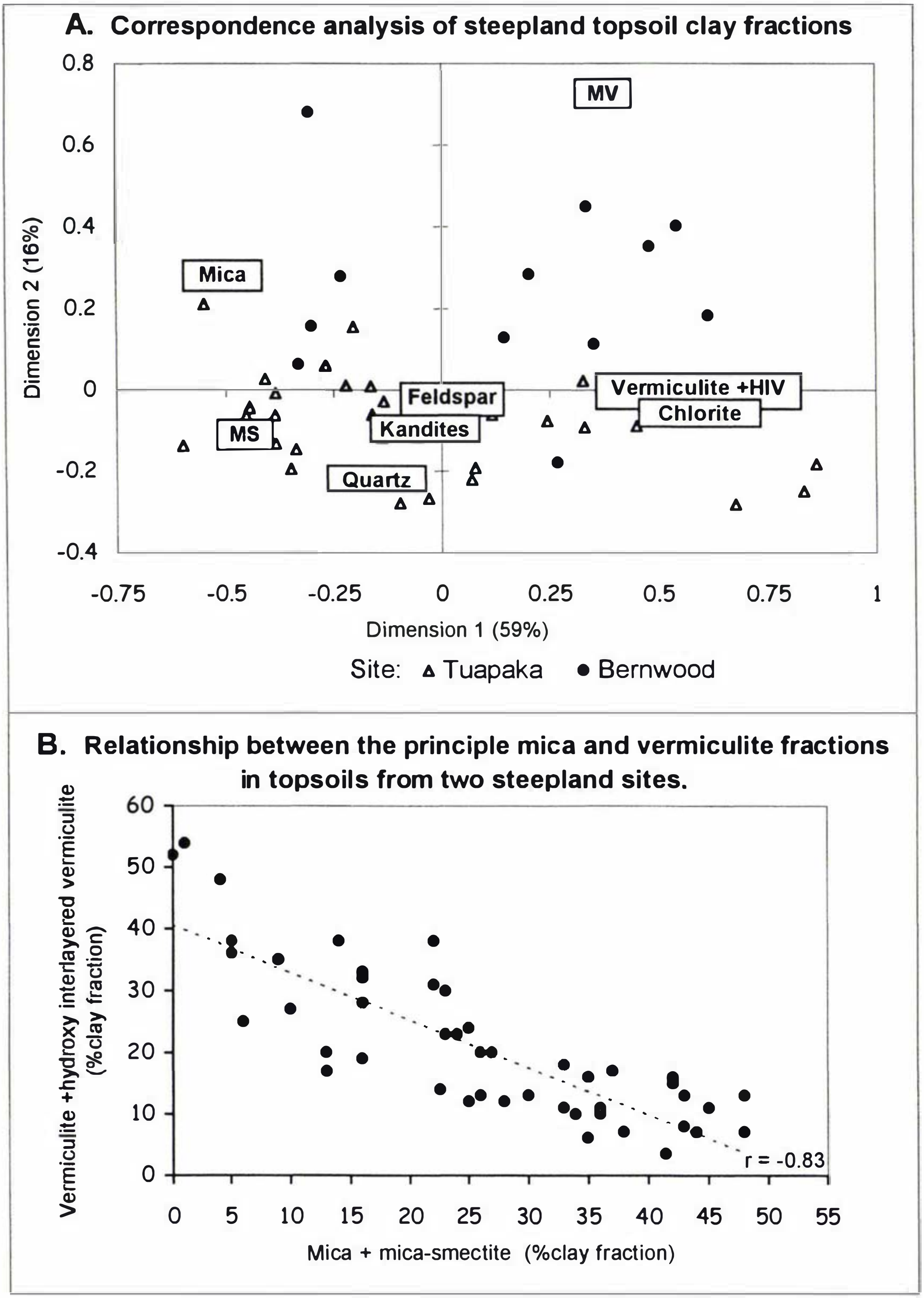


Figure 4.4: Correspondence analysis of the mineralogical analysis of the clay fraction of the topsoils in two steepland pasture sites, Tuapaka and Bernwood. MS = mica-smectite. MV = mica-vermiculite. HIV= hydroxy interlayered vermiculite. (A). Relationship between the principal vermiculites (vermiculite + HIV) and micas (mica + MS) in the clay fraction of steepland topsoils (B).

2:1 layer silicate sequence suggested that the kandites are more likely to be the weathering products of the feldspar and/or have been inherited from the greywacke, than to be weathering products of the 2:1 silicates.

Churchman (1980) examined a sequence of South Island micaceous high country soils and found mica and chlorite dominated profiles in dry areas. In higher rainfall areas, MV and MS were dominant under tussock and smectite and vermiculite formed under the more acid and stronger podzolising conditions of beech forest. Harrison et al. (1990) found similar trends in two other sequences of micaceous high country soils.

Wells and Furkert (1972 & 1973) surveyed the mineralogy of topsoils on Taita Research Station in New Zealand. The site mainly consisted of soils developed in loess on solid greywacke, very similar to the Tuapaka site in this study. A very similar mix of quartz, feldspar, kandites, mica, vermiculite, irregularly stratified 2:1 layer silicates and amorphous material was found. The variability was also similar. The principal 2:1 layer silicates had an average c.v. of 74% within each soil type, and a less variable content of quartz, feldspar and halloysite. It may be concluded that highly variable mixtures of 2:1 layer silicates are typical of steepland soils with sedimentary parent materials, at a moderate rainfall and altitude. It is interesting that the mineralogy of the Bernwood site was quite similar to the mineralogy of the Tuapaka and Taita sites, even though the soil parent materials were rather different.

A conventional way of representing the various 2:1 layer silicate clays found in the present study would probably be a weathering sequence of mica ⇒ MV⇒MS⇒vermiculite ⇒HIV⇒chlorite, with mica ⇒ MV⇒MS⇒smectite ⇒chlorite in wetter areas (Tributh, 1987). However, the clays in a soil probably exist as a continuous 2:1 layer silicate complex rather than as discrete units (Churchman, 1980). This approach was supported by the correspondence analysis and correlation results in this study, in particular where the combined mica and MS clay fractions had a strong negative correlation to the vermiculites. The 2:1 layer silicates identified in each topsoil were thought to be part of a clay complex that varied throughout the landscape from a relatively highly charged complex, with many K rich micaceous interlayers and some smectitic interlayers, to a moderately charged complex, with some micaceous interlayers and many vermiculitic interlayers, which were low in K and rich in hydroxy polymers.

4.3.4.4 Mineralogy and the steepland environment

The relationship between the nature of the 2:1 silicate complex in a topsoil and the position of a topsoil in a steepland landscape could be explored by comparing the mineralogy with the soil extraction results, which were more extensively surveyed at the the two sites (Chapter 3). The clay fraction content of mica, MS, both mica fractions added together, and the vermiculites (vermiculite and HIV) were compared with the Quick test K, Step K and Kc values of the whole soil in the same samples (Tables 4.4 and 4.5). When all the mineralogy data was considered, Step K and Kc had strong correlations with the principal 2:1 layer silicates, although they were not exactly the same. Step K had a stronger correlation to mica, compared to the other minerals, while Kc had a similar correlation to all the mineral components. There was no linear relationship between Quick test K value and the composition of the clay fraction.

Table 4.4: Various correlations of clay mineralogy with soil tests for K, at the Tuapaka site only, between both sites, and separated into the steep slopes and flatter areas of both sites (see Chapter 3 for information on the soil tests and statistics).

	Tuapaka only n=32		**Tuapaka and Bernwood,** n=48		**Step K**	
	Step K	**Kc**	**Quick test K**	**Step K**	**≤ 20° slope** n=16	**>20° slope** n=32
Mica	0.87 (p=0.0001)	0.79 (p=0.0001)	0.35 (p=0.02)	0.79 (p=0.0001)	0.63 (p=0.009)	0.88 (p=0.0001)
MS	0.70 (p=0.0001)	0.71 (p=0.0001)	0.09 (p=0.51)	0.57 (p=0.0001)	0.52 (p=0.04)	0.57 (p=0.0007)
Mica + MS	0.82 (p=0.0001)	0.78 (p=0.0001)	0.27 (p=0.06)	0.79 (p=0.0001)	0.69 (p=0.0032)	0.83 (p=0.0001)
Vermiculites +HIV	-0.68 (p=0.0001)	-0.79 (p=0.0001)	-0.2 (p=0.17)	-0.68 (p=0.0001)	-0.60 (p=0.01)	-0.71 (p=0.0001)

The strong relationship between the Step K test results and mica content of the clay fraction could be used to link the relationships that were previously found between Step K value and position in a steepland pasture landscape (Chapter 3), to the trends in the clay mineralogy. The mineralogy results were divided into soil samples from sites that had greater than or less than 20° of slope (Table 4.4). These two groups corresponded to the difference between the rolling or flat topography on the shoulder slopes and ridge-tops and the steep topography on the main slopes of the ridges. This division was previously found to provide a good separation of soil on the flatter areas that may be

Table 4.5: Clay mineralogy of topsoils from various areas of the Tuapaka and Bernwood sites (Figures 4.1 and 4.2 for location maps). The mineralogy results are presented as a percentage of the clay fraction, as well the sums and ratios of the principal mica and vermiculites. Dotted underlining in lines A and I indicates the presence of irregularly interstratified material in the expanded 2:1 layer silicate fraction. Associated soil test information is also shown for whole soils of the same samples; exchangeable K (Quick test K), plant available non-exchangeable K (Step K), the combined test (Acid K), long term reserve K (Kc), Olsen P, pH, slope and soil moisture.

Line reference and soil sample location descriptions	No. Samples	Slope (degrees)	Soil pH	Acid K test (mgK/gsoil)	Quick test K (mgK/gsoil)	Step K test (mgK/gsoil)	Kc test (mgK/gsoil)	Olsen P (µgP/gsoil)	Soil miosture (%)	Quartz	Feldspar	Kandites*[1]	Chlorite	Smectite	MV	MS	Mica	HIV	Vermiculite	Total Mica *[2]	Total Vermiculites*[3]	Ratio: micas /vermiculites *[4]
										% of clay faction												
TUAPAKA FARM																						
A Ridge top: vector J, transect 3	6	9	5.7	1.50	0.48	1.0	0.16	51	52	11	4	36	0.3	0	2	20	21	0	8	41	8	5.1
B Ridge top, seep zones, vectors H&D	2	15	5.4	0.65	0.21	0.44	0.12	.	.	11	4.5	39	5	0	5	8	5	0	19	13	19	0.7
C Steeper slopes with south aspect	10	25	5.4	0.74	0.22	0.52	0.13	23	67	11	4	33	4	0	5	13	11	0	18	24	18	1.3
D Ridge top: dry soils, transect 1	1	5	5.2	1.83	0.48	1.36	.	55	43	8	1	43	2	0	0	18	18	0	11	36	11	3.3
E Steeper slopes on dry NE aspect.	9	38	5.5	1.01	0.12	0.89	0.19	29	40	14	6	31	1	0	1	16	19	0	14	35	14	2.5
F Ridge top: wet Korokoro soil, transect 2	1	20	.	0.63	0.29	0.34	.	31	65	6	4	29	4	11	0	15	8	.	23**	23	23	1
G Steeper slopes, wet Korokoro soils	3	30	5.3	0.49	0.13	0.36	0.06	15	58	12	6	27	6	2	6	9	9	.	25**	18	25	0.72
H Vector O, alluvial toe slope	3	22	5.6	0.34	0.20	0.14	0.03	16	61	5	4	30	7	0	0	1	0	.	51**	1	51	0.02
BERNWOOD FARM																						
I Ridge top: Peg site 58 and 59	2	7	5.7	1.68	0.88	0.80	.	34	46	4	3	24	2	2.5	8	12	31	0	15	43	15	2.9
J Ridge top: Peg sites 43 and 44	2	8	5.4	0.86	0.33	0.53	.	26	51	5	6	26	2	0	10	5	14	23	12	19	35	0.5
K All upper slopes, transects 2&3	5	37	5.5	0.52	0.11	0.42	.	22	46	5	6	26	4	2	8	7	8	21	13	15	34	0.4
L Conglomerate band, peg sites 49 & 51	2	48	5.5	0.75	0.09	0.66	.	30	45	4	5	23	4	8	0	16	26	5	11	42	16	2.7

*[1] Kandites=kaolinite and halloysite *[2] Mica and MS *[3] Vermiculite and HIV *[4] Total Micas/Total Vermiculites **HIV included with the vermiculite

affected by animal camping and soil on the steep slopes that had no marked effects of animal camping (Chapter 3.4).

Mineralogy on the steep slopes

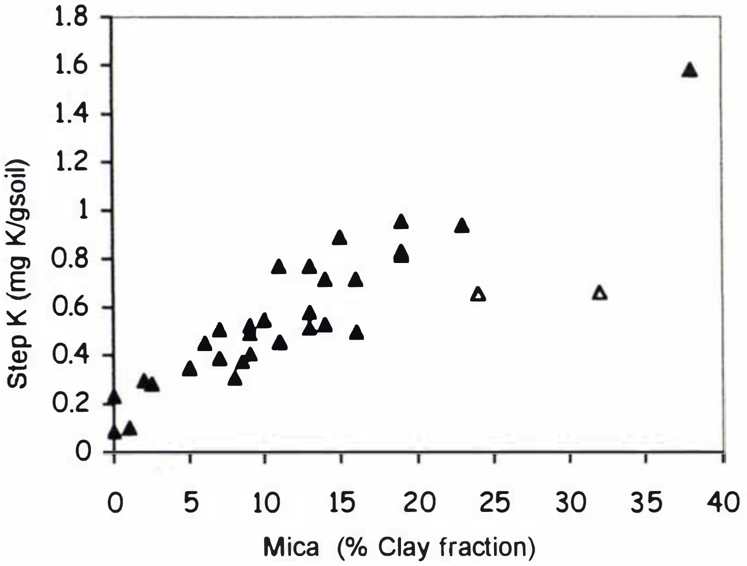
The correlations between the principle 2:1 layer silicates (particularly mica) of the clay fraction of a soil and the Step K value of the whole soil were very strong on the steep slopes (Table 4.4, Figure 4.5a).

Where Step K was previously found to be high (>0.6 mgK/gsoil) on a northeasterly slope with dry soils at the Tuapaka site, the soils had a relatively high mica content (10-38 % mica), and a relatively high mica:vermiculite ratio (between 1 and 8) (Table 4.5, line E). The soils in this area were reasonably stable, with no recent slip scars or tunnel gully formations in the area that was sampled, so the high mica content did not appear to be the result of the exposure of fresh parent material. The soil weathering environment in these slopes has evidently been gentle enough to conserve a 2:1 silicate complex of relatively high charge and high K content. The mica and MS in the clay fraction may have been present in the current form in the original parent materials or it may be the secondary weathering product of less stable clay, silt or sand sized micas, such as biotite, which were present in the soil forming parent materials and have since reassembled to a more stable mica structure, such as a dioctahedral illite, illite-smectite complex (Righi et al., 1995).

The majority of the soils on the slopes at both sites were associated with wetter soils and a medium range of Step K values (0.2-0.6 mgK/gsoil). These soils were found to have a mica content that ranged between 2 and 16 % of the clay fraction, and mica:vermiculite ratios between 0.1 and 3 (Table 4.5, lines C, G and K). A mica and MS dominated complex is thought to be weathering to a vermiculite and HIV dominated complex in these soils.

One small patch of soil at the Tuapaka site was associated with low Step K values (<0.2mgK/gsoil). These soils had 0-1% mica in the clay fraction, which mainly consisted of HIV (Table 4.5, line H). The soils were thought to be formed in a mixture of alluvial basaltic and greywacke parent materials (Section 4.3.5).

A. Step K and mica on slopes of more than 20 degrees, both sites



B. Step K and mica on slopes less than or equal to 20 degrees, both sites

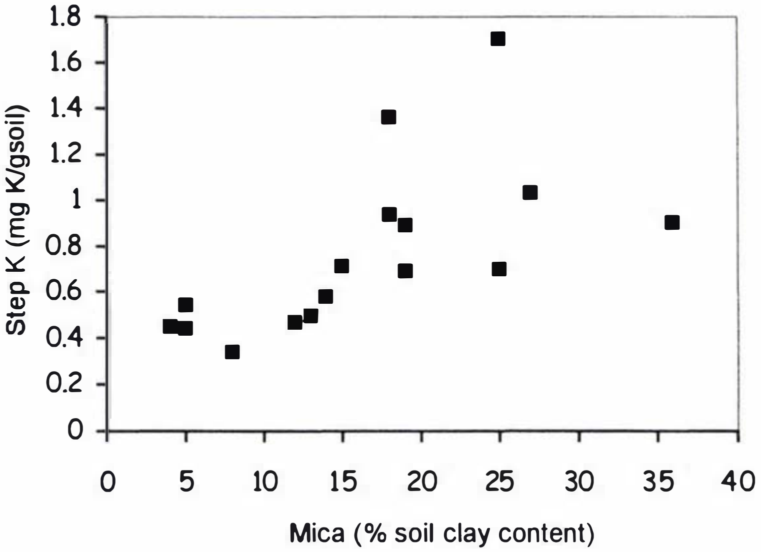


Figure 4.5: Relationship between mica in the clay fraction and Step K value of the whole soil, from slopes of greater than 20 degrees (A) or slopes of less than or equal to 20 degrees (B), in samples from both the Tuapaka and Bernwood sites. Two anomalous points that had large amounts of mica in the silt and clay fractions, but had relatively low Step K values are marked with unfilled triangles, plot A.

Two soils from an eroding conglomerate band in the lower slopes of the Bernwood site had an anomalous relationship between Step K and mica (Figure 4.5a, Table 4.5, line L). These soils contained 24 and 26% mica and and mica:vermiculite ratios of 2.6 and 2.8. There was also a relatively large quantity of mica, MS and MV in the silt fraction (Section 4.3.3). The soil parent materials were unstable and were thought to have been exposed to the surface relatively recently. These soils had about half the Step K value of corresponding soils at the Tuapaka sites, which had the same mica content in the clay fraction and only trace amounts of mica in the silt fraction (and similar total K, Section 4.3.5). Anomalously low Step K results have previously been recorded in similar New Zealand micaceous soils. Some reabsorption of K during the extractions, possibly by the expanded layers, was suggested (Lee et al., 1978).

Mineralogy on the flatter areas

On the flatter areas (≤ 20° of slope), the Step K values ranged from medium to extremely high values. There were no significant correlations between 2:1 layer silicates and Step K (Figure 4.5b), indicating that the significant correlation of the whole set was mainly due to the strong relationship between Step K and the mineralogy on the steeper slopes. In these soils the mica content ranged from 4 to 36% of the clay fraction and the mica:vermiculite ratio varied from 0.4 to 12. The ratio range was high because less vermiculite was found in the soils that were high in mica compared to soils with similar mica levels on the steeper slopes.

The topsoils of the wetter areas on the broad loess covered ridge-tops (Table 4.5, lines B and F) had medium Step K values. In these soils the mica content ranged from 4-14% and the mica:vermiculite ratios ranged from 0.4-0.8, similar to the average conditions on the steeper slopes.

The relatively well drained soils on the ridge-tops have been previously associated in this study with some extremely high Step K values. These soils had mica contents that ranged from 15 - 36% and mica:vermiculite ratios between 2.2 and 12 (Table 4.5, lines A and I). These soils were also associated with poorly formed, irregularly interstratified, expanded 2:1 layer silicates and no HIV was recorded in these soils (Section 4.3.4.1).

The increase in mica in some ridge-top soils was rather in contrast to the results of Wells and Furkert (1972, 1973), who found that mica content tended to increase, and vermiculite to decrease, with increasing slope, and also to McLaughlin (1983), who found vermiculite-dominated profiles on nearby ridge-top sites. The difference appears to be the deliberate inclusion in this study of the well drained animal campsite areas, which would have been avoided by Wells and Furkert (J. Whitton, pers. com.) who were examining soil type differences and presumably also by McLaughlin, who was studying reference profiles for a soil map. The purpose of the present study was to examine the effects of animal transfer, so the animal campsites were deliberately included.

Some unusual effects have already been associated with the well-drained animal campsite soils. Quick test K, Step K and Olsen P sometimes evinced very large increases in these areas and sometimes did not, generating a wide range of results and extreme variability (Chapter 3.4). It was speculated that a high rate of dung and urine deposition followed by a relatively slow breakdown in well drained soils was producing this effect.

Multiple dung and urine depositions in relatively dry conditions are expected to cause very high, sustained, K and NH_4 concentrations in the soil solution. More K is generally expected in the urine, although sheep dung in particular has been found to contain appreciable K (Sakadevan, 1991). The presence of both in the soil has been associated with a sustained rise in the soil pH, to about pH 8 (Haynes and Williams, 1993), and an increased pH was found in the campsite soils of this study. Such a rise in the pH would neutralise any positively charged metal-hydroxide polymers and organic matter complexes in the interlayer spaces (Sparks and Huang, 1985). The dung will also release PO_4 into the soil solution, which has also been found to be an effective neutraliser of interlayer material (Stanford, 1947). The neutralisation of the hydroxy polymer material will expose more negatively charged mineral surface to soil solution, increasing the CEC, and facilitating an increased adsorption of K and NH_4 in interlayers of the vermiculites and smectites (Saha and Inoue, 1997).

Wetting and drying cycles in these relatively well-drained sites would then facilitate the collapse of expanded (hydrated) interlayers that are saturated with K and NH_4. The large mica:vermiculite ratios in the campsite soils, especially compared to adjacent ridge-tops, indicated some collapse of vermiculite had occurred, forming mica in the campsite soils. No tests were made for NH_4 which may have been in the interlayers. NH_4 saturated smectite has been found to collapse to illite less readily than K saturated smectite (Miklos and Cicel, 1993), which may account for some of the variability of these effects. The effect on the exchangeable surfaces of the K-NH_4 or Ca-K-NH_4 mixtures has also been found to be quite unpredictable, and the effect of such mixtures on interlayer collapse does not appear to have been explored (Evangelou et al., 1994; Barbayiannis et al., 1996). Some interlayers may also be propped open by material still in the interlayer spaces, allowing only partial collapse after fixation. Uneven collapse of the interlayers was indicated by the XRD traces for these soils.

After the interlayers have collapsed, "atolls" of hydroxide polymers are expected to re-form around the edges of the mineral as the soil solution pH drops. Where only a partial collapse has occurred and the interlayers are still exposed to the soil solution, the presence of the polymers on the edges of the minerals can trap K and NH_4 in the interlayers (Harris et al., 1988; Weaver, 1989; Shen et al., 1997). K trapped in the poorly collapsed material is liable to be extracted by the nitric acid more readily than from mica, which is a likely cause of the extremely high Step K and the poor correlation between Step K and the mica content of the campsite soils.

Ross et al. (1985) found similar changes in a soil after six years of heavy applications of liquid manure, applying approximately 850 kg K/ha/yr and 900 kg N/ha/yr (with approximately 40% as NH_4). Analysis of the clay fraction found that the mica:vermiculite ratio was less than one before manuring and more than one after manuring.

4.3.4.5 Summary of the clay mineralogy

The clay mineralogy of top soils at the two sites consisted of a mixture of 2:1 layer silicates, accompanied by quartz, feldspar and kandites. The principal 2:1 layer silicates identified in the clay fraction were mica, interlayered mica-smectite (MS), vermiculite and hydroxy interlayered vermiculite (HIV). The assignment of vermiculite and HIV was inconsistent between the two mineralogy sets analysed, so they were grouped together as vermiculites for correlation analysis. A very strong negative correlation was found between the proportions of the combined mica and MS in the clay fraction compared to the proportion of vermiculites in the clay fraction. A complex of 2:1 layer silicates appeared to exist in these soils, that varied from a relatively highly charged complex, rich in dehydrated micaceous interlayers, to a moderately charged complex dominated by expanded and hydrated vermiculitic interlayers. The range of mineralogy of the clay fractions of topsoil samples gathered from the two steepland sites was quite similar and was also similar to another study of steepland soils developed in greywacke derived parent materials.

On the steeper areas, the Step K value of the whole soil was highly correlated to the soil mica content, indicating that the relationships previously found between Step K and conditions on the slopes (Chapter 3) were also reflecting consistent changes in the amount of mica and the mica:vermiculite ratio in these soils. The ridge-top areas that were previously found to have an extractable K chemistry similar to the steeper slopes, including wetter, seep affected areas, also had a clay mineralogy that was similar to the average clay mineralogy of the steeper slopes.

The well drained ridge-top areas, that were previously associated with some large increases in Quick test K, Step K and Olsen P, were also found to be associated with increases in pH. In these topsoils, the proportion of mica and MS in the clay fraction increased, while vermiculite was reduced, compared to other ridge-top soils and no HIV was identified, at all. The expanded 2:1 layer silicates were poorly formed and irregularly interstratified, and there was no longer a good correlation between Step K and mica. These effects were consistent with the expected effects of adding large amounts of dung and urine to a soil under relatively well-drained conditions.

4.3.5 Major oxides

In the light of the pronounced animal campsite effects on the soil K chemistry and clay mineralogy, the total K and P of these soils and some soils from the steeper slopes were examined to check accumulation K and P caused by animal transfer onto the campsites. Haynes and Williams (1993) indicated that animal transfer could be moving 200 kg K/ha/yr from the slopes onto the campsite areas, accompanied by 30 kg P/ha /year. As both the sites in this study have been under standard fertiliser and production regimes, probably at Tuapaka since the 1950's and at Bernwood since at least the 1970's, this extent of transfer over more than 20 years should have caused a very marked build up in total K and P in the camp site topsoils. Certainly, there were marked changes in the chemistry and mineralogy of these soils (previous section, and Chapter 3).

The elemental analyses of topsoil samples (determined by XRF) from the two steepland paddocks were generally typical of soil with quartzo-feldspathic parent materials (Wells, 1968). An exception was one sample from an alluvial toe slope next to a stream at Tuapaka (Table 4.6, Vector O). The elevated proportions of Mn, Ti and Fe in this sample, compared to the other samples, indicated that the parent material was probably a mixture of basaltic and greywacke alluvium (Wells, 1968). The distinctive red colouring of weathered basaltic volcanic material, formed by an eruption on the sea floor as the sedimentary greywacke was forming, was observed in a road cutting about 30 m upstream of this particular alluvial slope (A.S. Palmer, pers. com.). A distinctive mineralogy and K chemistry have previously been noted in soil samples from this particular location. This sample was excluded from the remaining comparisons in this section.

The total K content of the topsoil samples ranged from 1% K_2O (0.85% K or 22 cmol K/kg soil) to 2.44% K_2O (2.1% K or 54 cmol K/kg soil). These results ranged from medium to very high compared to other New Zealand soils, in terms of the classes proposed by Metson (1980). The K content of topsoils from the two farms were similar (Table 4.5). There generally tended to be more Ca in the Bernwood soils, perhaps reflecting the regular application of lime as well as superphosphate at this site.

Table 4.6: Major oxides of the whole soil sample of topsoils. Results are expressed as weight % on oven dried basis.

	n	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	K_2O	MgO	TiO_2	P_2O_5	MnO	LOI*	Sum
Tuapaka	10	62.2	12.0	3.30	2.10	0.88	1.48	0.65	0.49	0.27	0.06	16.25	99.66
c.v.		6%	9%	14%	20%	15%	31%	21%	11%	32%	21%	23%	0.2%
Bernwood	8	64	11.2	3.4	2.43	1.73	1.27	0.78	0.54	0.24	0.05	14.06	99.70
c.v.		3%	5%	7%	8%	10%	11%	12%	14%	22%	15.12	20%	0.2%
Vector O	1	56.02	14.90	5.59	2.98	2.46	0.56	2.0	0.56	0.20	0.09	14.45	99.81

LOI = loss on ignition at 1000°C for 1 hour.

The main purpose of the spectrographic analysis was to compare total P and K levels on the slopes and ridge-tops. The results could be divided into either ridge-top samples or samples from the steep slopes. Total K and P per hectare was estimated for the top 75 mm, adjusted for an average bulk density of 0.87 in ridge-top soils and 1.01 in soils from the steeper slopes. These estimates were based on bulk densities found when larger soil cores were lifted for the leaching experiment (Chapter 6).

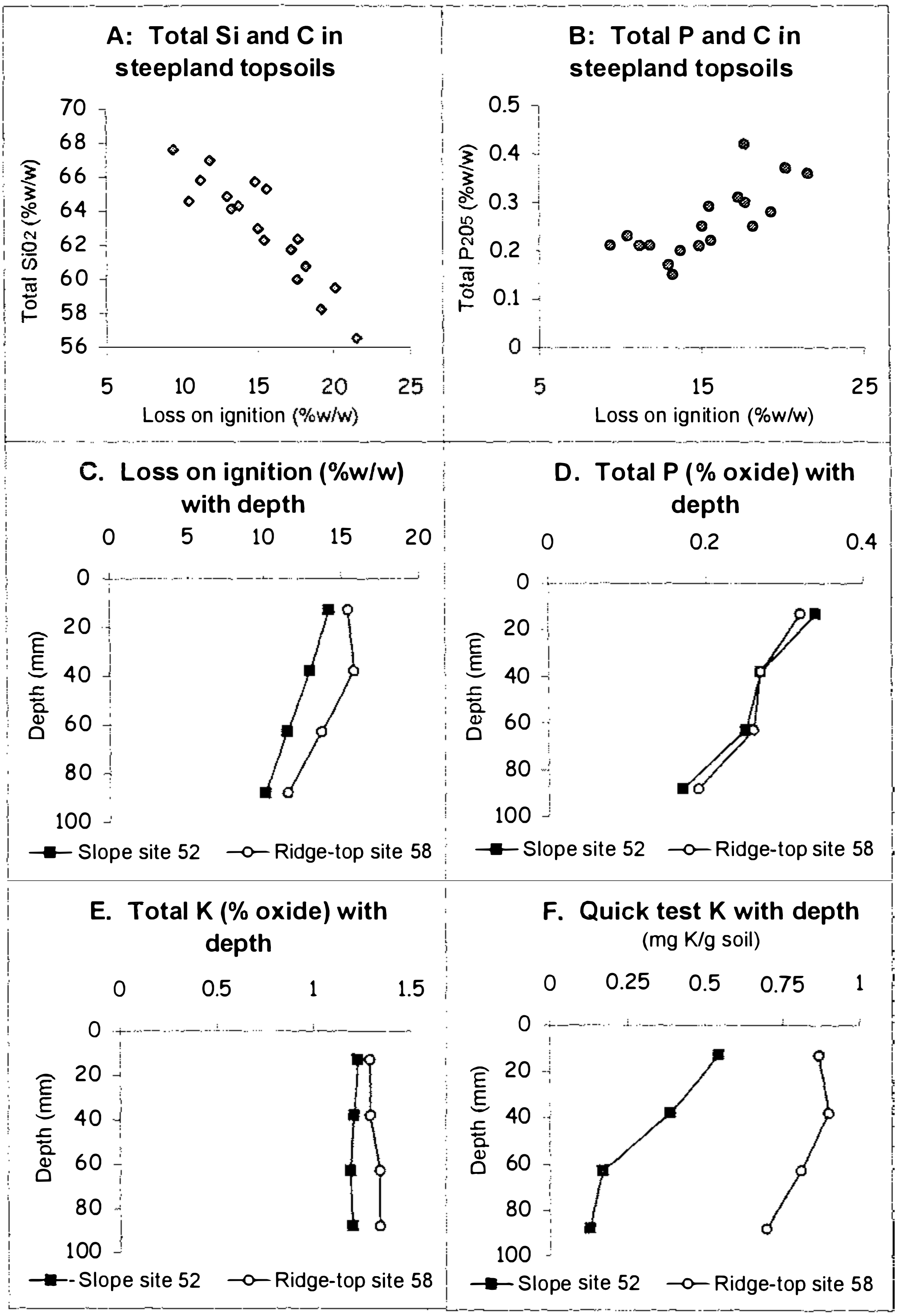
A comparison between ridge-top and slope samples found a consistent decrease in Si content, and an increase in organic matter (loss on ignition) and P on the ridge-tops (Table 4.7, Figure 4.6). Total P ranged from 0.5 to 0.77 t P/ha on the slopes, and 0.57 to 1.1 t/ha on the ridge-tops. Analysis with depth indicated that most of the P was in the top 75 mm of the soil, so recovery of the accumulated P was thought to be reasonable (Figure 4.6d). The average difference between the total P of slope and ridge-top samples, of about 200 kg P/ha, was smaller than might have been expected based on Haynes and Williams (1993) or Gillingham and During (1973). However the estimates did corresponded well to 30-50 years of the 1-11 kg/ha /year gains of P found on ridge-tops by Saggar et al. (1988), under an application rate of 125 kg/ha/year of superphosphate and where flatter areas constituted 23-37% of the area examined (on a dissected sedimentary landscape similar to the present study sites).

Table 4.7: Comparison of silicate content, loss on ignition (LOI), and P and K status of topsoil on the ridge-tops and steep slopes of steepland pasture.

		% w/w				T/ha**				
	n	SiO_2	LOI	P_2O_5	K_2O	Total P	Olsen P	Total K	Step K	Quick test K
Ridge-tops	12	61.6	17.2	0.29	1.36	0.83	0.033	7.5	0.64	0.43
Std. dev.		2.8	2.4	0.07	0.28	0.2	0.017	1.5	0.32	0.23
Steep slopes										
Weathered	4	65.4	12.3	0.19	1.19	0.62	0.017	7.7	0.29	0.09
Unweathered	2	66.1	9.9	0.22	1.96	0.73	0.030	12.6	0.85	0.11
All slopes	6	65.6	11.5	0.2	1.45	0.66	0.02	9.3	0.48	0.09
Std. dev.		1.4	1.5	0.03	0.5	0.1	0.01	3.3	0.37	0.04

**adjusted for bulk density of 1.01 on slopes and 0.87 on ridge-tops

Total K in the soils on the slopes ranged from 6.6 t K/ha on the weathered areas, and up to 15.7 t K/ha on the relatively unweathered or dry areas. The ridge-top soils ranged from 5.6 on the wetter soils, and up to 10.6 t/ha of K on well drained campsite areas previously associated with some big increases in extractable K and a modified clay mineralogy (previous section). Haynes and Williams (1993) indicated that an approximate 7:1 ratio of K to P is transferred on to animal camp-sites, so the accumulation of 200 kg P/ha onto the campsites would be expected to have been accompanied by approximately 1.4 t/ha K. Although the initial K status of the ridge-top



A: Total Si and C in steepland topsoils

B: Total P and C in steepland topsoils

C. Loss on ignition (%w/w) with depth

D. Total P (% oxide) with depth

E. Total K (% oxide) with depth

F. Quick test K with depth (mg K/g soil)

Figure 4.6: Total oxides analysis of selected steepland topsoils (75 mm depth), showing the relationship found between total Si and P and the loss on ignition or total C (A and B). Two soil cores, at slope site 52 and ridge-top site 58 respectively, were also fractioned into depths of 0-25 mm, 25-50mm, 50-75mm and 75-100mm, and measured for total carbon (C), total P (D), total K (E) and exchangeable K (F).

soils before grazing development is not known, it seems probable that the K status of all the ridge-top soils was similar or less than the total K of the present day weathered slopes and ridge-tops that are not animal camps. Unlike total P, the average total K did not increase in the ridge-top soils compared to the weathered soils on the steeper slopes (Table 4.7), so, even the relatively small accumulation expected in association with the P could not be confirmed. Leaching studies (Chapter 6) indicated that an increased rate of K leaching under animal campsites could reduce the build up of total K in the ridge-top soils. A reduced accumulation could have been easily masked by the variability of these results.

Overall, high rates of accumulation of K and P were not indicated, although this was not a comprehensive study. Animal transfer from the steeper areas was thought to be occurring at a relatively slow rate compared to some other studies. This was a rather surprising conclusion in view of the marked effects of animal camping on the soil chemistry and mineralogy of the campsite soils. One of the original objectives of this study was to examine whether or not animal transfer was a significant mechanism for the loss of K from the slopes of these steepland pasture systems. These results indicated that the transfer losses were relatively small, and not likely to cause significant depletion of K from the slopes. A low rate of transfer combined with the relatively large total K reserves in these soils indicated that the current practise, of not applying K fertiliser to these soils, would be sustainable well into the future. It is thought that erosion would probably expose fresh parent material on the steeper slopes long before total K in the topsoil was significantly reduced by animal transfer (perhaps 1-2000 years).

4.4 Conclusions

(1) The mineralogy of the topsoil of two steepland pastures with mainly sedimentary parent materials had very similar patterns. The sand and silt fractions were dominated by quartz, and feldspar. Little micaceous material was present in the sand and silt fractions, except in topsoils from rapidly eroding sites. The clay fraction mainly consisted of quartz, feldspar, kandites and 2:1 layer silicates. The 2:1 layer silicates constituted about two thirds of the clay fraction and mainly

consisted of a combination of mica, MS, vermiculite and HIV. Mica and MS were closely associated and the vermiculites could not be separated. The results suggested that each topsoil contained a single complex of 2:1 layer silicate clays. Within the landscape, this 2:1 layer silicate complex varied from a K saturated form dominated by micaceous interlayers to a complex that was dominated by vermiculitic interlayers, which contained hydroxy polymers and much less K.

(2) On the steeper slopes, Step K was a good indicator of the proportion of mica present in the clay fraction and the mica:vermiculite ratio, indicating that the previously ascertained relationship between Step K and the soils on the slopes (Chapter 3) was also reflecting consistent changes in the soil mineralogy. Soil moisture as determined by aspect and the location of seeps, and the pattern of the soil parent materials, were all related to large variations in the proportions of mica and vermiculite in the topsoils.

(3) Some very distinctive mineralogy was found in well drained ridge-top soils that were previously associated with large increases in Quick test K, Step K and Olsen P. In these topsoils, the proportion of mica and MS in the clay fraction increased compared to other ridge-top soils, while vermiculite was reduced and no HIV was identified. The expanded 2:1 layer silicates were poorly formed, MV and MS were irregularly interstratified, and there was no longer a good correlation between Step K and mica. These soils were also associated with increases in pH. These effects were consistent with the expected effects of adding large amounts of dung and urine to a soil under relatively well-drained conditions. A reversal of the apparent mica to vermiculite weathering sequence found on the slopes was apparently occurring in the topsoil under animal campsites.

(4) Analysis of total K and P found only very limited evidence of the accumulation of K and P under animal campsite, despite the marked effects on the chemistry and mineralogy. An average increase of approximately 200 kgP/ha was found under animal campsites, compared to the steeper slopes. This P was thought to have accumulated over the last 30 to 50 years. A corresponding expected increase in total K, of approximately 1.4 t K/ha could not be confirmed.

Relationship between plant growth and K fertility in steepland pasture and glasshouse trials

Chapter 5

5.1 Introduction

The relationship between soil K fertility and pasture growth is examined in this chapter. A simple, exploratory fertiliser trial was undertaken in the field to see if a response to K fertiliser could be obtained in a typical pasture situation, where a wide range of soil K availability was previously found by soil testing (Chapters 2 and 3). The test sites were known to have soils that ranged from low to high ratings of measures of soil K (NH_4-exchangeable, plant available nonexchangeable, and total K) and responses were thought to be probable in the areas of low soil K.

Once the results of the field trial had been assessed, a second, more detailed, subtractive trial was undertaken in the glass house. Small amounts of various soils taken from the study sites were exposed to exhaustive growing conditions, with all nutrients supplied except K.

5.2 Fertiliser Experiment

Some preliminary examinations of the pasture growth patterns at the two sites were carried out in previous studies (Chapter 3). In the steepland pasture on Tuapaka farm, the dominant pasture species was found to change at least every 10 m, in association with small scale variations in the topography (Chapter 3.3.3.2). This was a larger scale of change than was found for soil exchangeable and nonexchangeable K, which varied sharply even at points 0.25 m apart.

An initial survey of autumn pasture regrowth was also made in two steepland pastures, on Tuapaka and Bernwood farms. The frequency distribution of pasture growth within the pastures was Normal, in contrast to the heavily skewed Quick test (exchangeable) K and Step (plant available nonexchangeable) K distributions at the two sites, (Chapter 3.2.1.1). Pasture regrowth was the only factor examined that varied distinctly between the two farms (Chapter 3.4.3.4.1). More pasture regrowth was obtained at the warmer, north orientated, Tuapaka farm site, compared to the colder, south orientated, Bernwood farm site. Plant available K and pasture regrowth did have a common pattern of increasing on the flatter ridge-top areas at both sites, but the exact relationship with ground slope was unique for each factor. Pasture regrowth increased steadily with decreasing slope, although variability was high and few significant differences could be identified when comparing the average results from the ridge tops and the adjacent steep slopes.

Evidently, there was little obvious relationship between the spatial variability patterns of pasture growth and soil K fertility. In this study, further attempts are made to relate the two factors.

5.2.1 Methods

32 of the 59 previously sampled peg sites (laid out on the sampling transects 10 m apart) were matched into 16 pairs with similar slope and soil K chemistry (Figures 5.1 and 5.2). A 5 m by 5 m square plot was marked out around each of the peg sites and fertiliser applied to one of the plots.

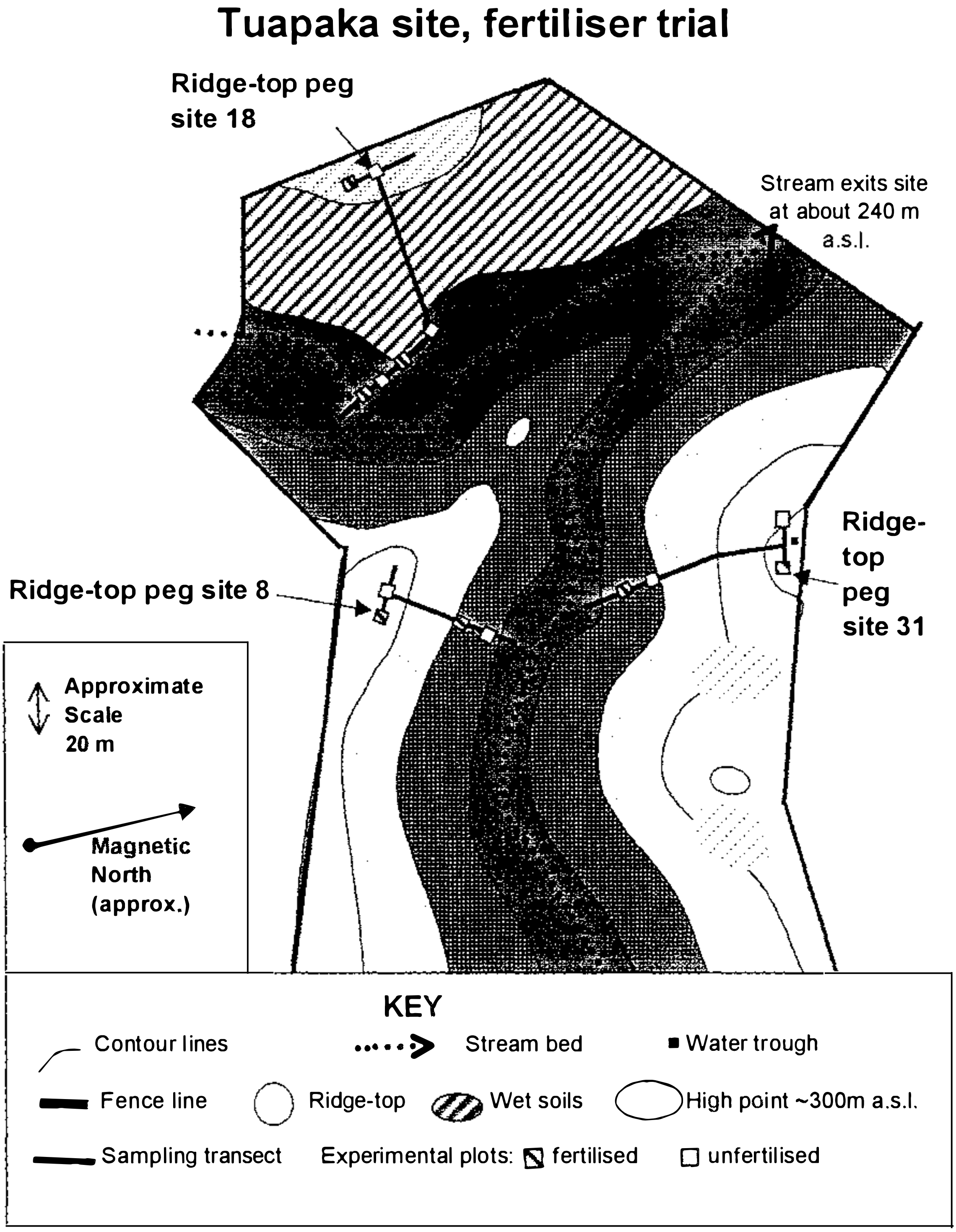


Figure 5.1: Diagram of the Tuapaka site, showing the layout of the fertiliser experiment plots in relation to the sampling transects of the second soil survey (Chapter 3.4) (lighter shades indicate increasing altitude).

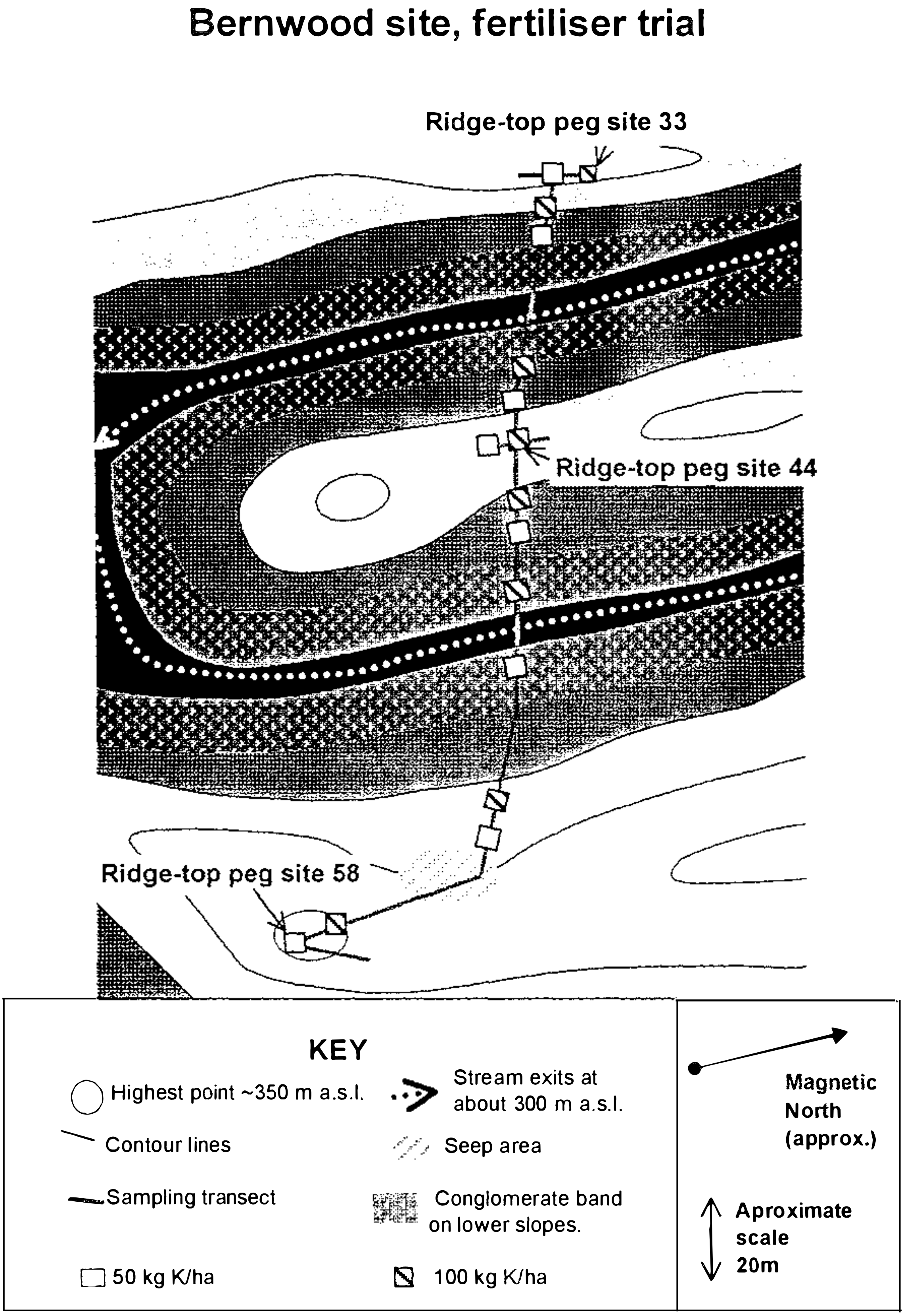


Figure 5.2: Diagram showing the layout of the fertiliser experiment plots at the Bernwood farm site, in relation to the sampling transects used in the second soil survey (Chapter 3.4) (lighter shades indicate increasing altitude).

An exclusion cage was laid randomly within each plot (Figure 5.3). At each harvest the cage was lifted and a test square (0.1 m^2) was cut from the protected pasture, cutting to the base of the leaf blades with scissors. The fertiliser trial was designed to run under normal grazing patterns, using stock exclusion cages that were shifted regularly to minimise any changes to stock grazing patterns. After each harvest the cages were shifted to a new position, which generally coincided with the end of a grazing rotation, otherwise, the pasture was trimmed before the cage was put down.

An initial pasture cut was taken from all the plots to establish the error levels. Fertiliser was then applied to every second plot at a rate of 50 kg K/ha (94.3 kg KCl /ha, 99.5% assay). This addition constituted about half the exchangeable K pool on the steeper slopes and about one tenth of the exchangeable pool on the ridge-top areas that were well frequented by animals (campsites) (see Chapter 4.3.5). The fertiliser for each plot was split into four bags of 59 g and applied by hand, in November (spring) 1995. Unfortunately, at the Bernwood site, about 350 kg/ha of 15% potassic super phosphate was applied by aerial topdressing to the whole site, about six days before the trial fertiliser was due to be applied. The exclusion cages were directly under a flight path, and superphosphate fertiliser appeared to be evenly spread over whole experimental area. Given the already large time investment at the site, it was decided to continue the experiment as planned, so the actual experimental application rates were zero and 50 kg K/ ha at Tuapaka, and about 50 and 100 kg K /ha at Bernwood. Two further pasture cuts were made about three weeks and eight weeks after the fertiliser was applied (Table 5.1).

Table 5.1: Harvest dates for the fertiliser experiment, run in spring, and early summer, 1995.

	TUAPAKA	BERNWOOD
Cages laid	7th September	7th September
Harvest 1	4th and 5th October	28th September
Fertiliser applied	25th October	26th October
Harvest 2	16th November	17th November
Harvest 3	20th December	21st December

After cutting, the herbage was dried overnight at 65°C and weighed. Dry matter collected in harvests prior to the fertiliser application, and immediately afterwards, was analysed for K, Ca and Mg content. The herbage was subsampled, ground for analysis, and 0.1g was digested in nitric acid (4ml HNO_3 conc.), at 150°C for 5-8 hours. The

Figure 5.3: Exclusion cage laid out for the fertiliser trial at peg site 12 on Tuapaka farm.

digest was then evaporated to dryness, redissolved in 5 ml 2M HCl, and diluted to 25 ml with deionised water. The solution was then analysed for K, Ca, and Mg by absorption /emission spectrophotometry (Williams, 1988; Surapaneni, 1994).[1]

The results of the fertiliser trial were evaluated using an unbalanced nested anova design with fixed effects. The frequency distributions of the herbage cuts were skewed for the first and second pasture cuts, and were log transformed as appropriate. Otherwise, the frequency distributions of the results did not require transformation. The results were nested according to farm, slope and fertiliser application. The categories were; the two farms- Tuapaka and Bernwood (level one of nest), two slope types- slope or ridge-top (level two of nest), and fertiliser rate (level 3 of nest). Unfortunately, the topdressing at Bernwood confounded the farm effect with the fertiliser effect. The model fit was good for the dry matter yield of the first pasture cut after the fertiliser was applied, and marginally acceptable for Mg content of the pasture and the accumulated harvests. Otherwise, the model fits were poor and the residual errors were high, resulting in poor separation of the means and few significant results.

5.2.2 Results and discussion

Prior to fertiliser

The results of the pasture cut that was made prior to the application of fertiliser were quite variable. There was no significant difference in pasture yield between the ridge tops and the slopes at the two sites, even though there was generally more dry matter cut from the ridge-tops, compared to the slopes (Table 5.2). No significant differences were found between the dry matter yields of the two farms, although yields were generally lower on the Bernwood site, as was previously found for autumn pasture regrowth (Chapter 3.4.3.4.1). The average yield of the paired plots did tend to be higher on the plots selected for the fertiliser application, although the effect was not statistically significant.

Prior to fertiliser application, the K content of the pasture was an average of 2.8% for both properties. The values ranged from 1.85% K to 3.6% K, with the highest and lowest values both found at the Tuapaka site. The lower end of the range was just

---

[1] Analysis of the herbage was carried out with the assistance of S. Weil

below the recommended minimum 2% K for mixed pasture and indicated a possible responsiveness to K fertiliser at some sites (Smith and Middleton, 1978). During (1984) suggested that because clover will suffer K deficiency earlier than the surrounding grass, that pasture levels may need to have 3% K or above to ensure that clover is not low in K. On this basis, more than half the sites tested had inadequate K levels in the pasture.

Table 5.2: Results from the fertiliser trial, showing yield rankings prior to the fertiliser application (H1) and three weeks after fertiliser application (H2), K, Ca and Mg content of the pasture at H2, mean yields two months after fertiliser application (H3), and the total average yield of all three harvests (H1-3).

	H1	**H2:One month after fertiliser application**				**H3**	**H1-3 TOTAL**
	D.M. (t/ha)*	**D.M. (t/ha)***	**%K**	**%Ca**	**%Mg**	**D.M. (t/ha)**	**D.M. (t/ha)**
TUAPAKA FARM							
Slope No fert.	0.73a	1.21a	2.9a	0.25a	0.15a	2.02a	3.99a
Slope, 50 kg/ha K	0.76a	1.09a	2.6a	0.22a	0.14a	1.84a	3.80a
Ridge-top, No fert.	1.20a	1.10a	3.1a	0.22a	0.16a	2.63a	4.95ab
Ridge-top, 50 kg/ha K	1.29a	0.86a	3.0a	0.19a	0.14a	3.08a	5.30ab
BERNWOOD FARM							
Slope, 50 kg/ha K	0.29a	1.59b	2.6a	0.26a	0.12b	2.10a	4.08a
Slope, 100 kg/ha K	0.37a	1.35a	2.9a	0.23a	0.12b	2.08a	3.86a
Ridge-top, 50 kg/ha K	0.69a	2.71b	3.2a	0.22a	0.14b	2.50a	6.15b
Ridge-top, 100 kg/ha K	0.80a`	2.45b	3.5a	0.23a	0.11b	2.47a	5.37ab
Average all sites	0.76	1.5	3.0	0.23	0.14	2.3	4.69
Range	0.07 - 1.9	0.07 - 3.4	1.6 – 3.7	0.17 – 0.31	0.1 – 0.17	1.4 – 3.2	2.8 – 6.9

a and b indicate a significant difference based on p-values <0.0005 of t-test between least-squares-means.
*D.M. values of H1 and H2 were back transformed after anova of ln transformed data (see section 3.4.3.4).

Yield after fertiliser was applied

KCl was applied to half the experimental plots, and potassic superphosphate was also flown onto the Bernwood site. At the Tuapaka site, the yields obtained from the slopes and the ridge-tops were similar (Figure 5.4a). There was no evidence of a dry matter response to the K fertiliser. In fact, yields on the fertilised plots tended to be lower than the yields on the unfertilised plots. At Bernwood the site, the yield on the ridge-tops was generally higher than on the steep slopes (Figure 5.4b). The plots on the steep slopes that had received about 100 kg K/ha had a significantly average lower yield, compared to the other Bernwood treatments, although the effect was rather uneven across the plots.

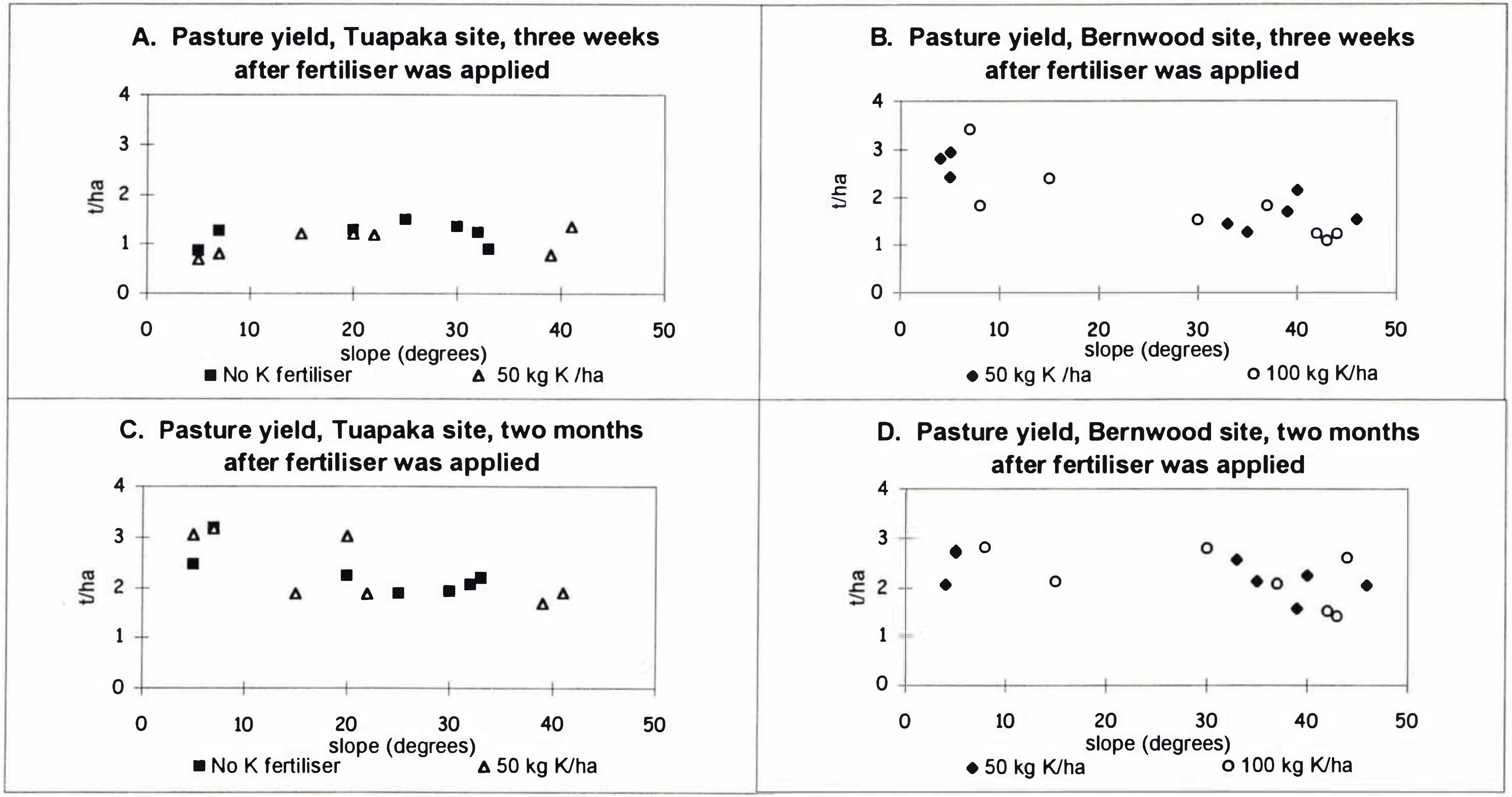


Figure 5.4: Pasture yields under exclusion cages on Tuapaka and Bernwood farms for two harvests after K fertiliser was applied in spring, 1995. The ridge-top sites all had ground slopes of less than 10 degrees.

Two months after the fertiliser was applied, there was still no evidence of a growth response to K (Figure 5.4c&d). The average yields were similar at the two farms and similar on the ridge-tops and slopes.

Only when all three harvests were amalgamated did some more consistent ridge-top and slope differences emerge (Table 5.2). The dry matter yields were typical of spring pasture growth in this region. The lack of difference at various times between the ridge-top plots and the yields from the steeper slopes was somewhat unusual, as ridge-top and slope differences tend to be very marked in the spring (Suckling, 1959; Roberts, 1987). The limited effects at these sites may have been caused by the particular orientation of sites. The ridge-top areas of both sites were noticeably exposed to cold northeasterly winds, while the valleys were more sheltered.

After fertiliser – K, Ca and Mg content

There was no significant increase in the K content of pasture on the fertilised plots at either site (Figure 5.5a&b). The average K content of the pasture and the range of values was very similar before and after the fertiliser was applied (Table 5.2). The lack of response in uptake even at the low end of the range was rather surprising. In fact, the lowest K content (1.6%) of the experiment was recorded at this harvest, in pasture from one of the fertilised plots at Tuapaka.

The application of K did coincide with a general drop in Ca and Mg content, although the only statistically significant difference was an average drop in Mg for the whole Bernwood site (Table 5.2, Figure 5.5c&d). The average Mg levels in the pasture were approximately 0.16% at both sites prior to the fertiliser application. After fertiliser was applied the average Mg content of the pasture at the Bernwood site dropped to 0.12 %, which is a low value for New Zealand pasture (During, 1984). A drop in Mg content is a typical effect of K fertilisation of pasture (Smith and Middleton, 1978). The effect may have been more pronounced at the Bernwood site because the soils contained less exchangeable Mg, compared to the Tuapaka site, although the levels were medium for New Zealand soils in general (Chapter 6.3.2).

Pasture K content has been found to have a broad pattern of increasing in the winter to a maximum in early spring and then falling sharply to lower levels in late spring. A general level of high variability is also maintained year round, that is thought to reflect

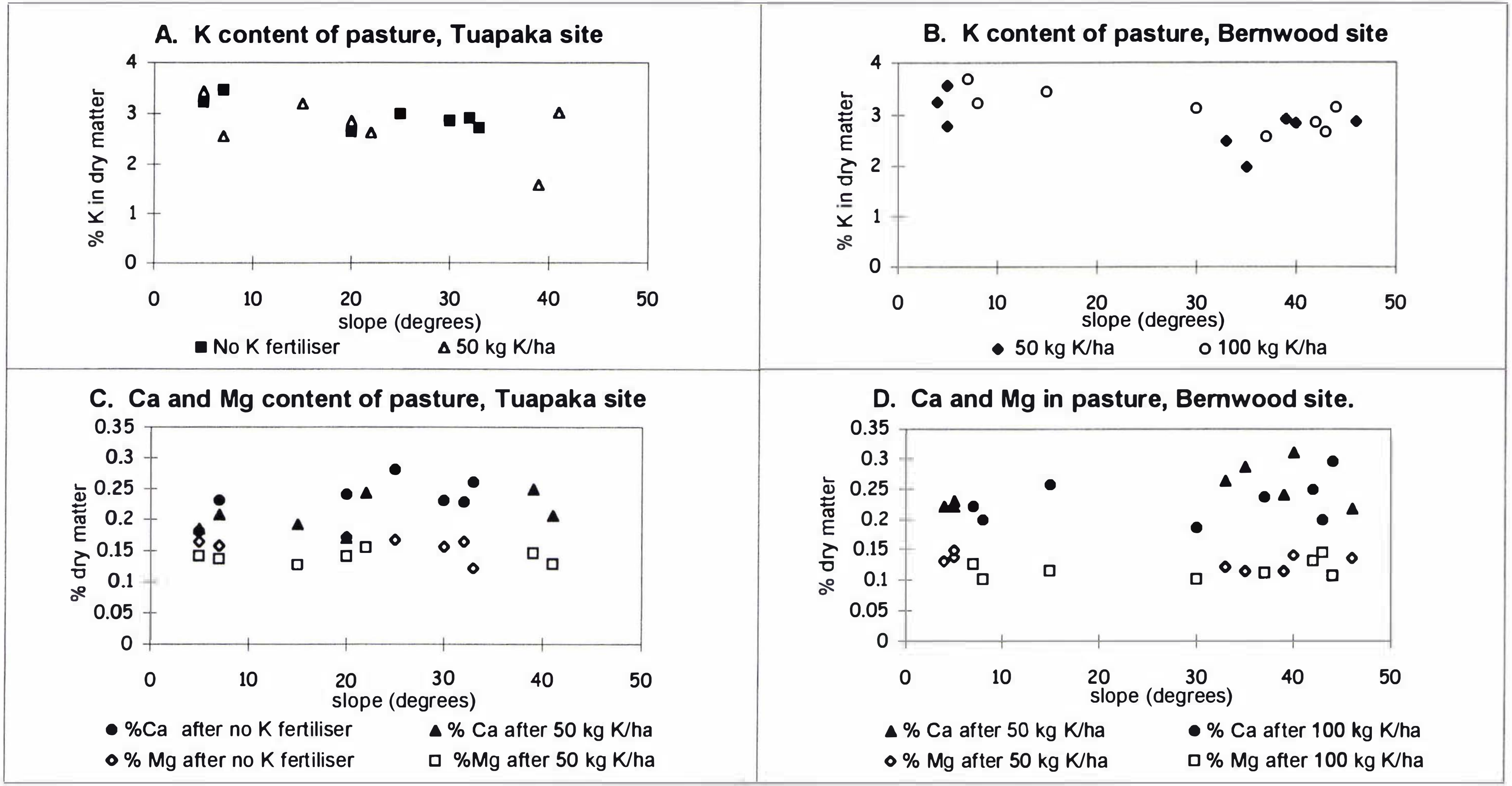


Figure 5.5. K, Ca and Mg content of steepland pasture in spring, three weeks after fertiliser was applied as specified at each site. The ridge-top sites were on slopes of less than 10 degrees.

the distribution of recent urine patches (Metson and Saunders, 1978; Roberts, 1987). In this experiment, conventional measures of pasture growth and K uptake, which effectively averaged the effect of the short range spatial variability, found no response to K fertiliser at the two study sites, regardless of the soil K status. The high spatial variability of plant available K in the soil and the spatial and temporal variability of the K content of the pasture were thought to have been inadequately accounted for by the trial design. Random soil sampling had indicated that up to 25% of the soil at these sites would have a very low exchangeable K status (Chapter 3), but the high spatial variability may mean that only detailed monitoring at fixed points of known exchangeable K could show a connection between the soil K fertility and pasture growth patterns.

5.3 Glasshouse experiment

The results of the fertiliser experiment indicated no response to K fertiliser under normal spring growing conditions, although high variability and poor environmental control dogged the experiment. This then raised the question as to whether the soil test values recorded in Chapters 3 and 4 were indeed reflecting differences in soil K fertility. To answer the question a more controlled experiment was undertaken in the glasshouse, with the objective of checking whether the soils from the two sites would give the expected differences in K supply, using a subtractive design that would limit nutrient interactions.

5.3.1 Methods

Small plastic pots with removable bases were filled with 400g of coarse acid-washed river sand and about 20 annual ryegrass seedlings were established in each pot, as per Surapaneni (1994). 1mg of K was added to each pot, to assist the early establishment. Distilled water and half strength standard -K nutrient solution was applied to the pots alternately, at two day intervals. Growth rates were initially good but became poor and some of the seedlings started to die off. Low pH and high E.C. in the pots indicated that a build up of salts and acidity around the roots had occurred. The uptake of NH_4 from the nutrient solution would have caused the release of H into the coarse sand matrix, which had a very limited buffering capacity. The effect was probably exacerbated by watering to weight, which did not flush the pots. The nutrient solution was modified by replacing NH_4NO_3 with $Ca(NO_3)_2.4H_2O$, and the pots were regularly flushed with water, until the soil treatments were added to the pots.

After three months, the grass plants were reasonably well established. There was quite a wide range of growth rates between the pots. An attempt to reduce the variability was made, by sorting them into low, medium and high yield groups. These groups were then used to form the blocks in a simple randomised block design. The bases of the pots were removed and 20g of soil (<2 mm) was added to each pot in a new base.

The soils tested in this experiment were chosen to represent the range of K chemistry and mineralogy (Table 5.3) that had been previously identified in soils from the Tuapaka and Bernwood steepland pasture sites (Chapters 3, 4). Each soil treatment was tested in three replicate pots. 20g of damp sand was placed in the control pots, which either received the same –K nutrient solution as the soil treatment pots or a solution with all nutrients.

Eight harvests were cut from the pots after the soil was added (Table 5.4). Each pot was trimmed to the base of the leaf blades. The cut herbage was dried overnight, at 65°C, and then weighed. Dried herbage was tested for K by an acid digest method (see Section 5.2.1, except the herbage was not tested for Ca or Mg content).

From harvests two to five the plant growth once again began to deteriorate. When the soils were added to the pots, drainage from the pots was stopped, and there appears to have again been a steady build up of salts and acidity. Growth was increasingly stunted in the pots, until, by the 5th harvest, all pots were yielding roughly the same. By the 5th harvest, plant roots had grown throughout the added soil. Holes were punched in the bottom of the pots and the pots were then regularly flushed with water, with minimal substrate loss. The growth patterns started to improve, so that by the 8th harvest there was a good range of growth rates between the pots.

The results were tested using a randomised block anova design. Variability remained high between the replicates throughout the trial, but no significant block effects were identified, so the variability could not be corrected.

Table 5.3: Treatment list for the glass house experiment. Transect and peg numbers refer to the origin of the soil in two steepland pasture sites, on Tuapaka and Bernwood farms (see Figures 5.1 & 5.2). Also shown is the total amount of Quick test K, Acid K and Step K that was in the 20 g of soil that was added to each pot.

TUAPAKA						
No.	**Terrain**	**Transect**	**Peg site**	**Quick test K** (mg K/20g soil)	**Acid K** (mg K/20g soil)	**Step K** (mg K/20g soil)
1	Slope	1	2	3.4	21.6	18.2
2	“”	2	11	2.6	15.0	12.4
3	“”	2	12	2.2	9.6	7.4
4	“”	2	14	3.1	9.4	6.3
5	“”	2	15	2.2	6.1	3.8
6	“”	3	24	3.3	7.1	3.7
7	Ridge-top	1	8	10.1	26.1	16.1
8	“”	2	18	5.8	12.6	6.8
9	“”	2	20	8.7	17.1	8.4
10	“”	3	31	9.7	19.9	10.2
BERNWOOD						
		Transect	**Peg site**	**Quick test K** (mg K/20g soil)	**Acid K** (mg K/20g soil)	**Step K** (mg K/20g soil)
11	Slope	1	35	4.7	14.3	9.6
12	“”	1	39	3.4	15.6	12.2
13	“”	3	53	1.9	7.9	6.0
17	“”	2	46	2.6	10.6	8.0
14	Ridge-top	1	33	3.2	19.0	15.9
15	“”	2	42	11.9	29.6	17.7
16	“”	2	44	9.6	21.1	11.5
18	“”	3	59	18.6	36.5	18.0
CONTROLS						
19	Control: Sand only, -K nutrient solution					
20	Control: Sand with all nutrients solution					

Table 5.4: Dates of harvests in the glass house experiment. Pots were trimmed and soil added on 28th January 1997.

HARVEST	DATE	DAYS SINCE SOIL ADDED
1*	21st February	31
2	3RD march	41
3	19th march	57
4	2nd April	71
5*	18th April	87
6	2nd May	101
7	26th May	125
8*	16th June	146

*herbage analysed for K

The frequency distributions of the herbage cuts were relatively normal for the first six experimental harvests, and required no transformation for anova testing. Herbage cuts seven and eight were skewed and required log transformation. The frequency distribution of K concentration in the herbage was Normal, not requiring transformation, but total K uptake was skewed and required log transformation before testing.

5.3.2 Results and discussion

Increases in dry matter yield, compared to the -K control pots, were observed for all the soil treatments at the first cut that was made after the soil was added to the pots. Significant dry matter increases were particularly associated with the soils obtained from the ridge-tops, which generally contained very high levels of NH_4-exchangeable K (Quick test K) and also plant available nonexchangeable K (Step K) (Table 5.5). Growth on the +K control pots was quite poor at this harvest, but subsequently improved.

An increase in the K content of the dry matter at the first harvest was also observed, compared to the -K control pots, mainly from pots containing ridge-top soils (Table 5.5). There was some correlation between Quick test K and K uptake at this harvest (Table 5.6, Figure 5.6a).

No significant anova fits were found for the treatments from the 2nd to the 7th harvests. By the 5th harvest, it was evident that a build up of salts was once again suppressing growth. There were some differences in the K concentrations the herbage at the 5th harvest, and a significant correlation to all three soil K tests was found (Table 5.6). The correlations were mainly generated by high K uptake in one outlier point associated with soil from peg site 58, which had a particularly high Quick test K value (Figure 5.6b).

After the 5th harvest holes were cut in the base of the pots and the pots were regularly flushed with water. By the 8th harvest plant growth had recovered. There was a visible difference between the treatments (Figure 5.7) and a significant fit to the anova model. The soils from the ridge tops were associated with the highest yields, although no pots were yielding as high as the +K control (Table 5.5).

Table 5.5: Results of the first and last (8th) cuts of ryegrass in a subtractive pot experiment. Total K (mg) removed was calculated from the total dry matter (DM) cut from the pot and the K content (%K) of the dry matter. An estimate was made of the amount of exchangeable K that was lost from the pots at each cut, based on the difference in total K between the pots with soil and the -K control pots, which had sand only. The difference in K content is expressed as a percentage of the total amount of Quick test K that was in the 20g of soil in each pot at the beginning of the experiment (%QTK). Peg# and Terrain refer to the locations that the soils were obtained from.

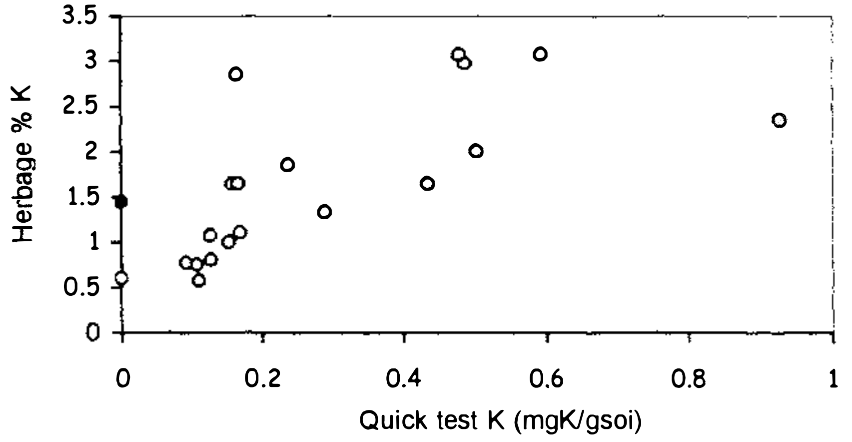
TUAPAKA									
		1ST HARVEST				8TH HARVEST			
Peg site	Terrain	DM (g/pot)	%K	Total K Removed	% QTK	DM (g/pot)	%K	Total K removed	% QTK
2	Slope	0.33*	1.1	3.6	62	0.58*	1.2	7.11	65
11	“”	0.30	0.8	2.4	35	0.40	1.5	5.11	6
12	“”	0.36*	0.8	2.7	55	0.37	1.5	4.92	0
14	“”	0.29	1.0	2.9	45	0.58*	1.0	6.44	34
15	“”	0.30	0.6	1.7	9	0.24	1.8	4.21	0
24	“”	0.27	-	-	-	0.39	1.6	5.67	22
8	Ridge-top	0.31	2.0	6.1	46	0.79*	1.2	9.04*	41
18	“”	0.34*	1.3	4.5	53	0.38	1.9	6.91	34
20	“”	0.39*	1.7	6.4	56	0.49*	0.8	4.74	22
31	“”	0.37*	3.0	11.1	99	0.68*	1.1	7.57	26

BERNWOOD									
		1ST HARVEST				8TH HARVEST			
Peg site	Terrain	DM (g/pot)	%K	Total K Removed	%QTK	DM (g/pot)	%K	Total K Removed	%QTK
35	Slope	0.37*	1.9	6.8	113	0.41	1.7	6.4	30
39	“”	0.33*	1.7	5.4	131	0.43*	1.7	7.3	66
46	“”	0.35*	1.1	3.7	85	0.39	1.9	7.6	100
53	“”	0.33*	0.8	2.6	55	0.30	1.8	5.2	14
33	Ridge-top,	0.35*	1.7	5.8	134	0.43	1.4	5.9	28
42	“”	0.39*	3.1	11.9	88	0.80*	1.5	12.5*	63
44	“”	0.37*	3.1	11.5	103	0.70*	1.4	9.6*	48
59	“”	0.37*	2.4	8.8	38	0.88*	1.0	9.0*	21

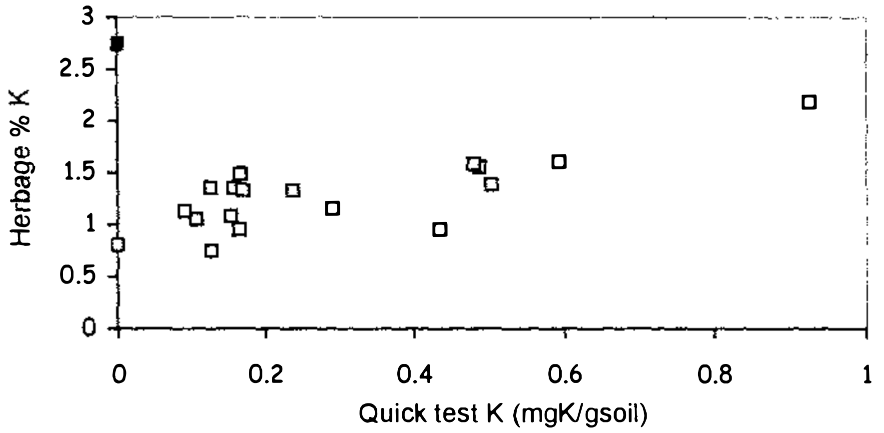
CONTROLS									
		1ST HARVEST				8TH HARVEST			
Peg site	Nutrient solution	DM (g/pot)	%K	Total K Removed		DM (g/pot)	%K	Total K removed	
	- K	0.25	0.6	1.5		0.32	1.3	5.0	
	+ K	0.21	1.5	2.9		1.39*	1.8	25.5*	

* Indicates a significant difference from the no K (-K) control, based on a significant model fit and significant Least-Significant-difference test (alpha=0.05) between the treatment means. Treatment means are presented for all variables, but significance rankings are based on an anova of ln transformed data for DM results in the eighth harvest and for total K removed. Otherwise, anova results are for untransformed data.

A. Quick test K and herbage K content, first harvest, each point is the combined value of three replicates



B. Quick test K and herbage K content, harvest 5, each point is the combined value of three replicates



C. Quick test and herbage K content, final harvest, all replicates shown

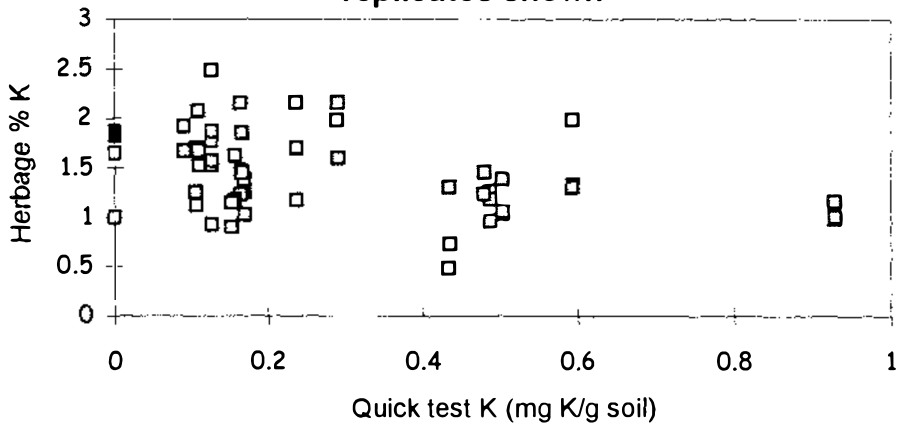


Figure 5.6: Comparison of initial Quick test K value of a soil and the K content of ryegrass, at various stages of a subtractive pot trial. The results from the control pots are shown on the Y axis, -K (clear marker), +K (black marker).

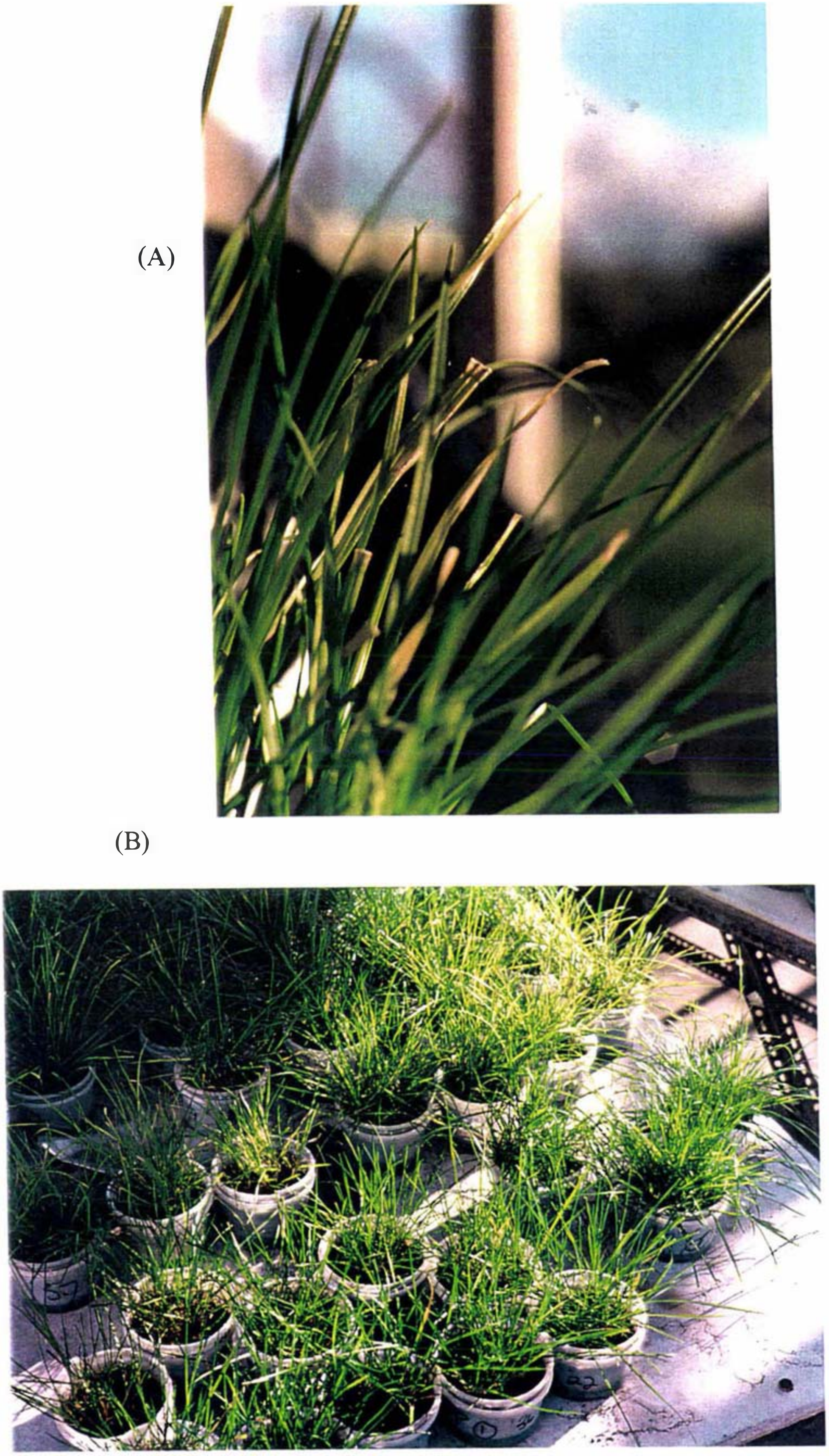


Figure 5.7: Subtractive pot trial of a range of soils from the Tuapaka and Bernwood sites, showing the development of apparent K deficiency symptoms on some leaves (A), and a good range of growth across the various pots (B), at the last harvest.

Table 5.6: Correlation between the initial soil test values and the dry matter yield and K content of ryegrass for the first, fifth and last harvests of a subtractive pot trial. Results are the Pearson correlation coefficient (upper number) and the statistical probability of a linear relationship between the soil tests (in brackets).

	Quick test	Acid K	Step K
Harvest 1, treatment averages			
Dry matter (g)	0.60 (p=0.0069)	0.63 (p=0.0037)	0.54 (p=0.0172)
Herbage K (%)	0.70 (p=0.0008)	0.61 (p=0.0053)	0.42 (p=0.0762)
Harvest 5, treatment averages			
Dry matter (g)	0.17 (p=0.4751)	0.23 (p=0.3471)	0.23 (p=0.3416)
Herbage K (%)	0.78 (p=0.0001)	0.81 (p=0.0001)	0.67 (p=0.0001)
Harvest 8, all replicates			
Dry matter (g)	0.71 (p=0.0001)	0.72 (p=0.0001)	0.59 (p=0.0001)
Herbage K (%)	-0.37 (p=0.0072)	-0.35 (p=0.0098)	-0.27 (p=0.0488)

The dry matter yields at the 8th harvest were significantly correlated to all three soil tests (Table 5.6). The correlation with Quick test K was reasonably consistent although the variability between the replicates was quite high (Figure 5.8a). The correlation between yield and Step K was mainly generated by three soils that had high Step K values (>17 mg Step K/20g soil in each pot). Two of these three soils were from ridge-tops (peg sites 42 and 59) and also had high Quick test K values, so it was difficult to separate the Step K effect from the Quick test K effect.

The K content of the grass ranged from 0.5% K to 2.5% K, which was similar to the other harvests, but now was inversely related to the soil tests (Figure 5.6c). This effect may have been indicating that soils in the pots were nearing exhaustion of the available K and were growing on K reserves that had been built up while growth was suppressed by the high salt levels. Some pots had been losing the equivalent of all of the Quick test K at every harvest, and most pots were expected to have lost all their available Quick test K at least once over the 8 harvests (Table 5.5). The apparent symptoms of K deficiency were observed on some leaf tips towards the end of the experiment (Figure 5.7). McNaught (1958) found that deficiency symptoms of grasses (tip burn of the older leaves) coincided with a K content of only 0.25% K, although 1.6% K was

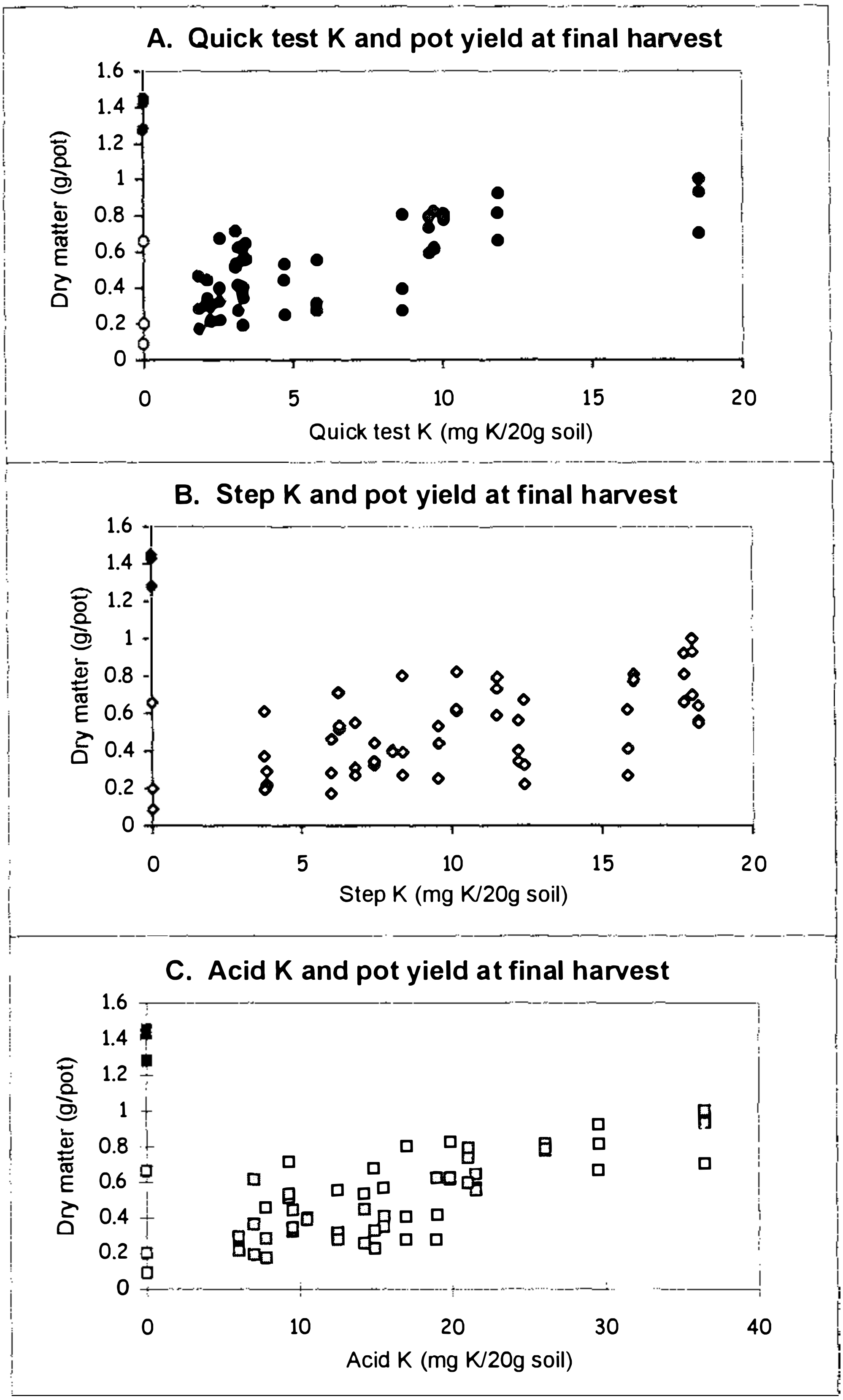


Figure 5.8: Comparison of the dry matter yield of pots at the final harvest (harvest 8) compared with the total amount of Quick test K (A), Step K (B) and Acid K (C) in the soil that was added to the pots. All replicate pots are shown for the treatments, including the controls on Y axis, - K (clear marker) + K (black marker).

considered the minimum level for near maximum growth. On this basis, many of the plants in the pots were inadequately supplied with K throughout the experiment.

A relatively large variability between the three replicate pots in each treatment was observed throughout the experiment. At the final harvest, two of the –K control pots had the lowest and the fourth lowest yields recorded at this cut, while the third replicate had a yield that was ranked 40th of the 69 pots. The wide variability may have been caused by a variable amount of K in the sand growth substrate.

A good correlation between growth and exchangeable K is a common observation from similar pot trials. Mengel and Uhlenbecker (1993) found that initial NH_4-exchangeable K was well related to K uptake by grasses after 2 years of pot trials, although the nonexchangeable K was also depleted. Ahmad et al. (1973) found NH_4-exchangeable was generally a better predictor than HNO_3 extraction of K uptake in maize over a wide range of soils from the West Indies. Surapaneni (1994) found that while NH_4-exchangeable K was a better predictor of K uptake than Step K, the combined extract (Acid K) was the best predictor of total yield and K uptake from ryegrass on micaceous soils.

In this study it was difficult to separate the effects of Quick test K and Step K. In general, Quick test K had the most consistent relationship to yield and K uptake. In these soils, the range of exchangeable K values was thought be largely determined by the exposure of the soil to urine. The objective of the study was to examine the K supplying power of a range of soils from two steepland pastures, which had returned no K response in a conventional fertiliser trial in the field. Certainly, a range of K availability was demonstrated in these soils throughout the glasshouse trial, with a conventional relationship to exchangeable K.

5.4 Conclusions

1. In two steepland pasture sites with mainly sedimentary soil parent materials, there was no evidence of a pasture growth response to K fertiliser, measured using conventional techniques. It appeared that even the areas of the paddocks that were associated with low exchangeable K values had sufficient plant available K to maintain an adequate

average pasture growth rate under field conditions. However, it is possible that the trial design disguised a relationship between the plant available soil K status and pasture growth.

2. Quick test K had a classical correlation to ryegrass yield and K content, in a subtractive pot trial of soils from the same site as the fertiliser trial. These findings confirmed that there was a range of K fertility across the paddocks, which could be identified using a range of soil tests.

Soil K leaching under steepland pasture

Chapter 6

6.1 Introduction

In this study, the chemical composition of the leachates of soils from the steep parts of a steepland pasture were compared with soils obtained from ridge-top areas where the animals tend to congregate. The soils on the steep slopes are expected to be only occasionally affected by excretal deposition, while many of the soils on the ridge-top areas are expected to have received many applications of urine over a long period of time.

The very different K chemistry of soils in these two parts of the landscape has previously been established (Chapters 3, 4 and 5). On the well drained ridge-top areas of these paddocks, distinct, but somewhat erratic, modifications to the chemistry of the top soil were found, particularly in association with drier soils and accumulations of dung (Chapter 3). The soil extractable K values were sometimes extremely high in soil from these areas, in association with increases in the soil Olsen P value and the soil pH. Topsoil in these areas was also found to have relatively large quantities of mica in the clay fraction, and to sometimes have a distinctively disordered expanded 2:1 layer silicate clay fraction (Chapter 4). All these changes, relative to the rest of the paddock, were consistent with the expected effects of large quantities of dung and urine deposition on to a well drained soil with mica – vermiculite clay mineralogy.

Previous studies have found that relatively little K^+ (see footnote [1]) is generally leached from pasture soils in the southern North Island with soil parent materials that are similar to the present study (Smith, 1979; Sakadevan et al., 1993; Parfitt et al., 1997). Even when urine is applied, the quantity of K^+ that is leached may be small, although large quantities of exchangeable Ca and Mg may be displaced from the CEC and leached (Williams and Haynes, 1994; Early et al., 1998). (The chemistry of this process was reviewed in Chapter 2).

6.2 Methods and materials

6.2.1 Soil source

Pairs of soil "stove pipe" cores were lifted from sites where previous soil samples had already been taken (Chapter 3). The sample sites of this study were chosen to represent the wide range of soil conditions presented by the sites, and to contrast the leaching processes of ridge-top soils and the soils on the steeper slopes.

At the Tuapaka site (Figure 6.1) two leaching cores were lifted from the midslope of the northern aspect of a ridge that was associated with relatively dry soils (peg site 3). Topsoils in this area were found previously to have average Quick test K values and very high Step K values, which were associated with a high soil mica content and a very high total K content, compared to the rest of the paddock (Table 6.1). The high mica and total K content was thought to be the result of a relatively mild soil weathering environment in the soils on this aspect.

Two leaching cores were lifted from a ridge-top area adjacent to the dry slope (peg site 7). Topsoil samples in this area were found previously to have very high Quick test K, Step K and Olsen P values and also a high mica content in the clay fraction, but much less total K compared to the adjacent slopes at peg site 3. The very high Quick test K and Olsen P values, and the high mica content, indicated heavy rates of dung and urine deposition on an animal campsite.

---

[1] In this study, ions marked with the appropriate ionic charge signify a fully hydrated and mobilised ion in soil solution

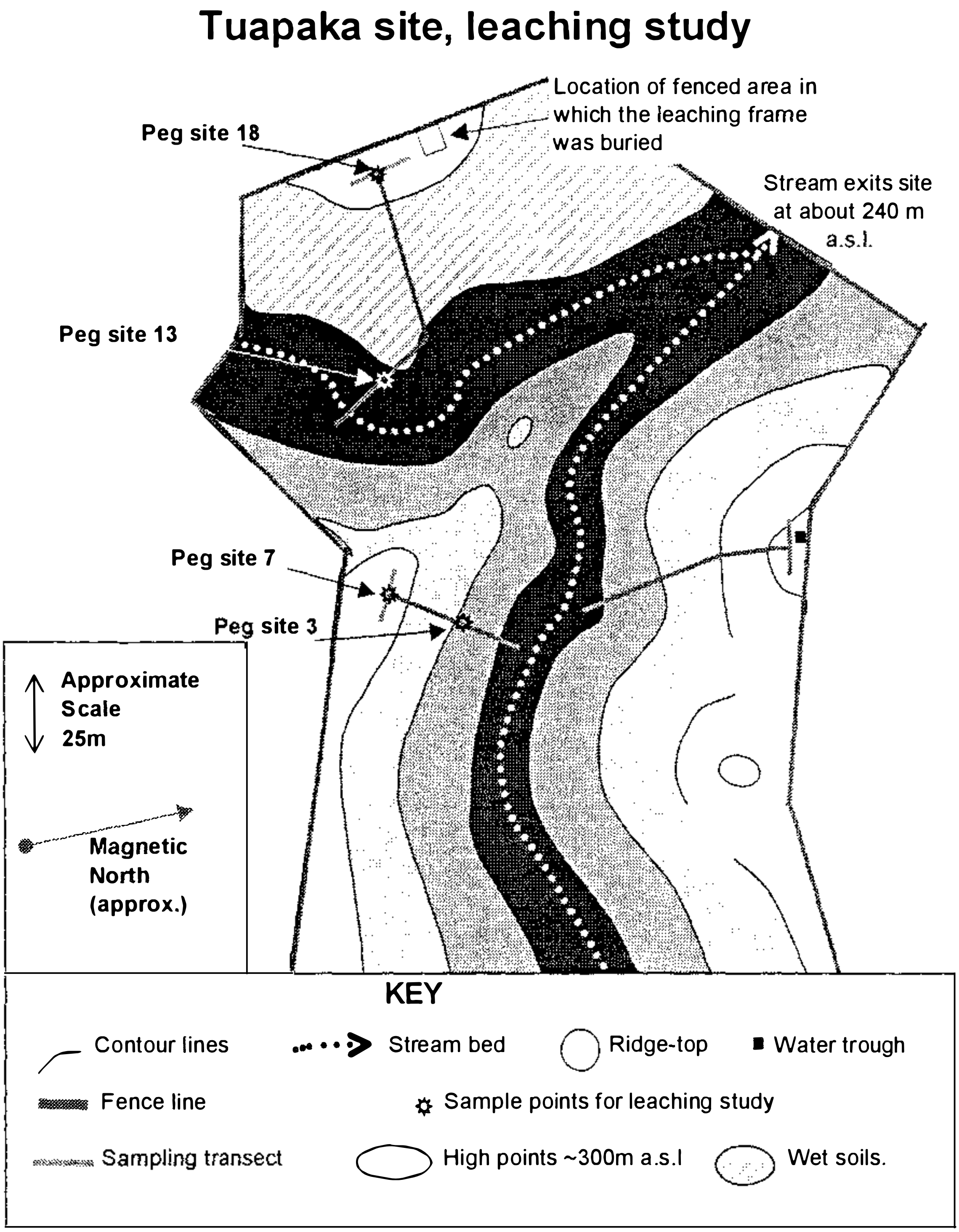


Figure 6.1: Diagram of the Tuapaka site, showing the approximate location of the peg sites where the "stove pipe" soil cores were lifted for the leaching study, in relation to the sampling scheme of the second survey (Chapter 3.4) (lighter shades indicate increasing altitude). The location of the fenced area where the Tuapaka leaching cores were reburied in a leachate collection frame is also indicated, along the western fence line.

Two soil cores were lifted from the lower slopes of an area associated with water seeps and wet, rush-infested soils (peg site 13). This site has previously been associated with low Quick test K, Step K and Olsen P values and medium total K. The clay fraction of soils from this area contained high proportions of vermiculite and hydroxy interlayered vermiculite (HIV) (Table 6.1). This area is thought to represent relatively well weathered topsoils on the slopes of the Tuapaka site.

A second pair of cores was lifted from the ridge-top adjacent to the wetter slopes (peg site 18). This area has been associated with wet seep-affected soils, with medium Quick test K and Olsen P values, and relatively low Step K values. The clay fraction contained an even mix of mica and vermiculite. The increases in Olsen P, Quick test K and mica, compared to the lower slopes, were thought to be the result of increased dung and urine deposition on the flatter areas, although the effect appeared to be limited by the wet environment.

Table 6.1: Summary of the soil properties found in the area of the various peg site locations at which soil cores were lifted for the leaching experiment. The soil K test results are drawn from Chapters 3 and 4. The clay mineralogy is from Chapter 4. The bulk density was measured at approximately 75 mm depth.

					Soil K values			2:1 layer silicates in the clay fraction (%)						
Peg site	**Terrain**	**Slope** (degrees)	**Bulk density** (g/cm^3)	**Olsen P** (ugP/gsoil)	**Quick test K** (mgK/gsoil)	**Step K** (mgK/gsoil)	**Total K_2O** (%)	**Mica**	**Mica-smectite**	**Vermiculite**	**HIV**	**Mica-vermiculite**	**Smectite**	**Mica/verm ratio**
Tuapaka farm														
3	Slope	39	0.94	29	0.12	0.88	2.4	21	20	8	0	0	0	5.1
13	Slope	38	1.09	15	0.15	0.26	1.0	9	9	25*	.	6	2	0.7
7	Ridge-top	5	0.86	61	0.72	1.43	1.6	18	18	11	0	0	0	3.3
18	Ridge-top	20	0.95	26	0.38	0.39	1.0	15	8	10	13	0	11	1
Bernwood farm														
47	Slope	35	0.94	19	0.09	0.40	1.2	9	12	13	19	5	2	0.7
52	Slope	44	1.06	26	0.12	0.44	1.2	8	8	13	24	7	4	0.4
43	Ridge-top	8	0.75	26	0.33	0.53	1.3	14	5	12	23	10	0	0.5
58	Ridge-top	4	0.91	37	0.91	0.79	1.3	31	12	15	0	8	3	2.9

*mixture of HIV and vermiculite

At the Bernwood farm site (Figure 6.2) two sets of leachate cores were lifted from the mid slopes of opposite sides of the same valley (peg site 47 on the eastern aspect and peg site 52 on the western aspect). These soils have previously been associated with low Quick test K and Step K values, and medium total K and Olsen P (Table 6.1). The 2:1 layer silicates in the clay fraction are generally dominated by vermiculite and HIV.

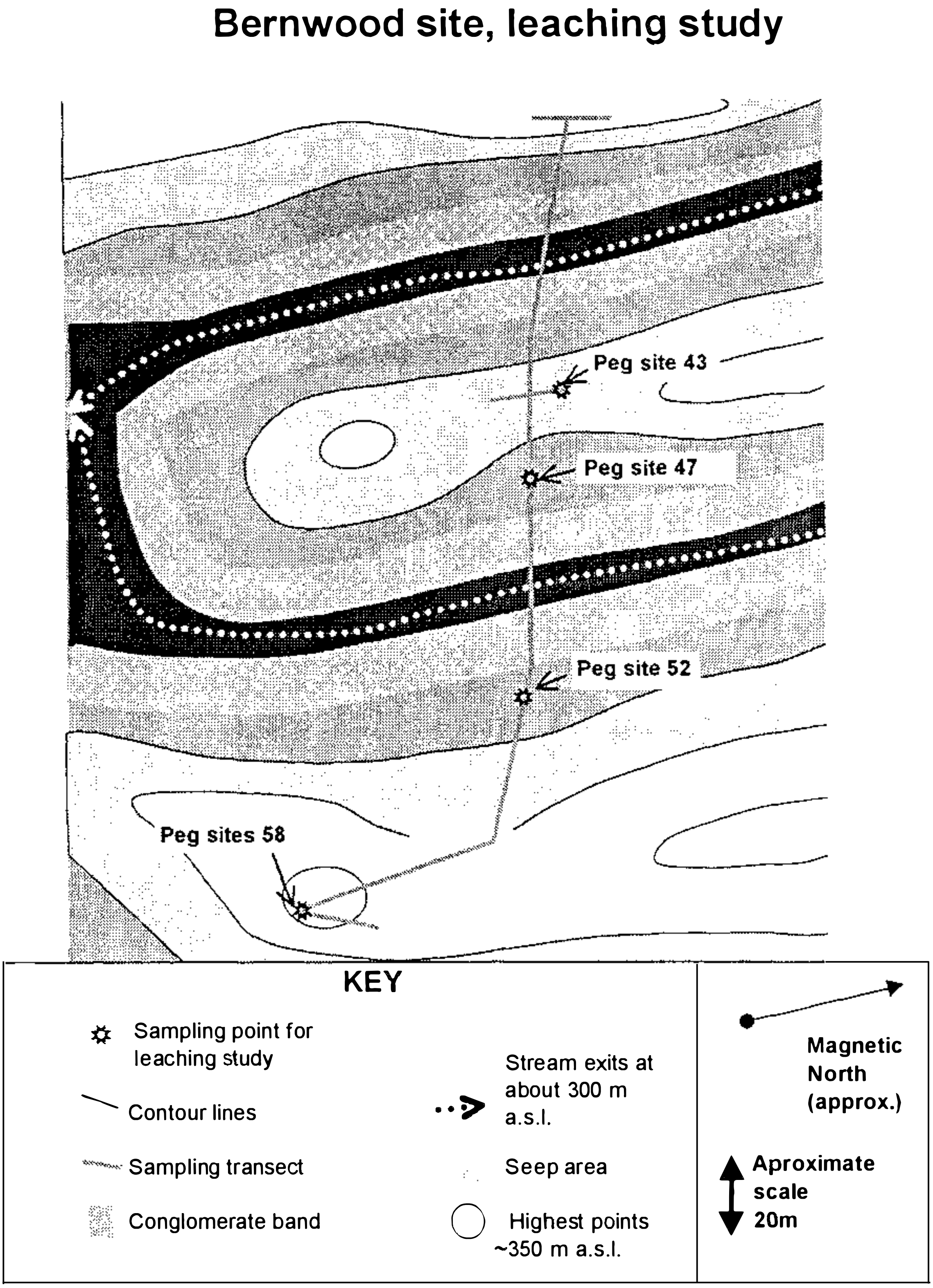


Figure 6.2: Site diagram for the leaching study at Bernwood farm, showing the approximate location of the peg sites where the "stove pipe" soil cores were lifted for the leaching study, in relation to the layout of the sampling transects used in the second survey (Chapter 3.4) (lighter shades indicate increasing altitude). The cores were reburied in a fenced area about 150 m north of the sampling area, in the same paddock.

Leaching cores were also lifted from the adjacent ridge-tops on either side of this valley. One pair of cores was lifted from the side of a small saddle on the crest of a ridge (peg site 43), which has previously been associated with medium Quick test K and Step K values. Olsen P values, soil pH, total K and the clay mineralogy were all quite similar to the soils on the adjacent slops. It is thought that some extra dung and urine deposition has occurred on this ridge-top site, but not enough to affect the soil clay mineralogy. The soils were thought to be a good example of a ridge-top site that would not be classed as an animal campsite.

In contrast, the ridge-top site sampled on the opposite side of the valley (peg site 58) was well frequented by stock. The soil in this area has been previously associated with extremely high Quick test K values, high Olsen P and high Step K values and an increased pH, compared to the soils on the slopes. The mineralogy of the soil in this area was also found to be distinctive. The clay fraction of these soils was characterised by a high mica content and 2:1 layer silicates with hydrated interlayers that were poorly formed. High rates of dung and urine deposition were thought to have caused very high concentrations of K and P in the soil, and the collapse, or partial collapse, of most of the hydrated interlayers in the 2:1 layer silicate clays (Chapter 4.3.4).

6.2.2 Lysimeter method

The soil leaching cores were constructed from 150 mm-diameter galvanised steel cylinders that were 150 mm long. At each designated peg site, two rings of galvanised "stove" piping were set side by side (next to the peg), tapped into the soil and then dug up. A third (100*100*100 mm) soil sample was then cut by spade from adjacent undisturbed soil. Bulk density cores were also lifted, by tapping two 90 cm^3 steel cylinders into the exposed soil profile, at about 75 mm depth.

In each paddock, the leaching cores were taken to a single convenient ridge-top location. A plastic cap and drainage ensemble was strapped onto the lower end of each core, which was then reburied in a leaching frame (Figure 6.3). The caps were 150 mm diameter plastic drain pipe caps. 50µm nylon mesh had been glued over a 22 mm drainage hole that was drilled into each cap. The drainage holes were attached by standard plastic drainage joints to plastic bottles. All pipes were sealed using silicate gel

“Stove pipe” soil cores collected from pasture and reburied at ground level in frame. Soil and turf replaced around cores.

Wooden leachate frame.

Below the frame the leachate is collected in sealed bottles that are protected from sunlight.

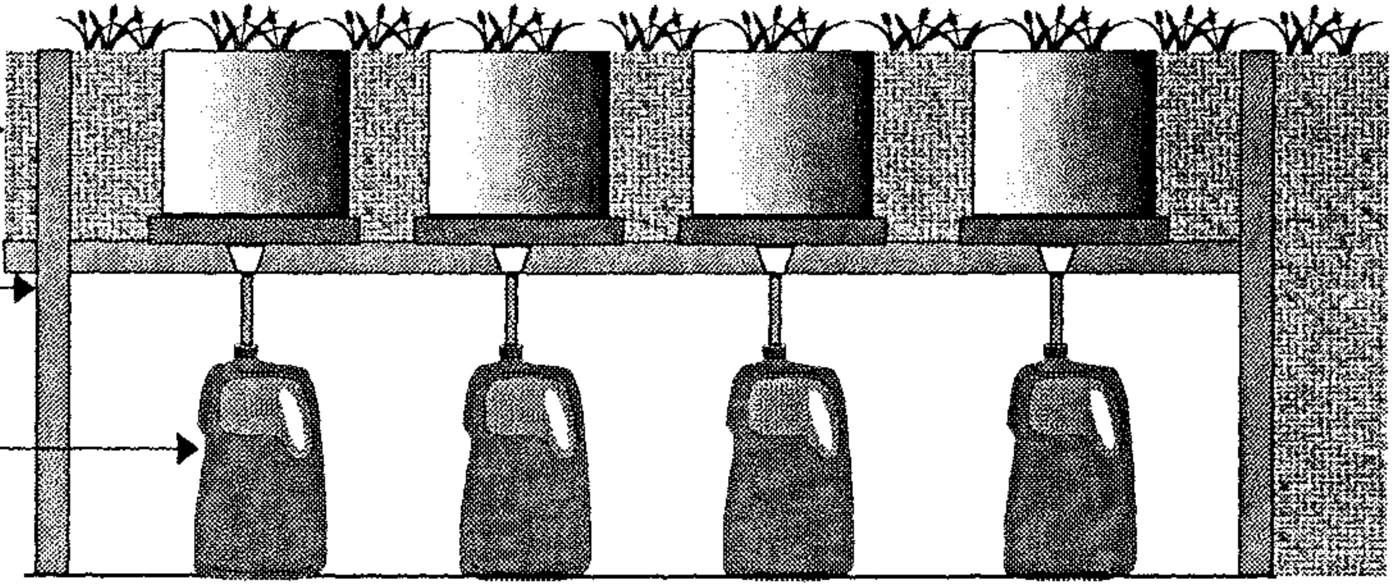


Figure 6.3: Diagram of one half of a leaching frame.

or plumbers tape (Figure 6.3) (method after Sakadevan, 1991). The lysimeters were protected from stock.

The collection bottles were dug in underneath the wooden frame, and were reburied under boards and turf after each collection of the leachate, to keep out the sunlight. The bottles were cleared at regular intervals, and after a significant rain event. The leachate was stored under refrigeration for subsequent analysis.

Locating the soil leaching cores in the field exposed them to realistic rainfall and temperature conditions but they were isolated from lateral subsurface and overland flows, and were removed from the micro-environmental conditions, such as aspect and grazing animal effects, which had formed the different soils at each peg site.

The cores were lifted and installed in the frames between 3 and 5 September 1995 (early spring). The collection bottles were checked weekly but it was quite a long time before a significant amount of rain fell and there was some leachate in the traps. The first collection was made at both sites on 11 October 1995 (Table 6.2). The leachates were then collected at about weekly intervals for the next two weeks at the Tuapaka site, and then not for another month. Little rain fell at the Bernwood site after the first collection and only small amounts of leachate were collected. These were added to a collection made after a significant rain event on the 17th of November, which was then analysed. The leachate traps continued to be maintained on this system until the end of the year. A final leachate collection was made one year after the experiment was established.

Table 6.2: Collection period (weeks) over which each leachate collection set was accumulated, with the last date of collection shown, for each set that was obtained from the two farms.

Tuapaka			Bernwood		
Set	Weeks		Set	Weeks	
1	5	11 October 1995*	1	5	11 October 1995*
2	1	18 October 1995	2	5	17 November 1995*
3	1	25 October 1995	3	2	29 November 1995
4	4	24 November 1995	4	3	2 October 1996*
5	3	1 October 1996*			

* indicates anions as well as cations were analysed in the leachate.

Cation concentrations were measured on five sets of collected leachate from the Tuapaka site and four sets from the Bernwood site (Table 6.2). Total cations and anions were measured in the leachate solutions collected at weeks 5 and 56 at the Tuapaka site and weeks 5, 10 and 56 at the Bernwood site.

6.2.3 Cation analysis

Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} concentrations in the leachates were measured in the water matrix, with 1.26 g/l CsCl and 2.41 g/l $SrNO_3$ added, and dilutions as necessary. Ca^{2+} and Mg^{2+} were measured by atomic absorption spectroscopy. K^{+} and Na^{+} were measured by flame emission spectroscopy.

6.2.4 Anion analysis method

Anion analysis was by ion chromatography, using an IC-PAK A anion guard column and an IC-PAK A anion chromatography column. The eluent used was a sodium gluconate/borate buffer (pH ~ 8.5) containing 1.48 mM sodium gluconate, 5.82 mM boric acid, and 1.30 mM sodium tetraborate. The working standard was a mixed anion standard containing 100 mg/L each of fluoride, chloride, nitrate, phosphate, and sulphate. Run conditions were an eluent flow rate of 1.2 ml/min, column temperature of 35°C, and injection volume of 25 microlitres. [2]

6.2.5 Soil exchangeable cations

Soil exchangeable cations were extracted using 2.5g soil in 25ml 0.2 M $BaCl_2$ - triethanolamine (TEA) solution at pH 8.2, shaken overnight, then centrifuged (Blakemore et al., 1987).[3] Exchangeable cations in the supernatant were analysed as per section 6.2.3, in a $BaCl_2$ matrix. The soils were also tested for Step K, a measure of plant available non exchangeable K (Chapter 3.3.2.5).

There was a very strong relationship between the exchangeable K values of soil samples analysed for Quick test K (2 minutes in ammonium acetate) and the same samples analysed by $BaCl_2$-TEA extraction (regression $R^2 = 0.99$), but the Quick test K value was, on average, 0.14 cmol K/kg soil less than the Ba-extractable value for the same soil. The effect was consistent with the lesser extraction of K expected for the shorter Quick test, and was not thought to be significant within the high level of variability generally found for soil tests of exchangeable K.

---

[2] Dr H. Percival at Landcare Research Ltd, Palmerston North, carried out the anion analysis.

[3] S. Weil carried out the $BaCl_2$-TEA soil extractions.

6.2.6 Statistical analysis

The frequency distributions of the leachate data sets were skewed. All data were log transformed, as appropriate, for probability tests and also the estimate of averages, as indicated. The statistical significance of the results was tested using simple nested anova models. The differences between pairs of soil cores from each peg site were regarded as treatment effects. The different leachate collection sets from each pair of cores were regarded as nested effects within each treatment. The two sets of results from each pair of soil cores were regarded as replicates within the nested effects.

Significant differences were found at the treatment level for concentrations of K^+ and Na^+ in the leachate. No significant differences were identified for Ca^{2+}, Mg^{2+}, total cations, or anion deficit (no significant model fits). Anion concentrations in the leachate were found to vary significantly between the different collection sets. All results from peg site 58 were also found to vary between the collection sets and were treated as outliers in the SAS models and reported separately.

6.3 Results and discussion

6.3.1 Leachates

6.3.1.1 Cations

Marked differences in the average K^+ concentration in the leachates were found, especially depending on the peg site location that each pair of soil leaching cores was obtained from (Table 6.3). There were some consistent differences between the two replicate cores, particularly the ridge-top soil cores from Tuapaka (Figure 6.4a), but the differences were on a smaller scale than the differences between the peg sites. There was no consistent pattern of changing K^+ concentration that was related to a particular leachate collection set, and K^+ concentration had a poor correlation to the total cation charge in solution (r=0.54).

At the Tuapaka site, a large average increase in K^+ concentration was found in the leachate of the soil cores that were obtained from the ridge-tops compared to the leachates of soil from the steeper slopes (Table 6.3). At the Bernwood site, the K^+

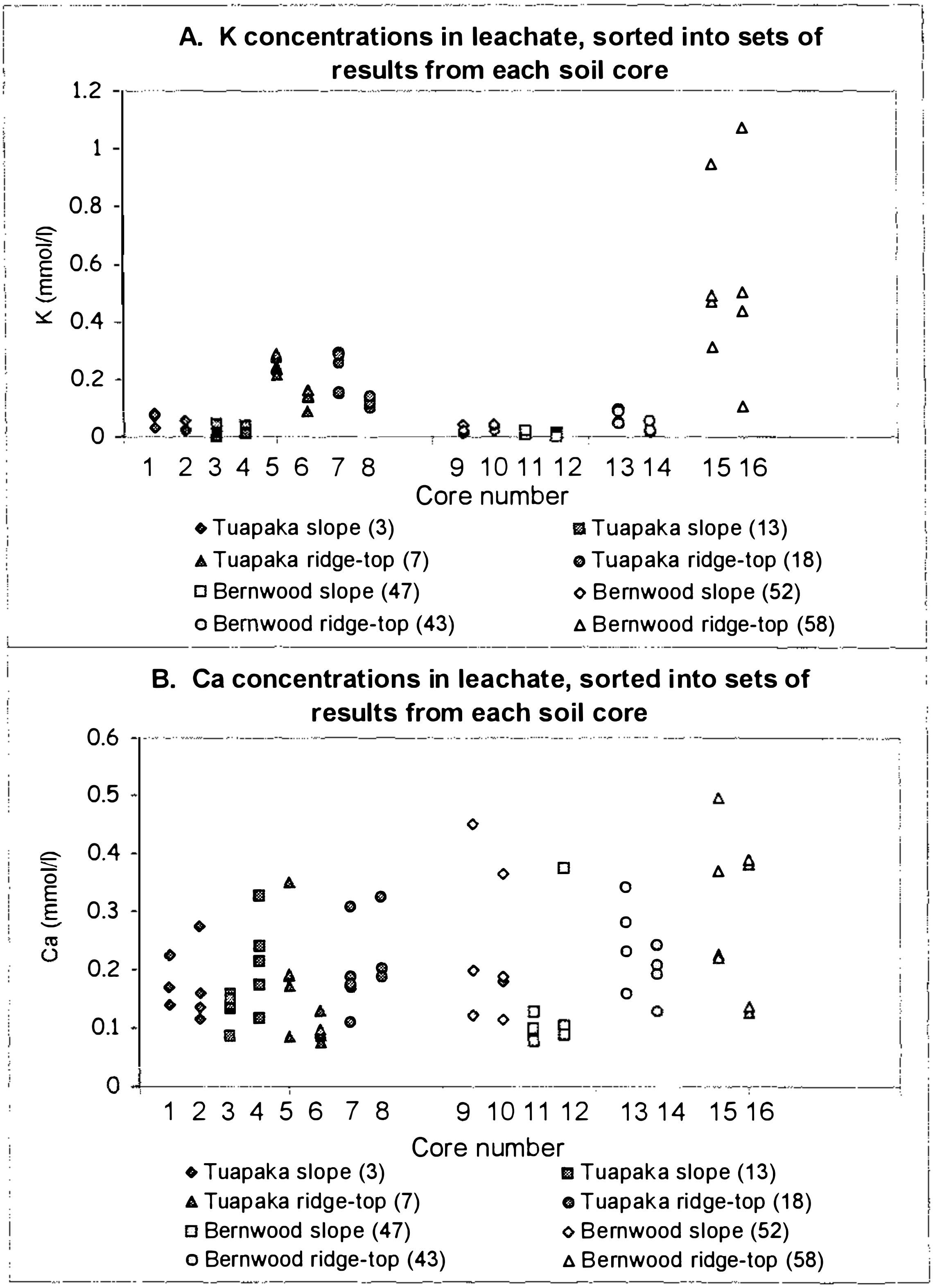


Figure 6.4: Leachate concentrations of K (A) and Ca (B) in all leachate solutions collected from 16 "stove pipe" soil cores exposed to rainfall. The cores were lifted in pairs from eight ridge-top or slope locations in two steepland paddocks. Leachates were collected between September 1995 and October 1996. All results are presented here, to illustrate the range of results obtained from the pairs of cores from each peg site

Table 6.3: Concentration and ratios of cations in soil leachates, spring 1995 and spring 1996, as well as total cation charge and the concentration ratio (CR_k) (see Chapter 2.2.4). The results show the median concentration of each cation for the whole experiment, as well as the ranges and anova results. The medians were calculated as back transformations of the anova treatment means of ln transformed data (see section 3.4.3.4). Significant differences were based on a least-squares-means t-test with p-values<0.0005 and a significant model fit.

Site of soil core collection	**Tuapaka farm**				**Bernwood farm**		
	Steep slope 3	**Steep slope 13**	**Ridge -top 7**	**Ridge -top 18**	**Steep slope 47**	**Steep slope 52**	**Ridge -top 43**
K^+ (mmol/l) Mean	0.04 b	0.02 ab	0.18 c	0.17 c	0.008 a	0.03 ab	0.04 b
Range	0.02 - 0.08	0.003 – 0.05	0.09 - 0.29	0.10 - 0.29	0.0005 - 0.02	0.01 - 0.04	0.02 - 0.10
Ca^{2+} (mmol/l) Mean	0.17 a	0.16 a	0.13 a	0.20 a	0.11 a	0.20 a	0.21 a
Range	0.11 - 0.27	0.09 – 0.33	0.08 - 0.35	0.11 - 0.32	0.08 - 0.37	0.11 - 0.45	0.13 - 0.34
Mg^{2+} (mmol/l) Mean	0.07 a	0.05 a	0.07 a	0.12 a	0.05 a	0.07 a	0.06 a
Range	0.05 - 0.11	0.03 – 0.09	0.04 - 0.21	0.06 - 0.19	0.03 - 0.16	0.04 - 0.14	0.04 - 0.09
Na^+ (mmol/l) Mean	0.28 b	0.12 a	0.22 ab	0.21 ab	0.13 a	0.10 a	0.14 a
Range	0.16 - 0.47	0.08 – 0.18	0.12 - 0.27	0.14 - 0.30	0.08 - 0.18	0.06 - 0.20	0.06 - 0.47
Ca/Mg Mean	2.34 b	3.60 c	1.79 a	1.64 a	2.46 b	3.00 b	3.59 c
Range	2-2.8	2.8-4.6	1.4-2.4	1.5-1.8	2.1-2.8	2.7-3.4	3.1-4.6
Total charge* Mean	0.81 a	0.57 a	0.84 a	0.99 a	0.47 a	0.68 a	0.75 a
Range	0.52 - 1.18	0.36 – 1.01	0.56 - 1.61	0.64 - 1.53	0.33 - 1.17	0.41 - 1.41	0.41 - 1.16
CR_k (mol/l)$^{1/2}$ **Mean**	0.003 b	0.0015 ab	0.013 c	0.01 c	0.001 a	0.0015 ab	0.0025 ab
Range	0.001 - 0.005	0.0008 - 0.004	0.008 - 0.024	0.004 - 0.017	0.00005 - 0.002	0.0006 - 0.003	0.001 - 0.006

* Total charge= $[K^+]+[Na^+]+2([Ca^{2+}]+[Mg^{2+}])$

N.B. The leachates of the soils from ridge-top peg site 58 and the anion concentrations were not included because these leachate concentrations varied strongly between different collection sets and consequently there was no valid average over the course of the experiment.

concentrations in the leachates were not so consistently related to slope. The K^+ concentration in the leachate of the soil cores obtained from ridge-top peg site 43, which was not an animal campsite, was similar to the K^+ concentration in the leachates of the soils from the steeper slopes.

In contrast, the K^+ concentration in the leachate of the soil from ridge-top peg site 58 was much greater than in any of the other leachates at the first collection (Appendix 2, Table 1). This difference subsequently decreased with time, so that by the end of the experiment, the K^+ concentrations in the leachate of the soil from peg site 58 was similar to the leachates of soil from the ridge-tops at the Tuapaka site (examined further in Section 6.3.1.3).

Ca^{2+} and Mg^{2+} concentrations varied considerably with time in leachate of the soil from each peg site. No statistically significant patterns could be identified, except that the Ca^{2+} and Mg^{2+} concentrations were well correlated to each other and were well correlated to the total cation charge in the leachate (r_{Ca} =0.81, r_{Mg}=0.90) (Table 6.3, Figure 6.4b)

The intensity ratio characterises the relative ability of a soil to maintain K^+ in solution compared to the Ca^{2+} and Mg^{2+} concentrations (Chapter 2.2.4). In this study, intensity ratios could be calculated for every leachate solution during the experiment. The cation concentrations were relatively low and activity effects were expected to be minimal, so a simple concentration ratio (CR_k) was calculated (equation 2, Chapter 2). The CR_k values of the leachate solutions in this study were found to be significantly different according to the different peg site sources of the soil cores (Table 6.3).

Na^+ was the dominant cation in the leachates in terms of the average molar concentration across the whole experiment, although some leachates contained higher concentrations of Ca^{2+} or K^+. Significantly greater Na^+ concentrations were found in the leachates of the soil cores lifted from peg site 3, a dry slope with a northeasterly aspect (Table 6.3) (see Chapter 3.4.3.4.2 for more information on this soil). No significant effects of collection set were identified and there was only a poor relationship between Na^+ concentration and total cation charge in solution (r=0.58).

6.3.1.2 Anions

Anion concentrations were measured in leachates collected in October 1995 and October 1996 from the Tuapaka site and in leachates collected at these times and also November 1995 from the Bernwood site (Figures 6.5-7). HCO_3^- was detected in many samples, but was not quantified, so the concentration of HCO_3^- and organic anions was estimated by calculating the anion deficit. The anion deficit estimate generally dominated the anion

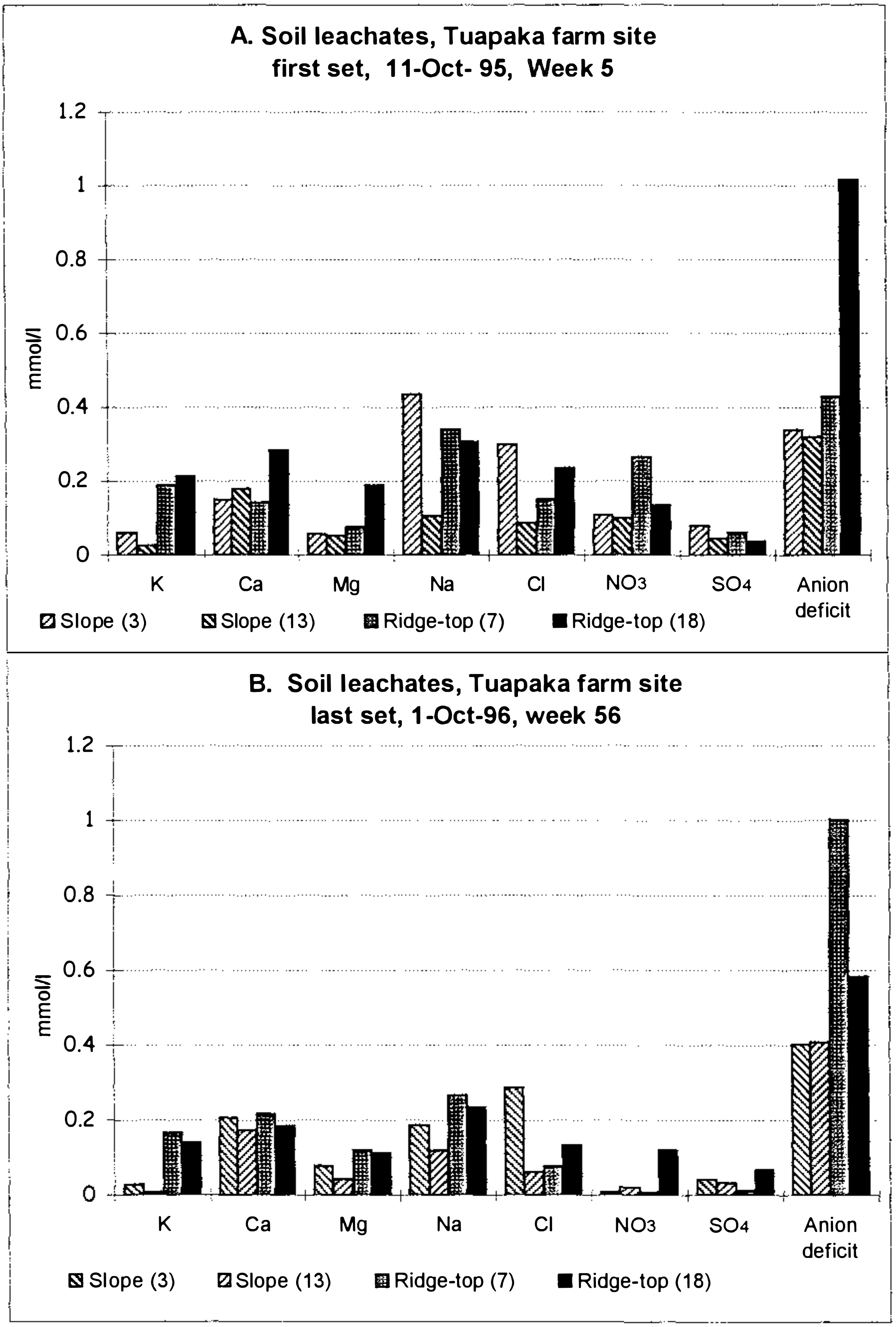


Figure 6.5: Cations and anions in leachates collected from soil cores drawn from four ridge-top or steeply sloping sites on Tuapaka farm, spring 1995 and 1996. Each result is an average of two replicate cores.

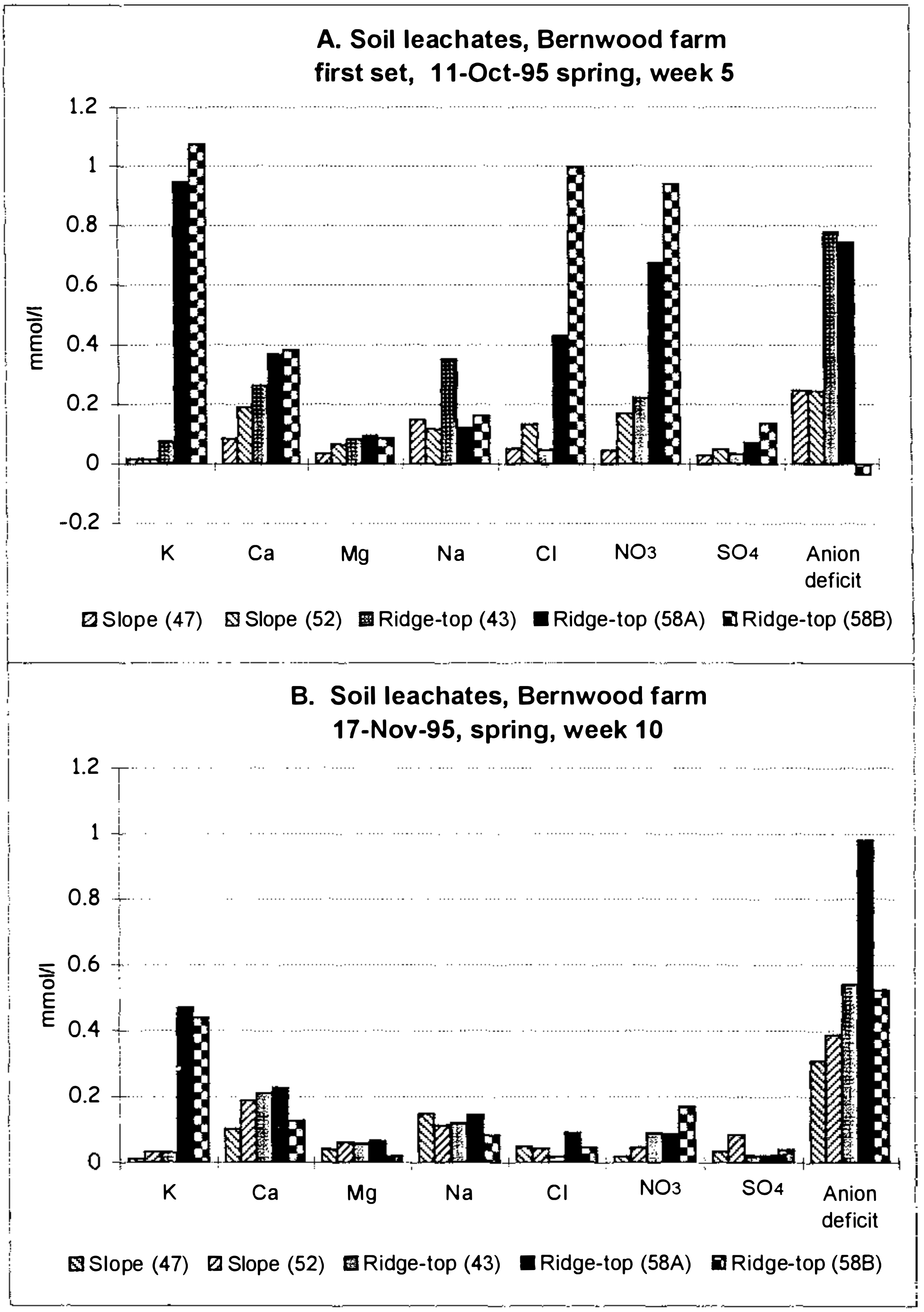


Figure 6.6: Cation and anion concentrations in leachates from soil cores collected from four ridge-top and steeply sloping sites on Bernwood farm, spring 1995. Results from the replicate cores for peg site 58, a ridge-top site, were dissimilar and are separated in the figure, otherwise, each column shows the average result from two replicate soil cores.

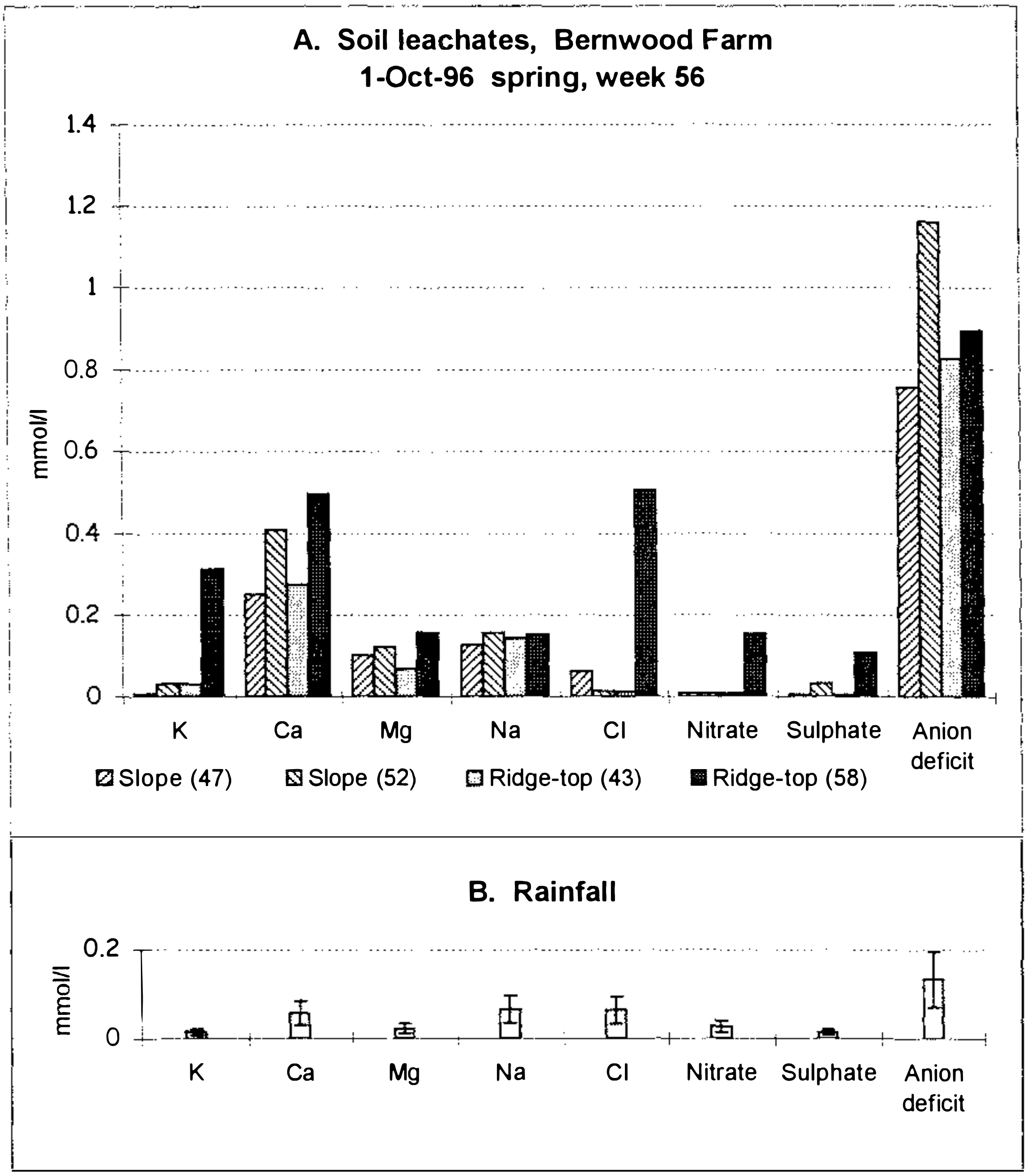


Figure 6.7: A: Cations and anions in leachate collected from lysimeters of soils drawn from four ridge-top and steeply sloping sites on Bernwood farm, spring 1996. Each column shows the average result from two replicate soil cores, including core 58.

B: Average composition of five samples of rain water, collected from both the Tuapaka and Bernwood sites, spring 1995.

concentrations found, followed by Cl^-, NO_3^- then SO_4^{2-}. Small amounts of NO_2^- were also detected in some samples.

In contrast to the K^+ patterns in the leachate, the anion concentrations changed considerably with time between the collection sets. Also, there were few consistent patterns that could be related to the source of the soil core. Cl^- concentrations were extremely high in the first leachate of the soil cores from peg site 58 (Figure 6.6a) and consistently high in the leachates of the soil cores from peg site 3 (Figure 6.5). Relatively high NO_3^- concentrations were associated with soil cores from the ridge tops, particularly peg site 58. SO_4^{2-} concentrations were consistently low in the leachate, compared to the other anions. The calculated anion deficits of the soil cores obtained from the steeper slopes at each site were usually similar but there were large variations in the anion deficits of the leachates from the ridge-top soil cores. This effect may have been caused by the presence in the leachate of cations that were not accounted for, such as NH_4^+.

Intensity ratio and anion load

A simple model to predict K^+ concentration in solution from the average CR_k for each peg site and the total cation charge of each leachate solution could account for much of the variation of K^+ concentration (R^2=0.71) (Equation 4, Chapter 2; Appendix 3, SAS model 1, excluding the leachates of peg site 58 which had no stable value over time). The strong correlation found in this study, between total cation charge and the concentration of Ca^{2+} and Mg^{2+} in the leachate and the poor correlation of K^+ concentration to total cation charge was also predicted by this relationship. Thus, the variations of cation concentrations in the leachates at each peg site with time appeared to have a reasonable relationship with the standard theoretical models, although 30% of the variability could not be accounted for, even when modelling at such a simple level.

A possible explanation for the variability in K^+ leaching over time, which could not be accounted for by the model, would be the effect of earthworms in the soil cores. Earthworms are expected to affect a considerable proportion of a topsoil, and the action of earthworms has been observed to modify the proportions of exchangeable K and Step K in soils that had a similar chemistry to the soils in this study (Basker et al., 1994). Earthworms may be causing sufficient variation to the exchangeable properties of the soil exposed in the macropores to cause the small-scale temporal variations in K^+ concentration in the leachate.

6.3.1.3 Core 58

A particular exception to the general patterns was found in the leachates of the soil cores from ridge-top peg 58 at Bernwood farm. These leachates had some distinct changes with time, particularly between the first and second collections of the leachate from the second replicate core (58B) (Figure 6.6). The first leachate from this core contained very high concentrations of K^+, NO_3^- and Cl^-, while Ca^{2+}, Mg^{2+}, Na^+ and SO_4^{2-} concentrations were similar to leachates from the other soil cores (Appendix 2, Table 1). This leachate was also notable for having an anion surplus rather than a deficit. At the second leachate collection, 5 weeks later, the K^+ concentration in the leachate from this soil core was reduced from 1.1 mol/l to 0.4 mol/l, and the Cl^- and NO_3^- concentrations were comparable to the other Bernwood soil cores. At this time, an anion deficit was estimated for both cores, although markedly less for core B.

A possible explanation for these effects is that the soil at peg site 58 was exposed to urine not long before the soil cores were lifted, and that the soil in core B was more affected than that soil in core A. The presence of large amounts of NO_3^- in the leachate was consistent with the expected conversion of urea in the urine to NH_4^+ then to NO_3^- (Williams and Haynes, 1994)(see Chapter 2.3.3 for more discussion). The measured anion surplus in the leachate of core 58B at the first collection could be explained as unaccounted for NH_4^+, which had yet to be converted to NO_3^-. Five weeks later, at the next collection, all the ionic concentrations had dropped and an anion deficit was recorded (Figure 6.6).

6.3.1.4 Comparisons with other studies

Another lysimeter study was in progress at the same time as this study, on similar New Zealand soils developed in greywacke parent materials and at a similar latitude (Parfitt et al., 1997). The sloped study site had a northeasterly aspect, similar to the location of the peg site 3 soils in this study. The soil exchangeable chemistry of the study site was also similar to the soils at peg site 3 in this study. The soil solution cations were dominated by Na^+, followed by Ca^{2+}, Mg^{2+} and K^+ respectively, as in the present study. HCO_3^- was quantified by Parfitt et al. (1997) and was the dominant anion in the macropore solutions, followed by the combined organic anions, Cl^-, and then relatively small amounts of SO_4^{2-} and NO_3^-. In the present study, the proportions of cations and anions in the leachate solutions of peg site 3 were very similar to those of Parfitt et al. (1997).

The error estimates in the study of Parfitt et al. (1997), and also in a different leaching study under pasture on New Zealand gibbsitic soils (Steele et al., 1984), were similar to the results of the present study, including a report of skewed distributions from Steele et al. (1984). Both studies used suction cups buried in the soil, with tension applied to maintain the continuity with the soil solution. In the present study, no tension was applied to the base of the lysimeters but comparable leachate concentrations, particularly for K, were obtained. The technique used in the present study therefore appears to have provided a reasonable estimate of the soil solution composition of the macropores.

6.3.1.5 Rainfall and volume

The incident rainfall at the two farms was analysed for cations and anions. Low concentrations of all the ion species identified in the soil leachates were found in the rainwater. While the soil leachate concentrations were generally much higher than the rain water, some soil cores may have been close to equilibrium with the rainwater. In particular, the composition of the first collection of leachate from the soil core 47B was quite similar to the composition of the rainfall, except that the SO_4^{2-} and Na^+ concentrations increased in the soil leachate (Appendix 2, Table 1).

The intention of this study was to examine the relative concentrations of K, and the other major cations, in leachate from topsoils taken from contrasting areas in hill country paddocks. The results can also, however, be combined with other published data (Parfitt et al., 1997) to estimate the order of magnitude of likely annual leaching losses of K.

The data indicated an approximate 9- fold range in K^+ concentration in leachates from soils collected from campsite areas and steep slopes (Table 6.3). Parfitt et al. (1997) estimated an annual leaching loss of 3.6 kg K ha^{-1} from a hill-country site under pasture. If their site was equivalent to an average site on the steep slopes in the current study, then a 9- fold increase in concentration would suggest that approximately 40 kg ha^{-1} yr^{-1} may be lost by leaching from campsite areas.

In fact, this is likely to be an upper estimate, as the site studied by Parfitt et al. (1997) was most similar to peg site 3 in the current study. This site had K^+ leachate concentrations approximately a quarter of those from the campsite areas. Applying this factor of four to the data of Parfitt et al. (1997) gives an estimated annual leaching loss of K^+ from campsite areas of 14-16 kg ha^{-1}.

Based on the accumulation of P under campsites (Chapter 4.3.5), between 28 and 50 kg K/ha/year was thought to be transferred onto the animal campsites on the ridge-tops of these sites. The expected resulting accumulation of K was not observed in the topsoils of the campsites in Chapter 4. The predicted scale of the leaching losses indicated that, while the variability of the process will be very high, much of K transferred to the ridge-tops could have been leached into the subsoil. This result is in contrast to most studies of urine leaching, which tend to find low losses of K, usually after a single application of urine to a previously unaffected profile. This study indicated that leaching losses of K^+ will increase where soils are regularly affected by urine.

6.3.2 Soil exchangeable cations

A soil sample (100*100*100 mm), similar in size to the leaching cores, was taken from each peg site at the same time that the leaching cores were lifted. Each sample was cut into 25 mm depth sections and analysed for Ba-exchangeable cations and Step K (nitric acid extract, Chapter 3.3.2.5).

In soils from the ridge-top sites, exchangeable K in the top 50 mm was in the very high range for New Zealand soils (Table 3.1) dropping to the high range at 50 - 100 mm depth (Figure 6.8.a). An exception was the level of exchangeable K in the soil of peg site 58, which was in the very high range throughout the profile (Table 6.4). The very high exchangeable K values were thought to be the result of successive urine events affecting the same soil profile (Chapters 3 & 4).

Table 6.4: Ba-exchangeable soil chemistry, average value of 0-100 mm depth, from samples collected adjacent to the eight leachate core collection sites.

	Tuapaka farm				Bernwood farm			
Site of soil core collection	**Steep slope 3**	**Steep slope 13**	**Ridge -top 7**	**Ridge -top 18**	**Steep slope 47**	**Steep slope 52**	**Ridge -top 43**	**Ridge -top 58**
K (cmol(+)/kg)	0.47	0.50	1.20	1.29	0.34	0.79	1.12	2.1
Ca (cmol(+)/kg)	8.0	6.4	7.3	7.5	10.0	6.0	7.9	7.5
Mg(cmol(+)/kg)	2.2	1.2	3.0	2.7	1.7	1.4	1.5	1.7
Na (cmol(+)/kg)	0.10	0.12	0.32	0.17	0.11	0.09	0.11	0.03
Ca/Mg	3.6	5.3	2.3	2.8	5.9	4.3	5.3	4.4
Ca+Mg	10.2	7.6	10.3	10.2	11.7	7.4	9.4	9.2
Q_k ratio	0.05	0.07	0.12	0.13	0.03	0.11	0.12	0.23

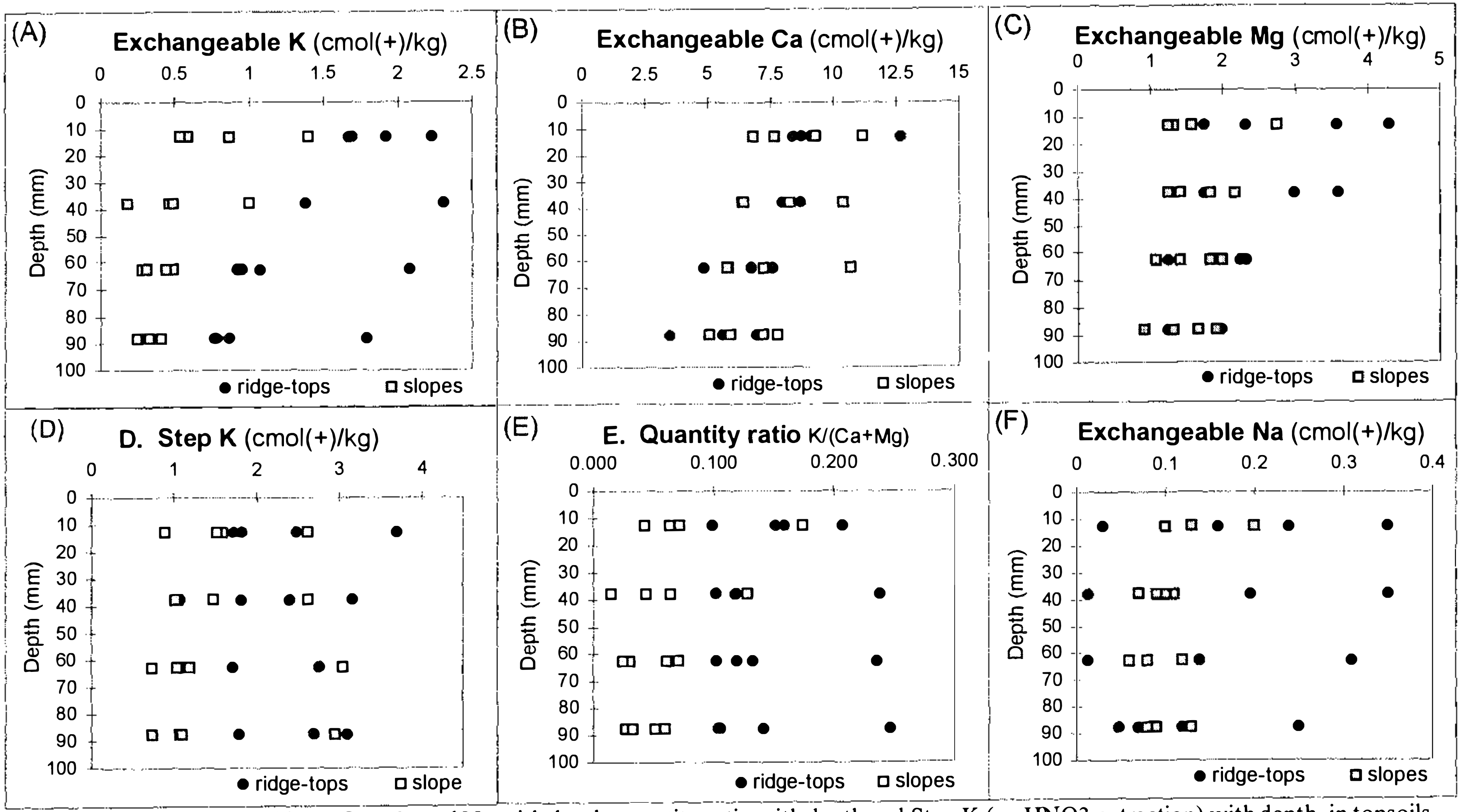


Figure 6.8: Ba-exchangeable K, Ca, Mg and Na with depth, quantity ratio with depth and Step K (an HNO3 extraction) with depth, in topsoils from ridge-tops and steep slopes in steepland pasture. Soill sample were 100*100*100 mm blocks cut into 25 mm depth sections.

Exchangeable K in the soils from the steeper slopes generally ranged from medium to high values in the top 25 mm, and low or very low values down the remainder of the profile. The exception was the soil from peg site 52 that was in the very high range in the top 25 mm, the high range in the top 25-50 mm and was in the low range down the remainder of the profile.

Comparisons with the New Zealand standard values for NH_4-exchangeable Ca and Mg (Blakemore et al., 1987) indicated that most of the exchangeable Ca and Mg values were in the medium range for New Zealand soils, with a few values in the high range, associated with the top 50 mm of the profile. The quantities of exchangeable Ca and Mg were quite similar in the soils of the different peg sites, compared to high variability of K and Na (Figure 6.8.b&c), as was also noted for the leachates. The Bernwood soils did tend to have less exchangeable Mg, which may be the result of regular liming on this property. Total Ca was also increased in these soils (Chapter 4.3.5)

The pattern of exchangeable Ca/Mg ratios had a general correspondence to the same ratio in the leachates (Table 6.3 and 6.4). The relatively low Ca/Mg ratios in the soil of peg sites 7 and 18 may reflect the increase in exchangeable Mg and loss of Ca that was found in a study of urine affected soils of similar mineralogy (Early et al., 1998). There was, however, no corresponding drop in Ca/Mg ratio in the soil from ridge-top peg site 58 at the Bernwood site, which was also evidently affected by urine.

The quantity ratios (Q_k= K/(Ca+Mg), see Chapter 2.2.4) followed the pattern of exchangeable K. This would be expected because Ca and Mg dominated the exchange surface, and neither Ca nor Mg changed greatly relative to the sharp changes in the quantities of exchangeable K found in the soils from the different locations in this study. The ratios also did not change greatly with depth (Figure 6.8e), as all the exchangeable cation values tended to decrease with depth.

Exchangeable Na values ranged from very low in the soil from ridge-top peg site 58, up to medium values in the upper profile of the ridge-top soil from peg site 7 (Figure 6.8f). The effect of increasing depth was generally less marked for Na, compared to K. There was a general disparity between the low exchangeable Na values and the relatively high concentration of Na^+ in the leachates. There was also a disparity between the pattern of exchangeable Na in the soil at the different peg sites and corresponding Na^+ concentrations in the leachate. In particular, the soil at peg site 3, which leached the highest concentrations of Na^+, had a low exchangeable Na value, similar to the other soils from the steep slopes.

6.3.3 Modelling K leaching

As has been demonstrated in this study, the measurement of K^+ leaching in hill country is a difficult exercise. This accounts for the paucity of published data on the subject. Furthermore, where cation leaching in hill country has been studied (Sakadevan et al., 1993; Parfitt et al., 1997), the measurements have, of necessity, been restricted to small localised points in the landscape.

An alternative approach would be to use soil test information in a model to predict leaching losses of K, rather than actually having to measure it.

6.3.3.1 Exchangeable K

The simplest modelling relationship that could be examined was between soil exchangeable K and K^+ concentration in the leachate (Khasawneh, 1971). In this study Ba-exchangeable K measured on the 100 * 100 * 100 mm third core sample had a moderate relationship with the K^+ concentration in the leachates (Figure 6.9a).

These soil samples, tested for Ba-exchangeable K, were taken after the leaching cores were lifted at each peg site, so were from soil about 500 mm from the peg. Other soil samples had been taken six months earlier, at the same point where the leaching cores were later lifted, by bulking four small soil samples. These samples were part of the second survey (Chapter 3.4) and were tested for Quick test K (NH_4-exchangeable K). The Quick test K values had an improved relationship to K^+ concentration in the leachates (Figure 6.9b), which was thought to be an indication of the high spatial variability of exchangeable K found at very short distances at these sites (Chapter 3.3). It does appear, therefore, that the high spatial variability of exchangeable K will make modelling of K^+ leaching difficult. This is because the measurements of exchangeable K have to be made on cores separate from those used to measure leaching.

It was noted that, in this study, the relationship to K^+ concentration in the leachate could be further improved by substituting the Ba-exchangeable K value (average to 75 mm) for peg site 18 into the Quick test K results. This peg site was in an area with relatively wet soils, which were expected to have only medium exchangeable K values, compared

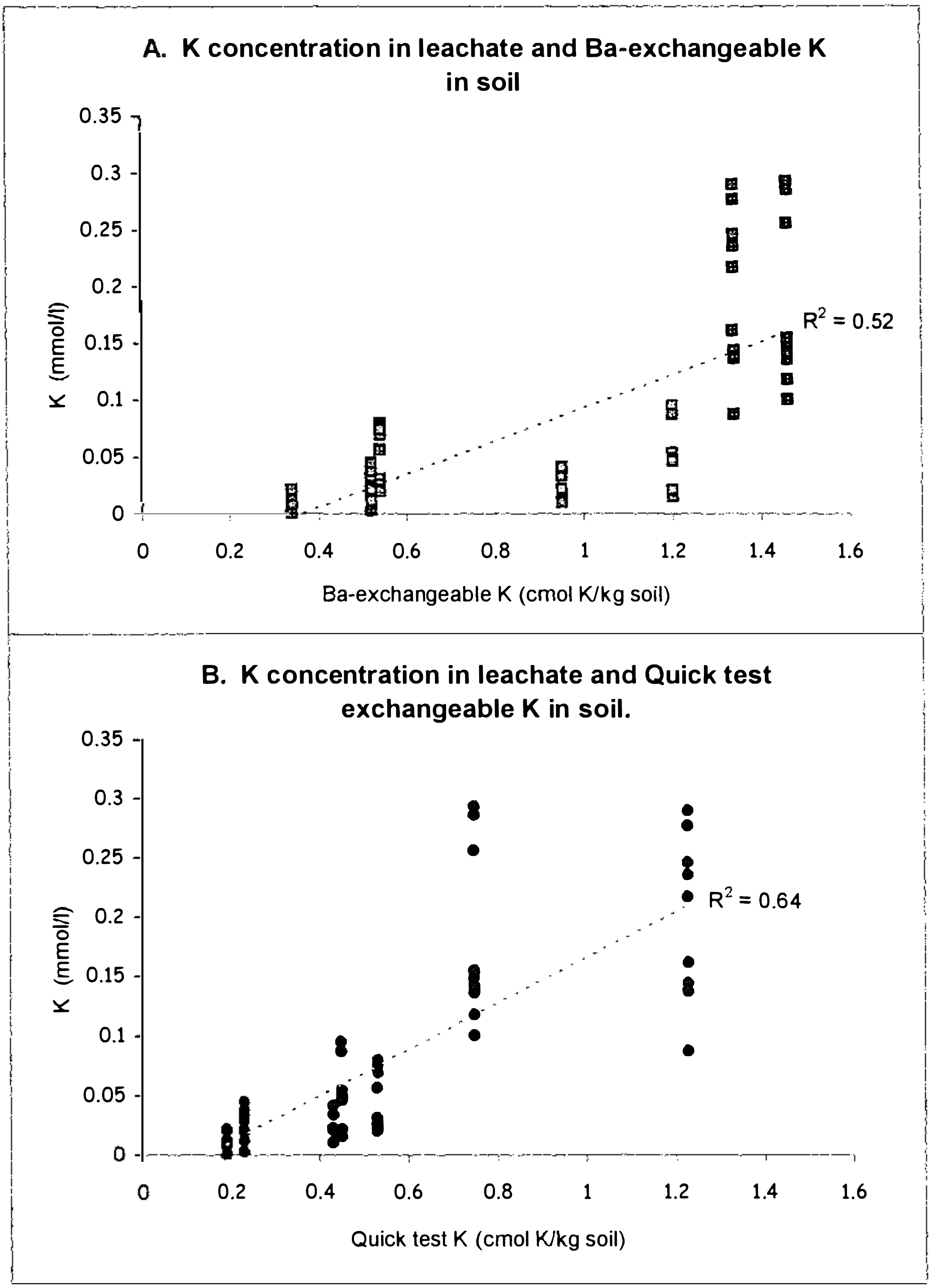


Figure 6.9: Relationship between K concentration in leachate and Ba-exchangeable K in soil adjacent to the leaching cores (A). Relationship between K concentration in leachate and Quick test exchangeable K in soil sampled from the leaching cores six months prior to leaching experiment (B).

to the drier ridge-top campsite areas like peg site 7, which had high exchangeable K values. Lower K^+ concentrations in the leachate might therefore have been expected at peg site 18, compared to peg site 7, but in this study the K^+ concentration in the leachates of these peg sites were similar. It was also noted that the Ba-exchangeable K value (to 75 mm) of the soil from peg site 18 was much higher than the Quick Test K value found six months earlier. At this site, both the Ba-exchangeable K soil sample and soil in the leaching cores may have been affected by urine relatively recently. Substituting the Ba-exchangeable K value for peg site 18 into the set of Quick test K values gave an empirically amended set of soil exchangeable K values that had an improved relationship to the pattern of K^+ leaching ($R^2 = 0.73$). This amended set of exchangeable K values, and the set of Ba-exchangeable values, was used in the following modelling section.

6.3.3.2 Cation exchange

In theory, the concentration of K^+ in solution is determined not only by soil exchangeable K but also by other exchangeable cations in the soil (see Chapter 2.2.4 for more information). Therefore, a simple cation exchange sub-model was developed to see whether this could further improve the prediction of K^+ concentration in a leachate. The ratio of the concentrations of the major cations in soil solution can be related to the ratio of the same cations on the exchange surfaces by a proportionality constant (k_x);

$$\frac{K_{ex}}{(Ca_{ex} + Mg_{ex})} = k_g \frac{K_l}{\sqrt{(Ca_l + Mg_l)}} \qquad (1)$$

where $_{ex}$ denotes exchangeable cations (cmol(+)/kg soil) and $_l$ denotes the concentration of the cations in soil solution (mol/l). Extension of this theory suggests that for any pair of cations (e.g. Ca and K) the relative quantities on the exchange surface and in solution are given by relationships such as;

$$\frac{Ca_{ex}}{K_{ex}} = k_3 \frac{\sqrt{Ca_l}}{K_l} \qquad (2)$$

where k_3 is a proportionality constant specific to the exchange between Ca and K (Robbins et al., 1980). Similar relationships will exist for each pair of cations, with a different proportionality constant for each of the possible pairs.

In this current study, equations similar to equation (2) were developed for the major cations (Ca, Mg, K and Na) and then used in a computer program to test whether the concentration of K^+ in the leachates could be predicted. To do this, each proportionality constant for each pair of cations needs to be known. Ideally, these constants would be obtained from independent experiments or from existing literature on similar systems. This was not possible in this study and so the constants were estimated from the trial data themselves.

The various proportionality constants (k_1-k_6) were calculated from a back-transform of the appropriate ln-transformed leachate concentration mean, and a simple average of the corresponding group of exchangeable cation values. These values were then used to predict the relative concentrations of K^+, Ca^{2+}, Mg^{2+} and Na^+ in each leachate, as total cation charge varied between each leachate and exchangeable K, Ca, Mg and Na varied between each peg site (full SAS model in Appendix 3, Model 2).[4]

If used unthinkingly, this approach of using the same data to both develop and test a model can be misleading. In this case however, the approach provides a useful test. If it is to be of any practical use, the same model needs to be able to predict K^+ concentrations in leachate from both highly enriched campsites and impoverished slopes. If it cannot do this and needs to be re-parameterised for each site then it will be of little or no practical value.

6.3.3.3 Modelling Results

The model was first run using the estimates of exchangeable cations, obtained by complete cation exchange (measured using barium (Ba) exchange) on the 100 * 100 * 100 mm 'core sized' soil samples collected immediately adjacent to each pair of leaching cores (Table 6.5).

Initial model runs divided the soil into separate 25 mm layers – each with its own level of exchangeable cations. However, the exchangeable cation ratios did not change much with depth (Section 6.3.2), and the inclusion of separate layers in the model appeared to

---

[4] SAS model supplied by Dr. D. Scotter

give little advantage. Subsequent model runs used simple averages of the exchangeable cation values.

In general terms, the model was able to differentiate those cores with low K^+ concentrations in leachate (e.g. cores from peg sites 3, 13, 47) from those with high K^+ concentrations (e.g. cores from peg sites 7 and 18) (Figure 6.10a). However, when viewed quantitatively the model did not closely match the experimental data and this was reflected in regression analysis where the model only accounted for 38% of the variation in the actual data. This result was worse than the prediction of K^+ concentrations in leachates from the same exchangeable K values alone (R^2=0.52).

Table 6.5: Proportionality constants for two simple cation exchange models using the Ba-exchangeable K values and the amended set of exchangeable K values, and a third model where the K/Ca and K/Mg proportionality constants were calculated for each peg site.

Leachate pair	Ca /Mg	Na/Ca	K/Ca	K/Mg	Na/Mg	Na/K
Constant	**K1**	**K2**	**K3**	**K4**	**K5**	**K6**
Simple model Ba-exchangeable K	0.4	0.7	0.05	0.02	0.27	13.4
Simple model Alternative K_{ex}	0.4	0.7	0.07	0.026	0.27	10
Peg site specific model, using Ba-exchangeable values						
3	"	"	0.052	0.02	"	"
13	"	"	0.02	0.007	"	"
7	"	"	0.096	0.054	"	"
18	"	"	0.07	0.032	"	"
47	"	"	0.022	0.006	"	"
52	"	"	0.016	0.006	"	"
43	"	"	0.02	0.007	"	"

Close inspection of the results (Figure 6.10a) revealed that deviations between the model and the actual data were not random. The model consistently overestimated the actual K^+ concentration in leachates of soil from several peg sites (e.g. peg sites 13, 43, 52), and consistently underestimated others (e.g. peg sites 7 and 47). This suggested that either there were systematic differences in the cation exchange behaviour of cores drawn from different parts of the paddocks, or that exchangeable K still was not estimated accurately enough.

The effect of a change in cation exchange behaviour could be examined by calculating separate K/Ca and K/Mg proportionality constants for each peg site (Table 6.5). When individualised proportionality constants were used in the model with the Ba-

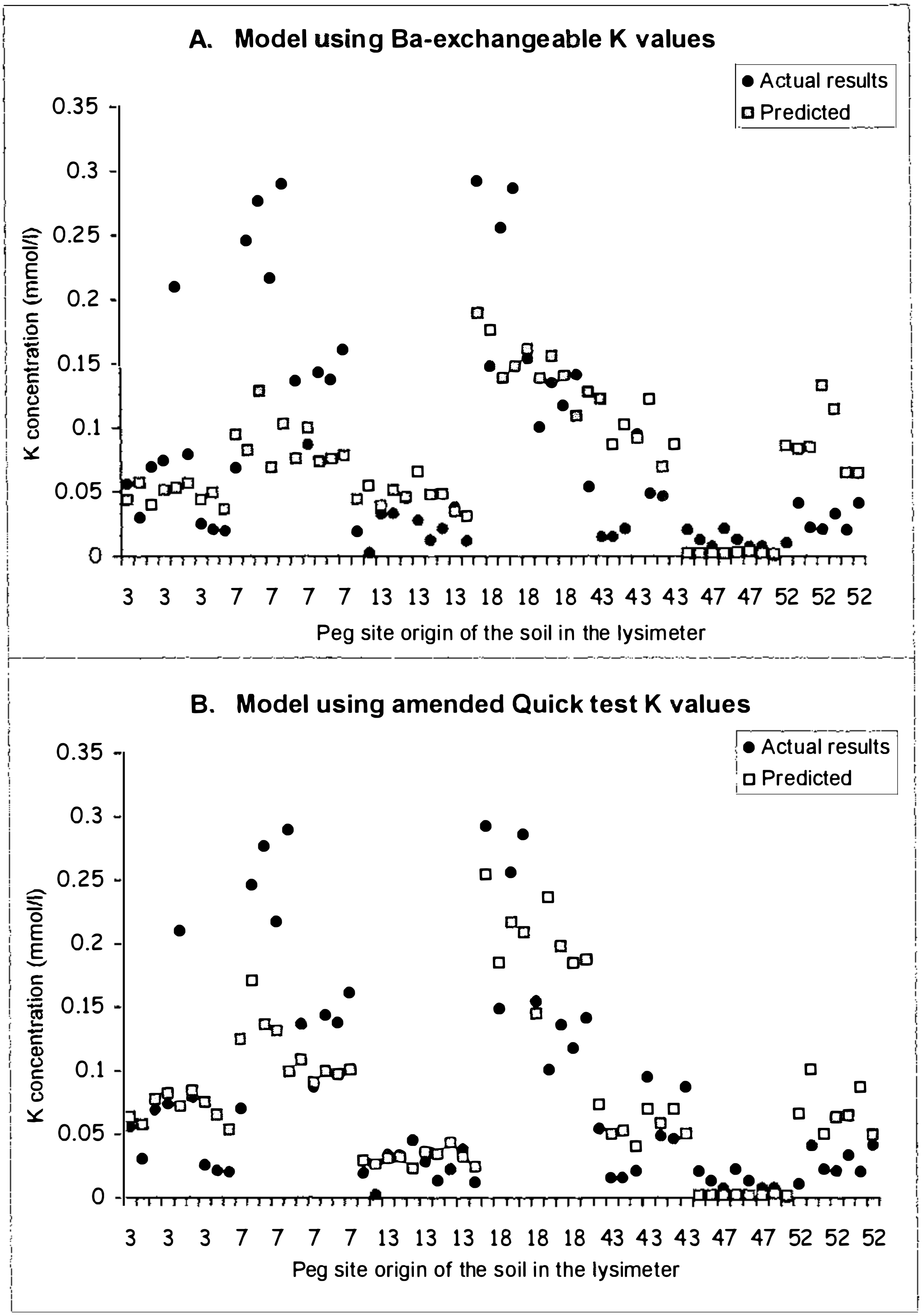


Figure 6.10: Comparison of predicted and actual K concentrations in the leachates of steepland topsoils. K concentrations were predicted using different exchangeable K inputs in a cation exchange model.

exchangeable values the fit between predicted and observed values did improve (R^2=0.70).

The effect of a more accurate estimate of exchangeable K could be illustrated by using the amended set of exchangeable K values (Section 6.3.3.1), which better matched the pattern of K^+ leaching. The proportionality constants were recalculated, using the amended exchangeable K values and the average Ba-exchangeable Ca, Mg and Na values (to 75 mm) (Table 6.5). Prediction of K^+ concentration in solution was reasonable (R^2=0.60, Figure 6.10b) but, again, did not predict K^+ concentration in solution as well as a simple regression between the amended exchangeable K values and K^+ concentration in the leachate (R^2=0.73). Evidently, even where the pattern of exchangeable K values matched the K^+ leaching pattern quite well, the consideration of other exchangeable cations in the modelling process did not improve the prediction of K^+ concentration in solution without significant adjustments to the proportionality constants at different peg sites.

The need to estimate separate selectivity coefficient for different parts of a paddock seriously erodes the potential utility of such a model. It is probable that the wide range in exchangeable K values across this landscape (Chapter 3), and the wide range in mineralogy, from mica dominated soils to vermiculite dominated soils (Chapter 4), will also correspond to a range in the nature of the cation exchange surfaces. Some cation exchange surfaces may be dominated by K exchange sites with a high specificity for K, while other exchange surfaces may be dominated by K exchange sites that have a low specificity for K (previously discussed in Chapter 2.2.4 as the difference between phase I and phase II sites). Such a change in site specificity may particularly have occurred in the soils under the animal campsites, so these soils will supply more K^+ into solution, relative to the amount of Ca^{2+} and Mg^{2+} in solution, compared to the soils in other parts of the paddock.

The concentration of K^+ in the leachate did generally increase as the exchangeable K value of the associated soil increased, so exchangeable K remained the most useful predictor of K^+ concentration in leachate across a steepland landscape. The extreme spatial variability of exchangeable K has previously been demonstrated (Chapter 3), so the spatial variability of K^+ leaching will be at least as high as the spatially variable of exchangeable K. Rainfall and soil moisture patterns, localised changes in the cation exchange behaviour, the presence of recent urine patches (such as peg site 58 in this study) and the smaller scale temporal variations (possibly caused by earthworms, see Section 6.3.1.2) will provide additional sources of spatial and temporal variability to the pattern of K^+ leaching. Therefore, the exact amount of K^+ leached at any one point at any one time will be difficult to predict in a steepland pasture. The accurate 'scaling up' of point measurements to an overall K^+ leaching loss per hectare, from the topsoil to the subsoil, will also be extremely difficult in a steepland landscape. However, leaching losses of K^+ were relatively small, compared to the total amount of K in the soil at the sites that were examined (Figure 6.11), so a very accurate estimate of the K^+ leaching loss may not be important.

This study did indicate some distinct stages in the leaching of urine, after deposition on to soils rich in 2:1 layer silicate clays. There may be an initial loss of pure urine by macropore flow into the subsoil. This effect was not explored in this study, but was examined by Williams and Haynes (1994) and thought to account for 15-25% of the losses of cattle urine into the subsoil. After the soil system has been flooded with urine, there is a second stage represented by core 58 in this study. During this stage, K^+ and NH_4^+ are adsorbed on to the exchange surface and some modifications to the exchange surface and the mineralogy may occur. Also, excess K^+ and NH_4^+, displaced Ca^{2+} and Mg^{2+}, and NO_3^- (as it is produced from the NH_4^+) will be flushing in relatively high concentrations from the topsoil to the subsoil. Eventually, the ionic concentration of the soil solution will drop and the soil exchange system will regain equilibrium. At this third stage, the cation exchange surface will again become the principle determinant of the concentration of K^+ in solution.

Most urine leaching studies examine the effect of a single urination on a previously unaffected soil and conclude that leaching losses are small because most of the urine K is conserved in the soil profile. This study indicated that K^+ leaching losses will increase under animal campsites, as the soil is exposed to multiple urination events and exchangeable K increases. The increased leaching losses under campsites are unlikely to be a problem in a steepland pasture system, because the amount of K^+ leached from the topsoil will still be relatively small and if it escapes the subsoil it will probably be transported by lateral flow to the side slopes, where the K depleted soils will "mop up" any extra K^+ in soil solution. Such effects may be more important under animal campsites on flatter land, especially where the soils are less conservative of K.

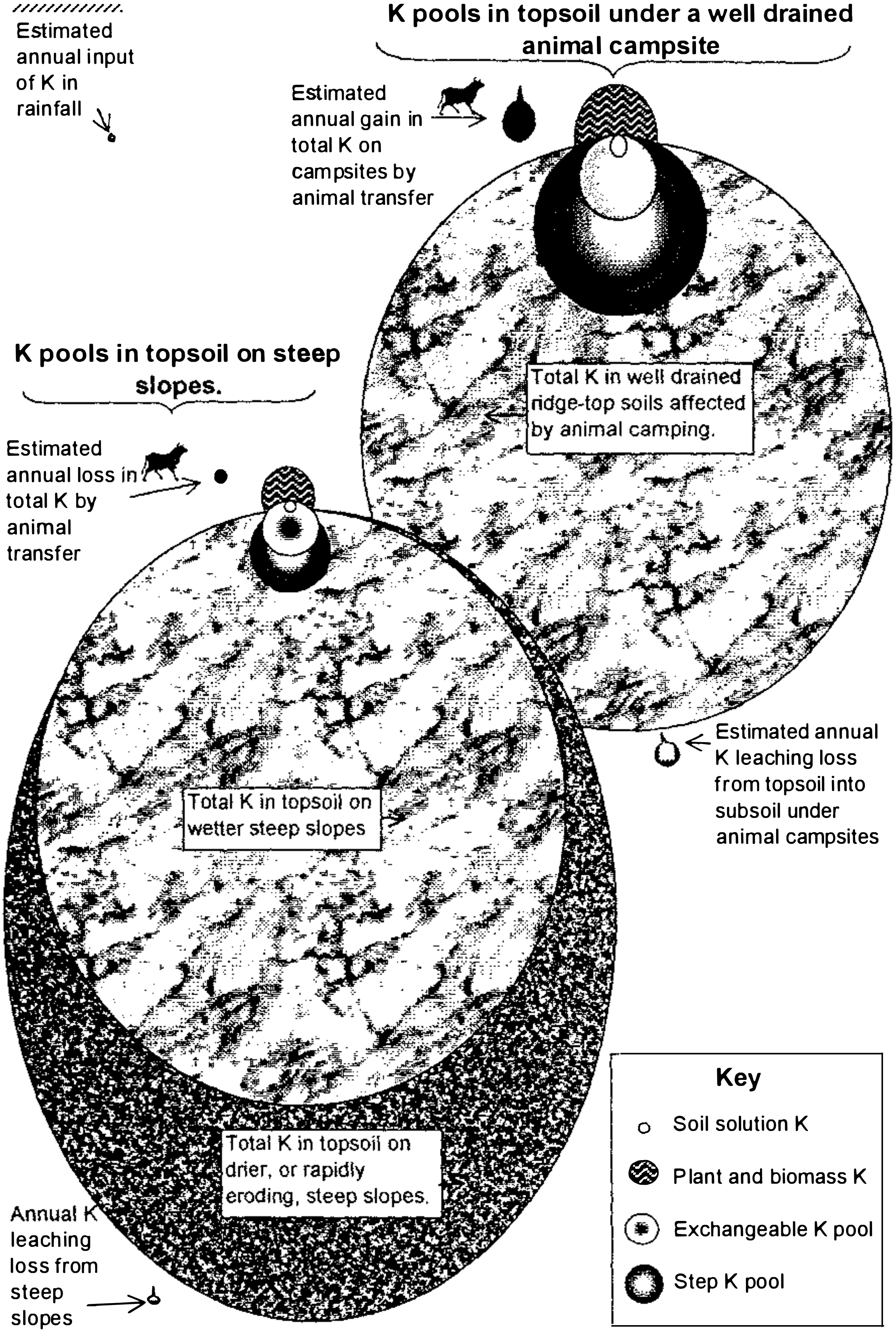


Figure 6.11: An indication of the relative size of K pools, in typical topsoils on the steep slopes and under a well drained ridge-top animal campsite, in a steepland pasture with micaceous sedimentary soil parent materials.

6.4 Conclusions

1. The K concentration in the leachates of soil from two steepland pastures varied from a lowest measured concentration of 0.0005 mmol/l to a highest concentration of 1.07 mmol/l. Otherwise, the principle cation in the leachates was usually Na^+ with lesser quantities of Ca^{2+} and Mg^{2+}. The principle anions appeared to be a combination of HCO_3^- and organic anions (calculated as measured cations less measured anions), with lesser concentrations of Cl^-, NO_3^- and SO_4^{2-}. This study did not include raw urine moving into the subsoil (up to 230 mmol K/l), which will further increase the range of possible K^+ concentrations in soil solution in the macropores.

2. K concentrations in leachate of soils from four locations on the steeper slopes were relatively low and were consistent over time, compared to the more variable Ca^{2+} and Mg^{2+} concentrations. K^+ leaching losses from the topsoil to the subsoil on the steep slopes were consistent with the results of other leaching studies on similar soils.

3. K^+ concentration in the leachate of soils from four different ridge-top locations varied markedly. Soil from a ridge-top location that was not an animal campsite had K^+ leachate concentrations that were similar to the soils of the steeper slopes. Soil leachate from ridge-top campsite locations contained relatively high concentrations of K^+. These soils were thought to have been affected by multiple urine depositions, which increased the exchangeable K, and modified the specificity of the exchange surface, so the campsite soils were now leaching consistently higher concentrations of K^+ than the soil from the steep slopes. Soil leachate from the fourth ridge-top campsite location contained extremely high concentrations of K^+ at the start of the experiment, which subsequently decreased time. This soil was thought to be have been exposed to urine immediately prior to the commencement of the experiment, and to be still regaining equilibrium.

4. The increased leaching of K^+ under ridge-top campsites was thought to be a significant loss mechanism for the K^+ that appears to be transferred from the slopes to these areas.

5. Where the soil systems were at equilibrium, and the cation exchange surface was thought to be largely controlling K^+ release, up to 70% of the variability of K^+ concentration in the leachate at each peg site could be explained by cation exchange models. Across the paddock as a whole, the best estimator of the concentration of K^+ in a leachate was exchangeable K. The relationship between K leaching and exchangeable K and the identification of additional sources of variability indicated that K^+ leaching processes would have a very high spatial variability and considerable temporal variability.

Summary and conclusions

Chapter 7

The soil K fertility relationships of two steepland pastures, located in the southern North Island Rangitikei and Manawatu regions of New Zealand, were investigated (Chapter 3.2.2). Both sites are part of well-established mixed stock grazing farms and have been receiving regular aerial topdressing with superphosphate for at least 30 years. One site on Tuapaka farm had soil parent materials that consisted of eroded loess and volcanic ash deposited on dissected greywacke bedrock (a quartz-feldspar-biotite sandstone). The second site, on Bernwood farm, had soil parent materials that consisted of eroded loess and volcanic ash deposited on a dissected sandstone band which capped a loose conglomerate.

Three soil K tests were investigated at the two sites. The first test was Quick test K, a two minute extraction of soil with NH_4, which is a standard New Zealand measure of plant available exchangeable K. The second test was Acid K, a single 20 minute extraction of soil in boiling HNO_3, which is a measure of the available NH_4-exchangeable K and some non-NH_4-exchangeable K. The difference between the two tests was termed Step K, a measure of plant available nonexchangeable K.

A preliminary survey of the spatial variability of the soil K tests was carried out at the Tuapaka site, investigating the distance dependence of soil samples collected from points that were between 0.25 m and 25 m apart (Chapter 3.3). These distances encompassed large variations in the small and medium scale topography and the pasture species. Each soil sample consisted of four standard soil cores (25 mm diameter and 75 mm depth) sampled from an area of approximately 100 mm^2. The Quick test K values ranged from 0.07 to

1.34 mg K/g soil, which was a range from very low to extremely high values for New Zealand soils (Blakemore et al., 1987). The Acid K values ranged from 0.12 - 2.43 mg K/g soil and the Step K values ranged from 0.05 - 1.70 mg K/g soil, but no standard comparisons were available. The distributions of the soil K test results were skewed, so that the arithmetic mean of the tests was higher than 60-70% of the results. No increase in spatial variability was found for the three tests as the sampling distance increased, indicating that the full range of variability found in one paddock (about 10 ha) could be found between samples that were only 0.25 m apart. The results were thought to be a classic example of the very high short-range variability that has previously been found in surveys of the exchangeable chemistry of developed soils (Beckett and Webster, 1971). Although the spatial variability of the soil K tests was very high, and regional variable theory could not be applied to map the trends, some relationships were identified between the Quick test K and Step K values and the position of a topsoil in the landscape. The main trends were identified by correspondence analysis in the preliminary survey and were examined in more detail in a targeted second survey (Chapter 3.4).

On the moderately steep to very steep slopes (>20°), the Step K value of a soil was related to the spring soil moisture status and to the pattern of the soil parent materials. Step K value increased in the drier soils, particularly on a ridge face at the Tuapaka site that had a warm northeasterly aspect. The Step K value also reflected large variations in the nature of the soil parent materials, particularly at the Bernwood site where Step K increased in the soil of a band of eroding conglomerate in the lower slopes of the Bernwood site. Quick test K and Olsen P value had no similar relationship to the position in the landscape of a soil on the steeper slopes.

On the strongly rolling to flat shoulder slopes and ridge-tops (0-20°), the mean and variability of the Quick test K, Step K and Olsen P tests increased, particularly in soils on the well-drained areas where the animals tended to congregate. Compared to the range of values of these soil tests obtained on the steep slopes, there was some increase in the lowest values that were obtained, and a very large increase in the highest values that were obtained (Table 7.1). This effect was particularly marked for Quick test K and occurred in soils on both the well drained shoulder formations (11-20°) and the well drained ridge-tops (<10°). In contrast, the range of the Step K and Olsen P values increased markedly only in soils obtained from slopes of less than 10°. The different behaviours of cattle and sheep, the relatively large amounts of K deposited in excreta compared to P, and the slower rate of breakdown and dispersal of excreta in drier conditions, were all thought to contribute to these effects.

Table 7.1: Comparison of the mean and range of Quick test K, Step K and Olsen P values in topsoil (0-75 mm) on the steeper slopes and flatter areas of a steepland pasture.

Slope	**21-50°**	**0-20°**
Quick test K (mg K/g soil)		
Mean	0.14	0.45
Range	0.06 - 0.32	0.11 - 1.18
Step K (mg K/g soil)		
Mean	0.49	0.69
Range	0.19 - 1.58	0.25 - 2.14
Olsen P (ug P/g soil)		
Mean	20	37
Range	6 - 45	11 - 101

The mineralogy of the topsoils at the two sites was also investigated (Chapter 4). The clay mineralogy was dominated by 2:1 layer silicates, accompanied by lesser quantities of quartz, feldspars and kandites. The 2:1 layer silicates largely consisted of a combination of mica, mica interlayered with smectite (MS), vermiculite and vermiculite interlayered with amorphous aluminium hydroxides (HIV). The topsoils formed a sequence, which ranged from a clay fraction that was dominated by mica and MS, to a clay fraction that was dominated by the vermiculite and HIV (summarised as the mica: vermiculite ratio). Little 2:1 layer silicate material was present in the sand and silt fractions, except in the apparently recently exposed soils of an eroding band of conglomerate, in the lower slopes of the Bernwood site.

The mineralogy of a soil could be related to its position in the landscape. On the steeper slopes, the proportion of mica in the clay fraction of a topsoil had a strong relationship to Step K value, indicating that the mica:vermiculite ratio of a soil depended on the original composition of the soil parent materials, the age of the soil profile, and the soil moisture conditions.

A wide range of clay mineralogy was also found in the soils on the shoulder slopes and ridge-tops (<10°). Soils with a low mica:vermiculite ratio were associated with the shoulder slopes and poorly drained ridge-tops. Soils with a high mica:vermiculite ratio were associated with well drained ridge-tops, and large but erratic increases in Quick test K, Step K, Olsen P and some increase in pH. A mica-dominated 2:1 layer silicate complex was thought to have formed from a vermiculitic 2:1 layer silicate complex, as the expanded interlayers collapsed under conditions of high pH and saturation with K and NH_4. The remaining expanded 2:1 layer silicates in these topsoils were poorly formed and irregularly interstratified, consistent with the partial collapse of HIV and the smectitic interlayers under the same conditions. Such conditions would be expected in soils affected by multiple depositions of dung and urine.

Concentrations of total K and P were investigated in the topsoils of the two steepland pastures (Chapter 4.3.5). The average difference between the total P of slope and ridge-top samples was about 200 kg P/ha, indicating a relatively small accumulation of P on the ridge-tops, following between 30 and 50 years of aerial topdressing on these pastures. An accompanying 1.4 t K/ha was also expected to have been transferred to the ridge tops but this effect could not be confirmed. A relatively low rate of K transfer, combined with the relatively large total K reserves in these soils, indicated that the current practise of not applying K fertiliser to these soils would be sustainable well into the future.

A fertiliser trial was conducted at the two steepland pasture sites, comparing the K responsiveness of soils with a previously identified range of K fertility (Chapter 5.2). Test plots (5 m^2) were matched by similar Quick test K and Step K values in the centre of the plot and K fertiliser was applied to one of the pair. Pasture growth was measured using exclusion cages that were moved to a random position within the plot after every cut. No response in K uptake or growth was identified at either site.

A second plant growth response trial was undertaken in the more controlled and exploitative conditions of the glasshouse (Chapter 5.3). Ryegrass was grown in pots containing a small amount of various soils sampled from the two sites and all nutrients were supplied except K. The Quick test K and Acid K values of the soils were well correlated to yield and K uptake but at different stages of the experiment. A range in the ability of the soils to supply K under exhaustive growing conditions was indicated. These findings confirmed that there was a range of K fertility across the field sites that could be identified using a range of soil tests. However, on the two paddocks investigated in this study it appeared that even those sites with the lowest K fertility levels had sufficient plant available K to maintain a conventionally measured pasture growth rate. It was thought that the spatial variability of the K fertility had been underestimated and that investigations at a smaller scale were needed to find a relationship between K fertility and plant growth in the field.

The cation leaching processes in steepland topsoils were examined in selected soils obtained from the ridge-tops and steep slopes (Chapter 6). Pairs of "stove pipe" soil cores (150 mm diameter and 150 mm long) were lifted from the study sites and transferred to a lysimeter frame that was exposed to rainfall and protected from stock. Cation and anion concentrations were measured in the leachates, and the cation concentrations were modelled. The principle cation in the leachate was usually Na with lesser quantities of Ca and Mg. K concentrations in the soil leachate varied from the lowest cation concentration measured (0.0005 mmol/l) to the highest concentration measured (1.07 mmol/l). The principle accompanying anions appeared to be a combination of HCO_3 and organic anions (calculated as measured cations less measured anions), accompanied by lesser concentrations of Cl, NO_3 and SO_4^2.

K concentrations in the leachates of soils from the steep slopes were relatively low, consistent over time compared to the more variable Ca and Mg concentrations, and also consistent with other leaching studies using similar soils. In contrast, the K concentration in the leachate of soils from four different ridge-top locations varied markedly, apparently mainly depending on how often and how recently the soil at each point had been exposed to urine.

Simple cation exchange models could account for up to 70% of the variation in K concentration in the leachate of a soil from a particular location, but between different locations exchangeable K alone was a better predictor of K concentration in the leachate. The increased leaching of K from soils with high exchangeable K values was identified as a significant potential loss mechanism for the relatively small amount of K that is apparently transferred to animal campsites in these pasture. However, an exact quantification of the leaching processes was expected to be very difficult, because the spatial variability of the K leaching processes was expected to be even higher than the spatial variability of exchangeable K, and some significant elements of temporal variability were also identified.

The principle conclusions from this study were:

1. **Soil sampling for K**

   The bulking of soil samples is a poor practise when measuring plant available K in steepland soils with a 2:1 layer silicate clay mineralogy. In New Zealand, the standard soil sampling practise is to analyse perhaps 3-5 samples per farm, which each consist of bulked soil core samples from a number of similar paddocks. An assumption implicit in this practice is that the soil fertility factors, which are tested in the samples, are from a population distribution that is Normal enough, and of a small enough range, for the single number generated by the analysis of the bulked sample to be representative of the entire area sampled. This assumption was not supported by this study, where the soil exchangeable K and plant available nonexchangeable K ranges were very wide and the population distributions were skewed. This study indicated that adequate sampling for K would involve the individual analysis of samples in order to characterise the range and skew of the field population. The large spatial variability within short distances, and the similarity of the population distributions at two different steepland sites, implied that a detailed characterisation of the K fertility within a small area could be sufficient to characterise the K fertility of large areas.

2. **Effect of animal campsites on K fertility**

   Topsoils under the very well frequented and well drained animal campsites had a distinctive mica-dominated clay mineralogy, as opposed to a vermiculite dominated clay mineralogy in most other areas of the paddock. The clay mineral weathering processes appeared to be reversed under animal campsites.

   The mean and spatial variability of soil exchangeable K increased sharply on the well drained shoulder slopes and ridge-tops. In contrast, the mean and spatial variability of Olsen P increased sharply only on the ridge-tops. The current procedures for soil sampling in hill country recommend avoiding the animal campsites, which are marked by the accumulation of dung. This study indicated that the soil K fertility patterns were strongly affected by the accumulation of urine in the profile over a much wider area than the obvious campsites. Only the steep slopes should be sampled if the campsite effect is to be avoided when testing for exchangeable K. The range of exchangeable K values was wide and the frequency distribution was skewed even on the steep slopes, so individual sampling was still recommended even in these areas.

Leaching of K into the subsoil also increased as exchangeable K increased. Past studies of urine leaching in New Zealand soils have generally focussed on the effect of a single application of urine on a previously unaffected soil profile. This study indicated that multiple applications of urine onto a well drained animal campsite would have an additive effect on K leaching losses. Ignoring such effects would cause underestimates of the movement of K from the topsoil into the subsoil.

3. K fertility management perspectives

Land can be managed from viewpoints that can range from the highly exploitive "taming of the land" attitude of the European settlers arriving in New Zealand during the last century, to the "alternative" belief that humans live in cooperation with a living system, which may be represented by one or more human-like personalities (Buck, 1987; Zweers, 1995).

Soil fertility management practises can reflect a similar range. During the development phase of New Zealand agriculture, the accepted practise has been to apply only those fertiliser nutrients for which an existing deficiency and a short-term economic response has been demonstrated. This is despite the fact that large quantities of many other nutrients are also depleted by the farming operation. More recently, this exploitive viewpoint has been largely replaced by the current conventional viewpoint that treats the soil as a nutrient bank. Under this viewpoint, a nutrient budget is constructed, by quantifying the gains and losses of the major nutrients and the estimated losses of the nutrients are systematically replaced with fertilisers. There is also a growing application of the "feed the soil not the crop" tenet of alternative agriculture, which argues that the soil is a living organism or community and should therefore be maintained in its own right, by assisting the natural growth and decay cycles (Doran et al., 1996).

Allen and Bernhardt (1995) found that farmers tend to occupy the middle ground with a mixture of both conventional and alternative viewpoints. A survey of farmers in

Nebraska found that, while they regarded farming as business rather than a lifestyle (conventional), they also thought that protecting the long-term productivity of the land was more important than immediate profit (alternative).

The common current practice of not applying K fertiliser to steepland pasture in the southern North Island without a proven economic response was regarded as a good practise when the exploitive viewpoint prevailed. Concerns have been raised over the suspected systematic depletion of K fertility on the steeper slopes and the possible development of an economic response. In this study, two typical steepland sites in this region were examined that have been under grazing, with regular applications of P and S fertiliser but no K, for at least 25 years. Large reserves of K remained in the topsoil at the sites examined and no response to K fertiliser was found, although measures of K fertility sometimes had low values. Therefore, the current practise was regarded as sound, under the exploitive viewpoint. The high spatial variability of the K fertility made an exact quantification of the gains and losses of K quite difficult in this landscape, so a strict application of the nutrient bank system could not be made. Because the risk of K running out on the slopes appeared to be small, it is thought that farmers who are using this system will be pragmatic, and will not apply K fertiliser unless further trials can prove an economic response. In terms of farming under alternative viewpoints of land management, the tendency of animals to congregate at campsites may be perceived as a highly effective natural means of enhancing the K fertility of the most potentially productive soils in steepland pastures, without seriously affecting the K fertility of the slopes in these and similar landscapes.

References

Adams, J.A., Wilde, R.H.; 1976. Variability within a soil mapping unit mapped at the soil type level in the Wanganui district. II. Chemical variation. *New Zealand Journal of Agricultural Research 19*: 435-442.

Ahmad, N., Cornforth, I.S., Walmsley, D.; 1973. Methods of measuring available nutrients in West Indian soils III. Potassium. *Plant and Soil 39*: 635-647.

Allen, J.C., Bernhardt, K.; 1995. Farming practices and adherence to an alternative-conventional agricultural paradigm. *Rural Sociology 60*: 297-309.

Aoudjit, H., Elsass, F., Righi, D., Robert, M.; 1996. Mica weathering in acidic soils by analytical electron microscopy. *Clay Minerals 31*: 319-332.

Ball, P.R., Luscombe, P.C., Grant.; 1982. Nitrogen on hill country. *In* Nitrogen fertilisers in New Zealand agriculture. *Ed.* Lynch, P.B. New Zealand Institute of Agricultural Science. Pp 133-148.

Bar, A., Banin, A., Chen, Y.; 1987. Adsorption and exchange of K in multi-ionic soil systems as affected by mineralogy. *In* Methodology in soil-K research. Proceedings of the 20th colloquium of the International Potash Institute, Baden bei Wien, Austria. Pp 155-170.

Barbayiannis, N., Evangelou, V.P., Keramidas, V.C.; 1996. Potassium-ammonium-calcium quantity/intensity studies in the binary and tertiary modes in two soils of micaceous mineralogy of northern Greece. *Soil Science 161*: 716-724.

Barber, S.A.; 1985. Potassium availability at the soil-root interface and factors influencing potassium uptake. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 309-324.

Basker, A., Kirkman, J.H., Macgregor, A.N.; 1994. Changes in potassium availability and other soil properties due to soil ingestion by earthworms. *Biology and fertility of soils 17*: 154-158.

Bautista-Tulin, A.T., Inoue, K.; 1997. Hydroxy-interlayered minerals in Japanese soils influenced by eolian deposition. *Soil Science Society of America Journal 61*: 631-640.

Beckett, P.H.T.; 1964(a). Studies on soil potassium I. Confirmation of the ratio law: measurement of potassium potential. *Journal of Soil Science 15*: 1-8.

Beckett, P.H.T.; 1964(b). Studies on soil potassium II. The "immediate" Q/I relations of labile potassium in the soil. *Journal of Soil Science 15*: 9-23.

Beckett, P.H.T.; 1972. Critical cation activity ratios. *Advances in Agronomy 24*: 379-412.

Beckett, P.H.T.; 1987. Spatial variability of soil K-status. *In* Methodology in soil-K research. Proceedings of the 20th colloquium of the International Potash Institute, Baden bei Wien, Austria. Pp 357-380.

Beckett, P.H.T., Nafady, M.H.M.; 1967(a). Studies on soil potassium VI. The effect of K-fixation and release on the form of the K: (Ca+Mg) exchange isotherm. *Journal of Soil Science 18*: 244-262.

Beckett, P.H.T., Nafady, M.H.M.; 1967(b). Potassium-calcium exchange equilibria in soils: the location of non-specific (Gapon) and specific exchange sites. *Journal of Soil Science 18*: 263-281.

Beckett, P.H.T., Webster, R.; 1971. Soil variability: a review. *Soils and Fertilisers 34*: 1-15.

Beringer, H., Nothdurft, F.; 1985. Effects of potassium on plant and cellular structures. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 351-367.

Blakemore, L.C., Searle, P.L., Daly, B.K.; 1987. Methods for chemical analysis of soils. New Zealand Soil Bureau Scientific Report 80.

Blaschke, P.M., Trustrum, N.A., DeRose, R.C.; 1992. Ecosystem processes and sustainable land use in New Zealand steeplands. *Agriculture, Ecosystems and Environment 41*: 153-178.

Bond, W.J., Verburg, K.; 1997. Comparison of methods for predicting ternary exchange from binary isotherms. *Soil Science Society of America Journal 61*: 444-454.

Bouma, T.J., Nielsen, K.L., Eissenstat, D.M., Lynch, J.P.; 1997. Estimating respiration of roots in soil: Interactions with soil CO_2, soil temperature and soil water content. *Plant and Soil 195*: 221-232.

Boyer, D.G., Wright, R.J., Feldhake, C.M., Bligh, D.P.; 1996. Soil spatial variability relationships in a steeply sloping acid soil environment. *Soil Science 161*: 278-287.

Bray, R.H., DeTurk, E.E.; 1938. The release of potassium from non-replaceable forms in Illinois soils. *Soil Science Society of America Proceedings 3*: 101-106.

Burrough, P.A.; 1993. Soil variability: a late 20th century view. *Soils and Fertilizers 56*: 529-562.

Buck, Sir P.; 1987. The coming of the Maori. Whitcoulls Ltd, New Zealand.

Campkin, R.; 1979. Potassium fertiliser requirements for pasture. *In* Annual report, Agricultural Research Division, New Zealand Ministry of Agriculture and Fisheries, 1978/79. Pp 97.

Campkin, R.; 1985. Model for calculating potassium requirements for grazed pastures. *New Zealand Journal of Experimental Agriculture 13*: 27-37.

Carey, P.L., Metherell, A.K.; 1997. Measuring non-exchangeable potassium in New Zealand soils. Conference proceedings, New Zealand Fertiliser Manufacturers' Research Association Inc., Invercargill, New Zealand. Pp 57-75.

Carran, R.A.; 1988. Influence of soil nitrogen transformations on cation uptake by urine-affected pastures. *New Zealand Journal of Agricultural Research 31*:65-69.

Churchman, G.J.; 1980. Clay minerals formed from micas and chlorites in some New Zealand soils. *Clay Minerals 15*: 59-75.

Cornforth, I.S., Sinclair, A.G.; 1984. Fertiliser and lime recommendations for pastures and crops in New Zealand, 2nd Edition. Ministry of Agriculture and Fisheries, Wellington, New Zealand.

Cowie, J.D.; 1978. Soils and agriculture of Kairanga County, North Island, New Zealand. New Zealand Soil Bureau Bulletin 33.

Crush, J.R., Evans, J.P.M.; 1988. Clay-fixed ammonium levels in four Manawatu pasture soils. *New Zealand Journal of Agricultural Research 31*: 71-75.

Dalal-Clayton, D.B., Robinson, D.A.; 1993. The experimental use of correspondence analysis to assess the relationship between soils and geomorphology in Eastern Zambia. *Catena 20:* 141-160.

DeRose, R.C., Trustrum, N.A., Thomson, N.A., Roberts, A.H.C.; 1995. Effect of landslide erosion on Taranaki hill pasture production and composition. *New Zealand Journal of Agricultural Research 38:* 457-471.

DeTurk, E.E., Wood, L.K., Bray, R.H.; 1943. Potash fixation in corn belt soils. *Soil Science 55*: 1-12.

Dobermann, A., Cassman, K.G., Sta. Cruz, P.C., Adviento, M.A., Pampolino, M.F.; 1996. Fertiliser inputs, nutrient balance, and soil nutrient-supplying power in intensive, irrigated rice systems. II: Effective soil K-supplying capacity. *Nutrient cycling in Agroecosystems 46*: 11-21.

Doran, J.W., Sarrantonio, M., Liebig, M.A.; 1996. Soil health and sustainability. *Advances in Agronomy 56*: 1-54.

Dreher, P., Niederbudde, E.-A.; 1994. Potassium release from micas and characterization of the alteration products. *Clay Minerals 29*: 77-85.

Duke, S.H., Collins, M.; 1985. Role of potassium in legume dinitrogen fixation. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 443-465.

During, C.; 1984. Fertilisers and soils in New Zealand farming. Government Printer, Wellington, New Zealand.

During, C., Mountier, N.S.; 1967. Sources of error in advisory soil tests. III. Spatial variance. *New Zealand Journal of Agricultural Research 10*: 134-138.

Early, M.S.B., Cameron, K.C., Fraser, P.M.; 1998. The fate of potassium, calcium and magnesium in simulated urine patches on irrigated dairy pasture soil. *New Zealand Journal of Agricultural Research 41*: 117-124.

Evangelou, V.P., Wang, J., Phillips, R.E.; 1994. New developments and perspectives on soil potassium quantity/intensity relationships. *Advances in Agronomy 52*: 173-227.

Ganesh, S.; 1994. Statistical analysis for researchers-Part 2. Study Guide. Department of Statistics, Massey University, New Zealand.

Gillingham, A.G.; 1974. Influence of physical factors on pasture growth on hill country. *Proceedings of the New Zealand Grassland Association 35*: 77-85.

Gillingham, A.G.; 1978. Phosphorus cycling in grazed, steep hill country. Ph.D. thesis, Massey University, New Zealand.

Gillingham, A.G.; 1982. Soils and fertilisers. *In* The Whatawhata way. *Ed.* Shimmins, M. Agricultural Promotion Associates Ltd, Wellington, New Zealand. Pp 9-19.

Gillingham, A.G., During, C.; 1973. Pasture production and transfer of fertility within a long-established hill pasture. *New Zealand Journal of Experimental Agriculture 1*: 227-232.

Goulding, K.W.T.; 1987. Potassium fixation and release. *In* Methodology in soil-K research. Proceedings of the 20th colloquium of the International Potash Institute, Baden bei Wien, Austria. Pp 137-154.

Gradwell, M.W.; 1974. The available-water capacities of some southern and central zonal soils of New Zealand. *New Zealand Journal of Agricultural Research 17*: 465-478.

Grant, D.A., Brock, J.L.; 1974. A survey of pasture composition in relation to soils and topography on a hill country farm in the southern Ruahine Ranges, New Zealand. *New Zealand Journal of Experimental Agriculture 2*: 243-250.

Grant, D. A., Rumball, P.J., Suckling, F.E.T.; 1973. Pasture improvement and potential productivity in southern North Island hill country. *Proceedings of the New Zealand Grassland Association 34*: 185-194.

Greenacre, M.J.; 1984. Theory and application of correspondence analysis. Academic Press, London.

Greenwood, D.J., Karpinets, T.V.; 1997. Dynamic model for the effects of K-fertilizer on crop growth, K-uptake and soil-K in arable cropping. 2. Field test of the model. *Soil Use and Management 13*:184-189.

Harris, W.G., Hollien, K.A., Yuan, T.L., Bates, S.R., Acree, W.A.; 1988. Nonexchangeable potassium associated with hydroxy-interlayered vermiculite from coastal plain soils. *Soil Science Society of America Journal 52*: 1486-1492.

Harrison R., Swift, R.S., Campbell, A.S., Tonkin, P.J.; 1990. A study of two soil development sequences located in a montane area of Canterbury, New Zealand. I. Clay mineralogy and cation exchange properties. *Geoderma 47:* 261-282.

Haylock, O.F.; 1956(a). A method for estimating the availability of nonexchangeable potassium. *Transactions of the 6th International Congress of Soil Science B*: 403-408.

Haylock, O.F.; 1956(b). A fractionation of acid-soluble non-exchangeable potassium in some New Zealand soils into available and non-available forms. Ph.D. thesis, Massey University, New Zealand.

Haynes, R.J., Williams, P.H.; 1993. Nutrient cycling and soil fertility in the grazed pasture ecosystem. *Advances in Agronomy 49:* 119-200.

Heerdegen, R.G.; 1982. Landforms of the Manawatu. *In* Landforms of New Zealand. *Eds*. Soons J.M., Selby, M.J. Longman Paul Ltd., Auckland, New Zealand. Pp 213-231.

Hewitt, A.E.; 1992. New Zealand soil classification. DSIR Land Resources Scientific Report No. 19.

Hinsinger, P.; 1998. How do plant roots acquire mineral nutrients? Chemical processes involved in the rhizosphere. *Advances in Agronomy 64:* 225-265.

Hinsinger, P., Jaillard, B.; 1993. Root-induced release of interlayer potassium and vermiculitization of phlogopite as related to potassium depletion in the rhizosphere of ryegrass. *Journal of Soil Science 44*: 525-534.

Hogg, D.E.; 1957. The assessment of available potassium in soils. *New Zealand Journal of Science and Technology A38*: 1015-1024.

Huber, S.C.; 1985. Role of potassium in photosynthesis and respiration. *In* Potassium in Agriculture. *Ed*. Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 369-396.

Imas, P., Bar-Yosef, B., Kafkafi, U., Ganmore-Neumann, R.; 1997. Phosphate induced carboxylate and proton release by tomato roots. *Plant and Soil 191*: 35-39.

Jones, D.L., Darrah, P.R.; 1994. Role of root derived organic acids in the mobilization of nutrients from the rhizosphere. *Plant and Soil 166*: 247-257.

Jones, D.L., Kochian, L.V.; 1996. Aluminium-organic acid interactions in acid soils. I. Effect of root-derived organic acids on the kinetics of Al dissolution. *Plant and Soil 182*: 221-228.

Jones, D.L., Prabowo, A.M., Kochian, L.V.; 1996. Kinetics of malate transport and decomposition in acid soils and isolated bacterial populations: The effect of microorganisms on root exudation of malate under Al stress. *Plant and Soil 182*: 239-247.

Journel, A.G., Huijbregts, Ch.J.; 1978. Mining Geostatistics. Academic press, London.

Kachanoski, R.G., Fairchild, G.L.; 1996. Field scale fertilizer recommendations: the spatial scaling problem. *Canadian Journal of Soil Science 76*: 1-6.

Kennedy, P.C., Roser, B.P., Hunt, J.L., Daly, B.K., Palmer, A.S.; 1983. A New Zealand interlaboratory comparison of analytical data for the CSSC reference soils. New Zealand Soil Bureau Scientific Report 59.

Khasawneh, F.E.; 1971. Solution ion activity and plant growth. *Soil Science Society of America Proceedings 35*: 426-436.

Kirkman, J.H., Basker, A., Surapaneni, A., MacGregor, A.N.; 1994. Potassium in the soils of New Zealand - a review. *New Zealand Journal of Agricultural Research 37*: 207-227.

Krishnamurti, G.S.R., Violante, A., Huang, P.M.; 1995. Influence of Fe on the stabilisation of hydroxy-Al interlayers in montmorillonite. *In* Clays, controlling the environment. Proceedings of the 10th International Clay Conference, 1993, Adelaide. *Eds*. Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. CSIRO Publishing, Melbourne, Australia. Pp 183-186.

Kuchenbuch, R.O.; 1987. Potassium dynamics in the rhizosphere and potassium availability. *In* Methodology in soil-K research. Proceedings of the 20th Colloquium of the International Potash Institute, Baden bei Wien, Austria. Pp 215-234.

Laird, D.A., Shang, C.; 1997. Relationship between cation exchange selectivity and crystalline swelling in expanding 2:1 phyllosilicates. *Clays and Clay minerals 45*: 681-689.

Lambert, M.G., Roberts, E.; 1976. Aspect differences in an unimproved hill country pasture 1. Climatic differences. *New Zealand Journal of Agricultural Research 19:* 459-467.

Läuchli, A., Pflüger, R.; 1978. Potassium transport through plant cell membranes and metabolic role of potassium in plants. *In* Potassium Research- Review and

Trends. Proceedings 11th Congress of the International Potash Institute. Pp 111-163.

Lebart, L., Morineau, A., Warwick, K.M.; 1984. Multivariate descriptive statistical analysis. Translated by E.M. Berry. John Wiley & Sons, New York.

Ledgard, S.F., Sheath, G.W., Gillingham, A.G.; 1982. Influence of some soil and pasture components on the growth of hill country pastures. 1. Winter and spring production. *New Zealand Journal of Experimental Agriculture 10*: 239-244.

Ledgard, S.F., Roach, C.G., Sowry, S.R.; 1997. N, P, K research at the Te Kuiti research station. Conference proceedings, New Zealand Fertiliser Manufacturers' Research Association Inc., Invercargill, New Zealand. Pp 160-170.

Lee, R.; 1973. The K/Ca Q/I relationship and preferential adsorption sites for potassium. New Zealand Soil Bureau Scientific Report 11.

Lee, R., Ross, E.R., Churchman, G.J.; 1978. Anomalous results in the determination of non-exchangeable potassium by the step K method: Note. *New Zealand Journal of Science 21:* 569-571.

Leigh, R.A.; 1989. Potassium concentrations in whole plants and cells in relation to growth. Proceedings of the 21st colloquium, International Potash Institute, Methods of K research in plants. Pp 117-126.

Leigh, R.A., Johnston, A.E.; 1983. Concentrations of potassium in the dry matter and tissue water of field-grown spring barley and their relationships to grain yield. *Journal of Agricultural Science, Cambridge 101*: 675-685.

Lou, G.Q.J., Huang, P.M.; 1995. Adsorption of hydroxy-aluminosilicate ions by vermiculite. *In* Clays, controlling the environment. Proceedings of the 10th International Clay Conference, 1993, Adelaide. *Eds*. Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. CSIRO Publishing, Melbourne, Australia. Pp 187-191.

McClean, E.O., Watson, M.E.; 1985. Soil measurements of plant-available potassium. *In* Potassium in Agriculture. *Ed*. Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 277-308.

Mackie-Dawson, L.A., Darbyshire, J.F., Wimaladasa, G.D.; 1995. Video-enhanced photography of lateral roots of perennial ryegrass, *Lolium perenne* L., with and without potassium fertiliser amendments. *European Journal of Soil Biology 31*: 81-86.

McLaughlin, B.; 1983. Tuapaka soil survey - an exercise in classification and detailed mapping in New Zealand hill country. M.Phil. thesis. Massey University.

McNaught, K.J.; 1958. Potassium deficiency in pastures 1. Potassium content of legumes and grasses. *New Zealand Journal of Agricultural Research, April*: 148-181.

Mathews, B.W., Sollenberger, L.E., Nkedi-Kizza, P., Gaston, L.A., Hornsby, H.D.; 1994. Soil sampling procedures for monitoring potassium distribution in grazed pastures. *Agronomy Journal 86*: 121-126.

Mengel, K.; 1975. The effect of potassium on the quality of plant products. *Potash Review 30th suite, 3*: 1-12.

Mengel, K.; 1985. Potassium movement within plants and its importance in assimilate transport. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 397-412.

Mengel, K., Uhlenbecker, K.; 1993. Determination of available interlayer potassium and its uptake by ryegrass. *Soil Science Society of America Journal 57*: 761-766.

Metson, A.J.; 1968. Potassium. *In* Soils of New Zealand, Part 2. *Soil Bureau Bulletin 26 (2)*: 82-94.

Metson, A.J.; 1980. Potassium in New Zealand soils. *New Zealand Soil Bureau Scientific Report 38*.

Metson, A.J., Saunders, W.M.H.; 1978. Seasonal variations in chemical composition of pasture I. Calcium, magnesium, potassium, sodium, and phosphorus. *New Zealand Journal of Agricultural Research 21*: 341-353.

Metson, A.J., Arbuckle, R.H., Saunders, M.L.; 1956. The potassium-supplying power of New Zealand soils as determined by a modified normal-nitric-acid method. *Transactions of the 6th International Congress of Soil Science B*: 619-627.

Miklos, D., Cicel, B.; 1993. Development of interstratification in K- and NH_4-smectite from Jelsovy Potok (Slovakia) treated by wetting and drying. *Clay minerals 28*: 435-443.

Morton, J.D., Baird, D.B.; 1990. Spatial distribution of dung patches under sheep grazing. *New Zealand Journal of Agricultural Research 33*: 285-294.

Morton, J.D., Roberts, A.H.C., Edmeades, D.C., Manning, M.J.; 1996. North Otago soils: physical properties and nutrient requirements for economic production. *Proceedings of the New Zealand Grassland Association 58*: 17-21.

Mountier, N.S., During, C.; 1967. Sources of error in advisory soil tests. IV. Discussion of total variance. *New Zealand Journal of Agricultural Research 10*: 139-142.

Mountier, N.S., Grigg, J.L., Oomen, G.A.C.; 1966. Sources of error in advisory soil tests. I. Laboratory sources. *New Zealand Journal of Agricultural Research 9*: 328-338.

Murphy, J., Riley, P.; 1962. A modified single solution method for the determination of phosphate in natural waters. *Analytica Chimica Acta 27*:31-36

NZLRI; 1979. New Zealand Land Resource Inventory, worksheets and extended legend. Produced for the National Water and Soil Conservation Organisation by the Water and Soil Division, Ministry of Works and Development. Government Printer, Wellington, New Zealand.

Nishimura, S., Scales, P.J., Tateyama, H., Tsunematsu, K., Healy, T.W.; 1995. An electrokinetic study of Li^+ ions fixed at the muscovite mica basal plane. *In* Clays, controlling the environment. Proceedings of the 10th International Clay Conference, 1993, Adelaide. *Eds.* Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. CSIRO Publishing, Melbourne, Australia. Pp 192-195.

Oliver, M.A., Webster, R.; 1986. Combining nested and linear sampling for determining the scale and form of spatial variation of regionalized variables. *Geographical Analysis* 18: 227-242.

Oliver, M.A., Webster, R.; 1987. The elucidation of soil pattern in the Wyre Forest of the West Midlands, England. II. Spatial distribution. *Journal of Soil Science 38*: 293-307.

Oliver, M.A., Webster, R.; 1991. How geostatistics can help you. *Soil Use and Management 7*: 206-217.

Olsen, S.R, Cole, C.V., Wanatabe, F.S., Dean, L.A.; 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. U.S.D.A. Circular no. 939.

Parfitt, R.L., Percival, H.J., Dahlgren, R.A., Hill, L.F.; 1997. Soil and solution chemistry under pasture and radiata pine in New Zealand. *Plant and Soil 191*: 279-290.

Paris, F., Botton, B., Lapeyrie, F.; 1996. In vitro weathering of phlogopite by ectomycorrhizal fungi. *Plant and Soil 179*: 141-150.

Parkin, T.B., Starr, J.L., Meisinger, J.J.; 1987. Influence of sample size on measurement of soil denitrification. *Soil Science Society of America Journal 51*: 1492-1501.

Petersen, R.G., Lucas, H.L., Woodhouse, W.W.; 1956(a). The distribution of excreta by freely grazing cattle and its effect on pasture fertility: I. Excretal distribution. *Agronomy Journal 48*: 440-444.

Petersen, R.G., Woodhouse, W.W., Lucas, H.L.; 1956(b). The distribution of excreta by freely grazing cattle and its effect on pasture fertility: I. Effect of returned excreta on the residual concentration of some fertiliser elements. *Agronomy Journal 48*: 444-449.

Pollok, J.A., McLaughlin, B.; 1986. A user friendly guide to the soils of Tuapaka farm. Tuapaka farm series, publication no.3, Massey University, New Zealand.

Poss, R., Fardeau, J.C., Saragoni, H.; 1997. Sustainable agriculture in the tropics: the case of potassium under maize cropping in Togo. *Nutrient cycling in Agroecosystems 46*: 205-213.

Preston, R.L., Linsner, J.R.; 1985. Potassium in animal nutrition. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 595-617.

Putman, R.J.; 1986. The pressure of grazing and its impact upon the vegetation. *In* Grazing in temperate ecosystems, large herbivores and the ecology of the New Forest. Croom Helm, London and Sydney. Pp 134-164.

Radcliffe, J.E., Young, S.R., Clarke, D.G.; 1977. Effects of sunny and shady aspects on pasture yield, digestibility and sheep performance in Canterbury. *Proceedings of the New Zealand Grassland Association 38*: 66-77.

Reynolds, S.G.; 1975. Soil property variability in slope studies: suggested sampling schemes and typical required sample sizes. *Zeitschrift fur Geomorphologie 19*: 191-208.

Rich, C.I., Black, W.R.; 1964. Potassium exchange as affected by cation size, pH and mineral structure. *Soil Science 97*: 384-390.

Richards, I.R., Wolton, K.M.; 1976. The spatial distribution of excreta under intensive cattle grazing. *Journal of the British Grassland Society 31*: 89-92.

Righi, D., Velde, B., Meunier, A.; 1995. Clay stability in clay dominated soil systems. *Clay Minerals 30*: 45-54.

Rijkse, W.C.; 1977. Soils of Pohangina county, North Island, New Zealand. New Zealand Soil Bureau Bulletin 42.

Robbins, C.W., Jurinak, J.J., Wagenet, R.J.; 1980. Calculating cation exchange in a salt transport model. *Soil Science Society of America Journal 44*: 1195-1200.

Robert, M.; 1992. K-fluxes in soils in relation to parent material and pedogensis in tropical, temperate and arid climates. *In* Potassium in ecosystems. Proceedings of the 23rd colloquium of the International Potash Institute, Prague, Czechoslovakia. Pp 25-44.

Robert, M., Tessier, D.; 1992. Incipient weathering: some new concepts on weathering, clay formation and organization. *In* Weathering, soils and paleosols, *Eds.* Martini, I.P., Chesworth, W. Developments in Earth Surface Processes 2: 71-104.

Roberts, A.H.C.; 1987. Seasonal variation in soil tests and nutrient content of pasture at two sites in Taranaki. *New Zealand Journal of Experimental Agriculture 15*: 283-294.

Robinson, D.L.; 1985. Potassium nutrition of forage grasses. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 895-914.

Ross, G.J., Phillips, P.A., Culley, J.L.R.; 1985. Transformation of vermiculite to pedogenic mica by fixation of potassium and ammonium in a six year field manure application experiment. *Canadian Journal of Soil Science 65*: 599-603.

Rowarth, J.S.; 1987. Phosphate cycling in grazed hill-country pasture. Ph.D. thesis, Massey University, New Zealand.

Saggar, S., Mackay, A.D., Hedley, M.J., Lambert, M.G., Clark, D.A.; 1988. The development of a nutrient transfer model to explain the fate of P and S in a grazed hill country pasture. Proceedings of the FLRC workshop: Towards the more efficient use of soil and fertilizer sulphur. *Eds.* White R.E., Currie, L.D. Occasional Report 2, Massey University, New Zealand. Pp 262-278.

Saha, U.K., Inoue, K.; 1997. Ammonium fixation by hydroxy-interlayered vermiculite and montmorillonite and its relation to potassium fixation. *Clay Science 10:*133-150.

Sakadevan, K.; 1991. Factors influencing the transformation and fate of sulphur and nitrogen in grazed hill country pastures. Ph.D. Thesis, Massey University, New Zealand.

Sakadevan, K., Mackay, A.D., Hedley, M.J.; 1993. Influence of sheep excreta on pasture uptake and leaching losses of sulphur, nitrogen and potassium from grazed pastures. *Australian Journal of Soil Research 31*: 151-162.

Sakurai, K., Huang, P.M.; 1998. Intercalation of hydroxy-aluminosilicate and hydroxy-aluminum in montmorillonite and resultant physicochemical properties. *Soil Science Society of America Journal 62*: 362-368.

Saunders, W.M.H., Sherrell, C.G., Gravett, I.M.; 1987. Calibration of Olsen bicarbonate phosphorus soil test for pasture on some New Zealand soils. *New Zealand Journal of Agricultural Research 30*: 387-394.

Sauvé, S., Hendershot, W.H.; 1995. Cation selectivity coefficient variations in acidic forest soils from Sutton, Québec. *Geoderma 68*: 301-308.

Scheinost, A.C., Sinowski, W., Auerswald, K.; 1997. Regionalization of soil buffering functions: A new concept applied to K/Ca exchange curves. *In* Soils and environment- soil processes from mineral to landscape scale. *Eds.* Auerswald, K., Stanjek, H., Bigham J.M. Advances in Geology 30: 23-38.

Serfass, R.E., Manatt, M.W.; 1985. Potassium in human nutrition. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 577-594.

Sheath, G.W., Boom, R.C.; 1985. Effects of November – April grazing pressure on hill country pastures. 3. Interrelationship with soil and pasture variation. *New Zealand Journal of Experimental Agriculture 13*: 341-349.

Sheldrick, W.F.; 1985. World potassium reserves. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 3-28.

Shen, S., Tu, S-I., Kemper, W.D.; 1997. Equilibrium and kinetic study of ammonium adsorption and fixation in sodium-treated vermiculite. *Soil Science Society of America Journal 61*: 1611-1618.

Shibata, M., Yui, M., Ishikawa, H., Watanabe, T.; 1995. The alteration of charge location in expandable layers at the initial stage of illitisation of smectite. *In* Clays, controlling the environment. Proceedings of the 10th International Clay Conference, 1993, Adelaide. *Eds.* Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. CSIRO Publishing, Melbourne, Australia. Pp 225-230.

Smith, C.M.; 1979. Leaching and runoff losses of sulphur and potassium from a Tokomaru soil. Masters thesis, Massey University, New Zealand.

Smith, G.S., Middleton, K.R.; 1978. Sodium and potassium content of topdressed pastures in New Zealand in relation to plant and animal nutrition. *New Zealand Journal of Experimental Agriculture 6*: 217-225.

Sparks, D.L., Huang, P.M.; 1985. Physical chemistry of soil potassium. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 201-265.

Sposito, G., Prost, R.; 1982. Structure of water adsorbed on smectites. *Chemical Reviews 82*: 553-573.

Stanford, G.; 1947. Fixation of potassium in soils under moist conditions and on drying in relation to type of clay mineral. *Soil Science Society of America Proceedings 11: 167-171.*

Steele, K.W., Judd, M.J., Shannon, P.W.; 1984. Leaching of nitrate and other nutrients from a grazed pasture. *New Zealand Journal of Agricultural Research 27*: 5-11.

Stewart, J.A.; 1985. Potassium sources, use, and potential. *In* Potassium in Agriculture. *Ed.* Munson, R.D. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America. Pp 83-98.

Suckling, F.E.T.; 1959. Pasture management trials on unploughable hill country at Te Awa. II. Results for 1951-57. *New Zealand Journal of Agricultural Research 2*: 488-543.

Surapaneni, A.; 1994. Potassium releasing and supplying power of selected yellow grey earth soils of New Zealand. Ph.D. Thesis, Massey University, New Zealand.

Taylor, A.B., Velbel, M.A.; 1991. Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge II. Effects of botanical uptake terms. *Geoderma 51*: 29-50.

Taylor, C.R.; 1950. Potash deficiency in land in Rotorua district. *New Zealand Journal of Agriculture 81*: 21-22.

Tillman, R.W.; 1991. Solute movement associated with intermittent soil water flow. Ph.D. Thesis, Massey University, New Zealand.

Timlin, D.J., Pachepsky, Ya., Snyder, V.A., Bryant, R.B.; 1998. Spatial and temporal variability of corn grain yield on a hillslope. *Soil Science Society of America Journal 62*: 764-773.

Todd, M.D.; 1986. A soil-landforms model for a selected area of hill country in Kiwitea county. Honours thesis, Massey University. New Zealand.

Tonkin, P.J.; 1985. Studies of soil development with respect to aspect and rainfall, eastern hill country, South Island, New Zealand. *In* Proceedings of the soil dynamics and land use seminar, Blenheim. New Zealand Society of Soil Science and New Zealand Soil Conservators Association. *Ed.* Campbell, I.B. Blenheim Printing Co. Ltd. Pp 1-18.

Tonkin, P.J., Cameron, K.C., McLaren, R.G., Horn, A.H., Rowland, I.; 1982. A report on the survey of the soils and soil fertility status of part of the Lincoln college hill country property, "Hunua", North Canterbury. Occasional report No.1, Department of Soil Science, Lincoln College, New Zealand.

Tributh, H.; 1987. Development of K containing minerals during weathering and suitable methods for their determination. *In* Methodology in soil-K research. Proceedings of the 20th colloquium of the International Potash Institute, Baden bei Wien, Austria. Pp 65-83.

Tributh, H., v. Boguslawski, E., v. Lieres, A., Steffens, D., Mengel, K.; 1987. Effect of potassium removal by crops on transformation of illitic clay minerals. *Soil Science 143*: 404-409.

Verberg, K., Baveye, P.; 1995. Influence of quasi-crystal formation and intercrystalline swelling on cation exchange hysteresis in smectites. *In* Clays, controlling the environment. Proceedings of the 10th International Clay Conference, 1993, Adelaide. *Eds.* Churchman, G.J., Fitzpatrick, R.W., Eggleton, R.A. CSIRO Publishing, Melbourne, Australia. Pp 173-177.

Vogler, I.; 1997. The convection dispersion equation- not the question, the answer! Ph.D. thesis, Massey University, New Zealand.

Weaver, C.E.; 1989. Clays, Muds and Shales. Developments in Sedimentology 44. Elsevier Amsterdam, New York.

Webster, R.; 1985. Quantitative spatial analysis of soil in the field. *Advances in Soil Science 3*: 1-70.

Webster, R., Oliver, M.A.; 1990. Statistical methods in soil and land resource survey. Oxford University Press, England.

Webster, R., Oliver, M.A.; 1992. Sample adequately to estimate variograms of soil properties. *Journal of Soil Science 43*: 177-192.

Weeda, W.C.; 1979. Transfer of fertility from sprinkler-irrigated pasture under two cattle grazing systems. *New Zealand Journal of Experimental Agriculture 7*: 289-293.

Wells, N; 1968. Element composition of soils and plants. *Soil Bureau Bulletin 26 (2)*: 115-131.

Wells, N., Furkert, R.J.; 1972. Mineralogy of parent materials, topsoils, and erosion products of Taita Experimental Station. *New Zealand Journal of Science 15*: 141-155.

Wells, N., Furkert, R.J.; 1973. Mineralogical and chemical data for Taita Experimental Station, New Zealand. New Zealand Soil Bureau Scientific Report 7.

Wesselink, L.G., Grosskurth, G., van Grinsven, J.J.M.; 1994. Measuring and modeling mineral weathering in an acid forest soil, Solling, Germany. *In* Quantitative modeling of soil forming processes. *Eds*. Bryant, R.B. and Arnold, R.W. SSSA Special publication No. 39, Catena Verlag, Germany. Pp 91-110.

West, C.P., Mallarino, A.P., Wedin, W.F., Marx, D.B.; 1989. Spatial variability of soil chemical properties in grazed pastures. *Soil Science Society of America Journal 53*: 784-789.

Whitton, J.S., Churchman, G.J.; 1987. Standard methods for mineral analysis of soil survey samples for characterisation and classification in N.Z. Soil Bureau. New Zealand Soil Bureau Scientific Report 79.

Williams, P.H.; 1988. The fate of potassium in grazed dairy pastures. Ph.D. Thesis, Massey University, New Zealand.

Williams, P.H., Haynes, R.J.; 1994. Comparison of initial wetting pattern, nutrient concentrations in soil solution and the fate of ^{15}N-labelled urine in sheep and cattle urine patch areas of pasture soil. *Plant and Soil 162: 49-59.*

Williams, P.H., Morton, J.D., Jackson, B.L.J.; 1986. Chemical soil test prediction of pasture responses to potassium on recent soils of the South Island west coast. *New Zealand Journal of experimental agriculture 14*: 411-415

Wright, N. A.; 1998. Soil fertility variograms from "true point sampling" TM on 20.0, 0.9, and 0.1 meter grids in two fields. *Communications in Soil Science & Plant Analysis 29*: 1649-1666.

Woodcock, J.W.; 1936. Some aspects of potash manuring of pastures. *New Zealand Journal of Agriculture 53*: 193-199.

Yanai, J., Linehan, D.J., Robinson, D., Young, I.M., Hackett, C.A., Kyuma, K., Kosaki, T.; 1996. Effects of inorganic nitrogen application on the dynamics of the soil solution composition in the root zone of maize. *Plant and Soil 180*: 1-9.

Zweers, W.; 1995. Ecological spirituality as point of departure for an intercultural dialogue. *In* Agriculture and Spirituality: Essays from the Crossroads conference at Wageninen Agricultural University. International Books, the Netherlands. Pp 64-83.

Appendix 1

Table 1: Cross-tabulation of sampling vector and Quick test extraction category (mgK/gsoil), used in the correspondence analysis of the results of the first survey. The arithmetic mean of each vector class is also included for comparison.

		EXTRACTION CATEGORY				
VECTOR	MEAN	0-0.19	0.2-0.39	0.4-0.59	0.6-0.79	1.2-1.39
A	0.132	5	1	0	0	0
B	0.107	6	0	0	0	0
C	0.157	5	1	0	0	0
D	0.445	1	4	0	0	1
E	0.571	0	2	0	4	0
F	0.225	1	5	0	0	0
G	0.252	3	2	0	1	0
H	0.148	5	1	0	0	0
I	0.175	4	2	0	0	0
J	0.480	0	3	1	2	0
K	0.143	6	0	0	0	0
L	0.235	3	3	0	0	0
M	0.145	5	1	0	0	0
N	0.192	4	2	0	0	0
O	0.171	4	2	0	0	0

Table 2: Cross-tabulation of vector and Step K extraction category (mg K/g soil), used in the correspondence analysis of the results of the first survey. The arithmetic mean of each vector class is also included for comparison.

		EXTRACTION CATEGORY								
VECTOR	MEAN	0-0.19	0.2-0.39	0.4-0.59	0.6-0.79	0.80-0.99	1.0-1.19	1.2-1.39	1.4-1.59	1.60-1.79
A	0.993	0	0	0	1	2	2	1	0	0
B	0.796	0	0	1	1	4	0	0	0	0
C	0.872	0	0	0	4	1	0	0	1	0
D	0.550	0	2	3	0	0	1	0	0	0
E	0.550	0	1	3	1	1	0	0	0	0
F	0.565	0	0	5	0	1	0	0	0	0
G	0.577	0	1	3	2	0	0	0	0	0
H	0.356	0	3	3	0	0	0	0	0	0
I	0.326	0	5	1	0	0	0	0	0	0
J	0.993	0	0	0	2	2	1	0	0	1
K	0.470	0	1	5	0	0	0	0	0	0
L	0.620	0	1	3	1	0	1	0	0	0
M	0.451	0	2	3	1	0	0	0	0	0
N	0.227	1	5	0	0	0	0	0	0	0
O	0.154	4	2	0	0	0	0	0	0	0

Table 3: Cross-tabulation of vector and Acid K extraction category (mg K/g soil) used in the correspondence analysis of the results of the first survey. The arithmetic mean of each vector class is also included for comparison. Note jumps between the last three categories.

		EXTRACTION CATEGORY										
VECTOR	**MEAN**	0-0.19	0.2-0.39	0.4-0.59	0.6-0.79	0.80-0.99	1.0-1.19	1.2-1.39	1.4-1.59	1.60-1.79	2.0-2.19	2.4-2.59
A	1.125	0	0	1	1	2	0	2	0	0	0	0
B	0.904	0	0	0	1	4	1	0	0	0	0	0
C	1.029	0	0	0	1	3	1	0	0	1	0	0
D	0.995	0	0	1	2	2	0	0	0	0	0	1
E	1.121	0	0	0	1	1	1	2	0	1	0	0
F	0.790	0	0	1	2	2	1	0	0	0	0	0
G	0.829	0	0	1	2	2	1	0	0	0	0	0
H	0.505	0	2	3	1	0	0	0	0	0	0	0
I	0.501	0	2	3	1	0	0	0	0	0	0	0
J	1.473	0	0	0	0	0	2	1	1	1	1	0
K	0.613	0	0	2	4	0	0	0	0	0	0	0
L	0.855	0	1	0	2	1	1	0	0	0	0	0
M	0.596	0	0	5	0	0	1	0	0	0	0	0
N	0.419	0	2	4	0	0	0	0	0	0	0	0
O	0.325	1	3	2	0	0	0	0	0	0	0	0

Table 4: Pearson correlation coefficients (upper number) and probability of a linear relationship (in brackets) between the soil K tests of the first survey, using raw data and also the data transformed to the optimum transformation to normalise the set.

	Quick test K	**Acid K test**	**Step K test**	**Power transformed**	**Quick test K ($x^{-0.5}$)**	**Acid K test ($x^{-0.2}$)**	**Step K test (Log)**
Quick test K	1	0.69 (p=0.0001)	0.27 (p=0.0089)	**Quick test K** ($x^{-0.5}$)	1	0.56 (p=0.0001)	-0.24 (p=0.02)
Acid K test	0.69 (p=0.0001)	1	0.88 (p=0.0001)	**Acid K test** ($x^{-0.2}$)	0.56 (p=0.0001)	1	-0.92 (p=0.0001)
Step K test	0.27 (p=0.0089)	0.88 (p=0.0001)	1	**Step K test** (Log)	-0.24 (p=0.02)	-0.92 (p=0.0001)	1

Table 5: Correlation of soil tests and other results from the second survey, carried out at both Tuapaka and Bernwood farms. Both untransformed and log transformed data sets were tested. Results are the Pearson correlation coefficient (upper number) and the statistical probability of a linear relationship between the soil tests (in brackets).

	Quick test K	**Acid K test**	**Step K test**	**Olsen P**	**Slope**	**Log transformed**	**LnQuick test K**	**LnAcid K test**	**LnStep K test**	**LnOlsen P**
Quick test K	1	0.86 (p=0.0001)	0.61 (p=0.0001)	0.57 (p=0.0001)	-0.57 (p=0.0001)	**LnQuick test K**	1	0.85 (p=0.0001)	0.61 (p=0.0001)	0.57 (p=0.0001)
Acid K test	0.86 (p=0.0001)	1	0.93 (p=0.0001)	0.72 (p=0.0001)	-0.46 (p=0.0001)	**LnAcid K test**	0.85 (p=0.0001)	1	0.94 (p=0.0001)	0.66 (p=0.0001)
Step K test	0.61 (p=0.0001)	0.93 (p=0.0001)	1	0.69 0.0001	-0.29 (p=0.023)	**LnStep K test**	0.61 (p=0.0001)	0.94 (p=0.0001)	1	0.62 (p=0.0001)
Olsen P	0.57 (p=0.0001)	0.72 (p=0.0001)	0.69 (p=0.0001)	1	-0.47 (p=0.0002)	**LnOlsen P test**	0.57 (p=0.0001)	0.66 (p=0.0001)	0.62 (p=0.0001)	1
Soil moisture	-0.01 (p=0.91)	-0.28 (p=0.023)	-0.42 (p=0.0008)	-0.12 (p=0.35)	-0.13 (p=0.33)	**Soil moist.** (not transf.)	0.025 (p=0.850)	-0.3 (p=0.019)	-0.46 (p=0.0003)	-0.06 (p=0.65)
Harvest 2	0.44 (p=0.0006)	0.36 (p=0.006)	0.24 (p=0.07)	0.36 (p=0.006)	-0.6 (p=0.0001)	**Harvest 2** (not transf.)	0.55 (p=0.0001)	0.36 (p=0.0059)	0.19 (p=0.15)	0.31 (p=0.018)

Table 6: Correlation of soil tests and other results from the second survey, split into ≤ 20 and > 20 degrees of slope. Results are the Pearson correlation coefficient (upper number) and the statistical probability of a linear relationship between the soil tests (in brackets). There was no significant relationship between pasture regrowth and the other factors when the data sets were split into the slope zones.

≤ 20 degrees of slope					
	Quick test K	**Acid K test**	**Step K test**	**Olsen P**	**Slope**
Quick test K	1	0.88 (p=0.0001)	0.66 (p=0.0001)	0.42 (p=0.03)	-0.18 (p=0.37)
Acid K test	0.88 (p=0.0001)	1	0.94 (p=0.0001)	0.68 (p=0.0001)	-0.40 (p=0.03)
Step K test	0.66 (p=0.0001)	0.94 (p=0.0001)	1	0.76 (p=0.0001)	-0.50 (p=0.007)
Olsen P	0.42 (p=0.03)	0.68 (p=0.0001)	0.76 (p=0.0001)	1	-0.28 (p=0.15)
Soil moisture	-0.22 (p=0.26)	-0.41 (p=0.03)	-0.5 (p=0.007)	-0.36 (p=0.06)	-0.13 (p=0.33)
> 20 degrees of slope					
	Quick test K	**Acid K test**	**Step K test**	**Olsen P**	**Slope**
Quick test K	1	0.68 (p=0.0001)	0.56 (p=0.0009)	0.29 (p=0.1)	-0.01 (p=0.96)
Acid K test	0.68 (p=0.0001)	1	0.99 (p=0.0001)	0.48 (p=0.007)	0.25 (p=0.17)
Step K test	0.56 (p=0.0009)	0.99 (p=0.0001)	1	0.48 (p=0.007)	0.29 (p=0.11)
Olsen P test	0.3 (p=0.1)	0.48 (p=0.007)	0.48 (p=0.007)	1	0.22 (p=0.24)
Soil moisture	-0.22 (p=0.23)	-0.53 (p=0.0022)	-0.55 (p=0.0013)	-0.19 (p=0.3)	-0.34 (p=0.06)

Appendix 2

Table 1: Full results of the first leachate collection, 11 October 1995, including all replicates. The presence of HCO_3^- was recorded in most samples but could not be quantified.

Peg No.	Terrain	Replicate cores	Volume (ml)	Concentration (μmol/l)							Charge		
				K^+	Ca^{2+}	Mg^{2+}	Na^+	CL^-	NO_3^-	SO_4^{2-}	Cation charge	Anion charge	Anion deficit
Tuapaka Farm													
3	Slope	A	710	69	187	70	435	423	137**	76	1018	712	306
		B	474	51	112	45	435	175	81**	87	800	430	370
13	Slope	A	404	23	142	45	91	59	105	42	488	278	240
		B	422	31	217	62	122	116	97	49	711	311	400
7	Ridge-top	A	630	230	152	86	300	172	177	63	1006	475	531
		B	853	151	134	66	383	130	353	63	934	609	325
18	Ridge-top	A	577	307	277	185	296	180	123	35	1527	373	1154
		B	409	120	292	193	317	290	150**	44	1407	528	879
Rain collector			1073***	13	72	17	39	42	48	-*	230	90	140
Bernwood Farm													
47	Slope	A	569	21	77	33	183	70	53	33	424	189	235
		B	418	13	90	37	113	34	37	25	380	121	259
52	Slope	A	239	10	200	70	113	144	202	63	663	472	191
		B	401	21	180	62	122	121	136	35	627	372	300
43	Ridge-top	A	355	54	242	74	474	39	182**	25	1160	271	1431
		B	455	95	282	91	230	56	257	43	1071	399	1470
58	Ridge-top	A	498	946	369	95	122	431	674	73	1627	1251	376
		B	364	1074	382	86	161	994	940	135	2171	2206	-35
Rain collector			-	10	92	29	30	42	24	-*	282	66	216
All slopes			455 (30%)	26 (52%)	151 (35%)	53 (28%)	202 (72%)	143 (85%)	106 (50%)	51 (43%)	639 (33%)	361 (51%)	288 (25%)
All ridge-tops			518 (32%)	368 (108%)	266 (43%)	50 (45%)	285 (40%)	287 (109%)	357 (83%)	60 (57%)	1363 (30%)	764 (86%)	766 (72%)

*below detection limit of 5μmol/l ** NO_2^- recorded ***Empty soil core used as a rain collector

Table 2: Volume of leachate, K concentration and total K in leachate collected from 150 mm diameter soil cores, including an empty core at each site that functioned as a measure of the rainwater that was deposited on to each soil core. Average total volume of leachate and the total amount of K(mg) lost from a core over the three leachate events was also calculated for the two replicate cores from each peg site.

Peg No.	**Terrain**	**Replicate cores**	**Volume (ml)**	**K^+** (µmol/l)	**Total K** (µmol)	**Volume (ml)**	**K^+** (µmol/l)	**Total K** (µmol)	**Volume** (ml)	**K^+** (µmol/l)	**Total K** (µmol)	**Average volume** (l)	**Total K** (mg)
Tuapaka Farm			**11-October 1995**			**18-October 1995**			**25-October 1995**				
3	Slope	A	710	69	49	59	69	4.0	167	74	12	0.9	2.5
		B	474	51	24	-	-	-	94	21	2		
13	Slope	A	404	23	9.3	120	33	4.0	166	33	5	0.6	0.7
		B	422	31	13	57	22	1.2	86	38	3		
7	Ridge-top	A	630	230	145	101	276	28	174	216	38	1.0	7.4
		B	853	151	129	87	143	12	189	137	26		
18	Ridge-top	A	577	307	177	132	256	34	150	286	43	0.7	6.4
		B	409	120	49	119	117	14	85	141	12		
Rain			1073	13	14	402	13	5	346	23	8	1.8	1
Bernwood Farm			**11-October 1995**			**17-November 1995**			**29-November 1995**				
47	Slope	A	569	21	12	455	8	3.6	173	22	4	1.2	0.34
		B	418	13	5	427	15	6.4	132	0.5	0.07		
52	Slope	A	239	10	2	478	-	-	205	22	5	1.1	1.3
		B	401	21	8	512	33	17	223	41	9		
43	Ridge-top	A	355	54	19	485	15	7	160	21	3	1.1	2.1
		B	455	95	43	584	49	29	104	88	9		
58	Ridge-top	A	498	946	471	-	471	-	112	493	55	1.0	26
		B	364	1074	390	527	440	232	65	503	33		
Rain			-	10	-	684	-	-	-	17	-	-	-

Appendix 3

1. SAS model for the changes in K$^+$ concentration in leachate (Kl) from the average concentration ratio CR$_k$ in the leachates from each peg site and total cation charge (Z) in each leachate solution from each peg site. Inputs were: K$^+$ in the leachate (Kl) (mol/l), Ca^{2+} in the leachate (Cal) (mol/l), Mg^{2+} in the leachate (Mgl) (mol/l), Na$^+$ in the leachate (Nal) (mol/l). These inputs were used to calculate the total cation charge (Z) in each leachate solution.

```
options nocenter;
data model;
input core mark $ CRk peg set Kl Cal Mgl Nal;
 A = CRk * CRk ;
Z = ((2 * (Cal + Mgl)) + Kl +Nal) ;
c = Z;
k = (-1 + SQRT(1 + ((8 * c) /A))) / (4/ A);
cards;
```

2. SAS program to predict changes in K$^+$ concentration in leachate between peg sites. Input as above and also; exchangeable K, Ca, Mg and Na (cmol/Kg) (Xk, Xca, Xmg, Xna), the proportionality constants for each cation pair; Ca/Mg=K1, Na/Ca=K2, K/Ca=K3 (equation 3 in text), K/Mg=K4 (equation 4 in text), Na/Mg=K5 and Na/K=K6.

```
options nocenter;
data model;
input obs core mark $ PEG set Xk Xca Xmg Xna Kl Cal Mgl Nal;
K1 =.4; K2 =.7; K3=0.05; K4=0.02 K5 =.27; K6 =13.4;
Z = (2 * Cal + 2 * Mgl + Nal + Kl) / 1000000;
aca = 2 + 2 * (Xmg / Xca / K1)**2;
bca = K3 * Xk / Xca + K2 * Xna / Xca;
```

Wallace, R.J. & Brammall, M.L. (1985). The role of different species of bacteria in the hydrolysis of protein in the rumen. *Journal of General Microbiology* **131**, 821-832.

Waller, P.J. (1994). The development of anthelmintic resistance in ruminant livestock. *Acta Tropica* 56, 233-243.

Wang, Y., Waghorn, G. C., Barry, T. N. & Shelton, I. D. (1994). The effect of condensed tannins in *Lotus corniculatus* upon plasma metabolism of methionine, cysteine and inorganic sulphate by sheep. *British Journal of Nutrition* **72**, 923-935.

Wang, Y., Douglas, G.B., Waghorn, G.C., Barry, T.N., Foote, A.G. & Purchas, R.W. (1996a). Effect of condensed tannins upon the performance of lambs grazing *Lotus corniculatus* and lucerne (*Medicago sativa*). *Journal of Agricultural Science, Cambridge* **126**, 87-98.

Wang, Y., Waghorn, G. C., McNabb, W. C., Barry, T. N., Hedley, M. & Shelton, I. (1996b). Effect of condensed tannins in *Lotus corniculatus* upon the digestion of methionine and cystine in the small intestine of sheep. *Journal of Agricultural Science, Cambridge* **127**, 413-421.

Woodward, S.L., Auldist, M.J., Laboyrie, P.J. & Jansen, E.B.L. (1999). Effect of Lotus corniculatus and condensed tannins on milk yield and milk composition of dairy cows. *Proceedings of the New Zealand Society of Animal Production* **59**, 152-155.