The effect of applying potassium as a countermeasure against radiocaesium in organic soils

By

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Abstract

Following the Chernobyl accident in 1986, a range of countermeasures has been developed to reduce the transfer of ^{137}Cs from soil to plant and from the plant into grazing animals. One such countermeasure is the application of potassium to the soil. However, little is known of any side-effects such an application may have on the ecosystem, the longevity of the application and the effectiveness in a range of soil types.

An application of potash (KCl) was made to four organic upland soils in Cumbria, England at two application rates of 100 and 200 kg K ha^{-1} in June 1997 and at a single site in June 1998. Following application, a range of parameters within the ecosystem were recorded, through the collection of monthly samples of soil, vegetation and water samples over a period of fifteen months.

The results indicate that the application was effective for at least one year following application, that a lag phase existed between potash application and any effect within each ecosystem and that the duration of this phase was site specific. The results also showed that the countermeasure was effective at all sites and there was little apparent difference between the two application rates. The parameters measured which included soil pH, plant biomass, changes in Cu, K, Mg, Mn and Ca concentrations within the soil and vegetation indicated only a relatively small effect of the application on the ecosystem as a whole. The application can be considered as a viable option for reducing the transfer of ^{137}Cs from soil to plant. The study also shows that the effectiveness of the application is dependent on the measurement used, i.e. concentration ratios, Tag values or a total flux approach. It is argued that the flux approach is the most appropriate basis for comparing the effectiveness of potash as a countermeasure between several sites.

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Table of Acronyms

AFCF	Ammonium-ferric-hexacyano-ferrate
Bq	Bequerel
CR	Concentration ratio
EDTA	Ethylene diamine tetra-acetic acid
FES	Frayed edge sites
IAEA	International Atomic Energy Agency
ITE	Institute of Terrestrial Ecology
MAFF	Ministry of Agriculture Fisheries and Food
NH_4Ac	Ammonium acetate
RIFE	Radioactivity in food and the environment
Tag	Total aggregated transfer

Chapter 1

Introduction

Radioactive material has been released into the environment since the late 1950's and early 1960's when around 400 nuclear test weapons were detonated in the atmosphere (International Atomic Energy Agency, 1994). Although global fallout constitutes the major source of radioactive contamination for most of the world, for some parts of Europe the Chernobyl accident also contributes significant additional contamination.

Following the accident at the Chernobyl nuclear power plant in 1986 (Hilton, 1997) over 10,000 km^2 were contaminated with radiocaesium (^{137}Cs) at levels greater than 500 kBq m^{-2} and within Europe most countries had areas which exceeded 10 kBq m^{-2} (De Cort, 1998). In the UK deposition of radioactive fallout predominantly occurred on upland areas in north west England, north Wales, Northern Ireland and southern Scotland (Coughtrey, Kirton and Mitchell, 1989(b)). The requirement to protect human health from the potential effects of this fallout generated a large amount of new research into countermeasures (e.g. Commission of the European Communities, 1992; Howard & Desmet 1993). In agricultural systems, countermeasures aim to reduce the transfer of radionuclides, in particular radiocaesium and radiostrontium (^{90}Sr), from soils to food products (International Atomic Energy Agency 1994; Roed, Anderson and Prip, 1995).

Within the UK, the Ministry of Agriculture Fisheries and Food (MAFF) invoked restrictions on the movement of sheep on large areas of land affected by deposition from Chernobyl. This was a response to increases in the concentration of radioactivity within the animals above an intervention level which was initially 1250 Bq kg^{-1} and subsequently reduced to 1000 Bq kg^{-1}. The majority of these restrictions were in Cumbria, south-west Scotland, Northern Ireland and north Wales. Fourteen years following the accident the transfer of ^{137}Cs from the soil into the sheep remains sufficiently high in some areas of the UK that restrictions remain in force (Food Standards Agency and Scottish Environment Protection Agency, 2000). As a consequence of these high transfer rates, a considerable effort has been made to evaluate countermeasures to mitigate the transfer of ^{137}Cs from soil to plants and animals (Beresford and Howard, 1988; Beresford et al., 1989; Coughtrey et al., 1989(a); Cawse, 1990; Jones et al., 1991, Oughton et al., 1991; Hove et al., 1993; Howard, 1993; Wilkins et al., 1993; Beresford et al., 1997; Andersson and Roed, 1994). One such countermeasure is the use of potassium (K) fertiliser. Potassium fertiliser is an effective method of reducing ^{137}Cs transfer from soil to plant in soils with a low K status (Coughtrey et al., 1989(b)). In comparison to other soil-based countermeasures for ^{137}Cs such as the application of clay minerals, Prussian Blue compounds or Ammonium-ferric-hexacyano-ferrate (AFCF), (Paul and Jones, 1995) it is relatively inexpensive and easily applied. The countermeasure is therefore a potentially practical option for reducing the transfer of ^{137}Cs from soil to sheep in upland ecosystems.

Although many pot experiments have quantified the effectiveness of potassium as a countermeasure there has been little work undertaken to determine the longevity, effectiveness and possible side effects of the countermeasure in a field situation.

This project supported by the Ministry of Agriculture Fisheries and Food (MAFF) (now the Food Standards Agency), represents one of the first studies in attempting to assess the effects of a potassium application in a field environment by collecting detailed information in a field trial.

1.1 The rationale and aims of this study

Many authors have discussed the use of K as a countermeasure to reduce ^{137}Cs transfer between soil and plant (Nisbet, 1995; Howard, 1993; Mitchell, Coughtrey and Kirton, 1990; Coughtrey et al., 1989(b); Jackson and Nisbet, 1990; Cawse, 1990). However, there have been relatively few studies that have been conducted in the field to determine the effect of K on ^{137}Cs transfer. The most notable of these studies were conducted by Paul and Jones (1995) and Rafferty, Dawson and Synnott (1998). Both of these studies demonstrated that the application of K was capable of reducing ^{137}Cs transfer from soil to plant on organic soil in an upland environment by between 20 and 70 %.

Organic upland soils encompass a wide diversity of soil types and associated vegetation communities. It may therefore be an inappropriate generalisation to presume that all upland communities would respond identically to an application of K. Furthermore, as countermeasures are primarily used to reduce radionuclide passage into the human food chain, it would be most likely that they would be deployed on soils used for the greatest intensity of grazing. Within upland areas in the UK, grassland communities that support the greatest intensity of grazing tend to occur on peaty soils, with an organic topsoil and a mineral sub-soil, rather than the bog habitats studied by Paul and Jones (1995) and Rafferty, Dawson and Synnott (1998).

Most upland organic soils have relatively low levels of nutrients when compared with most lowland mineral soils. A supplementary application of K would represent a significant input of nutrients to such systems. K can reduce the transfer of ^{137}Cs from soil to plant and thus reduce the ^{137}Cs activity within the vegetation. However, the addition of K may also disrupt the transfer of nutrients from the soil to the plant which are required for plant and animal nutrition. Any disruption in the transfer of nutrients between soil and plant will be strongly influenced by the longevity of the application within the soil system. However, the exact nature of this disruption may change according to the geochemical and physical properties of the soil.

This study was developed to provide data which would help to answer a number of specific questions relating to the potential effects of a potash application on an organic soil in a field application. These were:

1) Was the countermeasure effective in the field environment ?
2) Does the effectiveness of a K application depend on the depth of the organic horizon ?
3) Would an application of 200 kg K ha^{-1} have a significantly greater effect on the transfer of ^{137}Cs from soil to plant than an application of 100 kg K ha^{-1} ?
4) Would the longevity of the countermeasure within the soil be sufficient to remain effective at reducing ^{137}Cs transfer for greater than one year ?
5) Is there any difference in the effectiveness of application between two years ?

6) Are the nutrients affected by the potash related to the underlying geology of the sites ?
7) Would the potash application raise soil pH ?
8) Would the potash application stimulate biomass production ?

To address these questions data was collected through sampling of soil, vegetation and water from a number of experimental sites, followed by chemical analysis. The sites were located in Cumbria, England where the deposition of ^{137}Cs from Chernobyl (and other sources) was sufficiently large that the effects of the countermeasure on the ^{137}Cs transfer could be easily measured. Sites selected were within upland areas which were close to, or within areas where the movement of sheep was still restricted in 1996. A range of sites were selected with differing soil types, underlying geology, hydrological regimes and vegetation cover so that variation in the possible effects of the countermeasure depending on these environmental factors could be quantified. The study aimed to identify the most likely potential side effects of the potassium application. These were thought to be changes in biomass production, in soil pH, and in the nutrient availability with specific reference to the elements Ca, Cu, Mg, Mn and Fe. These elements were chosen for closer examination as any change in their concentration in the vegetation could induce nutritional problems within the grazing sheep.

In chapter 2 of this thesis current literature which details the sources, behaviour and effect of ^{137}Cs within the ecosystem, possible measures which may be taken to reduce the transfer of ^{137}Cs from soil to plant, together with studies which have been conducted using potassium as a countermeasure are reviewed. As this study represents one of the first studies of an application of potassium in a field environment the available specific literature is limited. However a review of many pot experiments which have been undertaken is included within this thesis.

Following details the current knowledge within this area of scientific research, a characterisation of the design of the project is detailed in chapter 3. The fourth chapter details the methods that were used to monitor the effects of the potassium application on the ecosystem. The results are presented in chapters 5 to 9. Chapter 5 consists of data which describes the control plots at each of the sites and the natural variation in the transfer of nutrients from soil to plant over the study period. This is followed by the results which examines the effects of the potassium application on the transfer of ^{137}Cs from soil to plant (chapter 6), the potassium within the soil and standing biomass (chapter 7), secondary effects of the potash application on the soil (chapter 8) and secondary effects of the application on the biomass (chapter 9). Within each of these result chapters there is a brief introduction that describes the objectives and hypothesis that will be tested in the chapter and a preliminary discussion of the data. Chapter 10 discusses the overall effects of the potassium application and the interdependence of the variables measured. An assessment of management implications of the data recommendations for the application and limitations are made. Areas requiring further research are also identified in chapter 10.

The thesis determined the effects of the potash application by statistical analysis. To allow statistical testing the aims of the study were interpreted into specific hypothesis which were subsequently tested. The result chapters present the outcome of the testing of these hypotheses, which were:

1) The countermeasure significantly reduces the transfer of ^{137}Cs from soil to plant in a range of organic upland soils.
2) The reduction in ^{137}Cs concentration in the biomass as a result of potassium application is not affected by the depth of the organic horizon.
3) An application of 200 kg K ha^{-1} has a significantly greater effect in reducing the transfer of ^{137}Cs from soil to plant than an application of 100 kg K ha^{-1}.
4) The countermeasure is capable of significantly reducing ^{137}Cs transfer for greater than one year.
5) There is no difference in the effectiveness of the countermeasure applied in different years.
6) The effect of the potassium application on other nutrients is dependent on the underlying geology.
7) The application of potassium significantly raises soil pH.
8) The potassium application does not cause a significant increase in biomass production.

The results of testing of these eight hypotheses are presented in Chapters 5,6,7,8 and 9 and within the general discussion in chapter 10.

Chapter 2

Literature review

2.1 Introduction

Chapter 2 places the research undertaken within this thesis into context with current research. It aims to identify research which has been undertaken to determine how ^{137}Cs behaves within a soil why it remains more available for plant uptake in organic upland soils than lowland soils. The literature review also includes studies that have examined the effect of countermeasures for reducing ^{137}Cs transfer into the food chain. The review also seeks to demonstrate that research into the effect of a potassium application has concentrated on the effect on the ^{137}Cs and that there have been few studies that have aimed to identify any secondary effects that such an application may have on the ecosystem as a whole. Thus the literature review will identify gaps within scientific knowledge which this study will address.

2. 2 Caesium-137

Cs-137 is a long lived radionuclide with a physical half-life of 30.17 years and a biological half-life of 110 days in men and 80 days in women (Eisenbud and Gesell, 1997). It is a beta emitter, but is most easily measured by the gamma emission of its ^{137m}Ba daughter through gamma-ray spectrometry (Eisenbud and Gesell, 1997). It is within the same homologous series as K^+ and NH_4^+ which are both weakly hydrated, monovalent ions (Shaw and Bell, 1991). However the Cs ions are more strongly adsorbed onto clay surfaces according to the Hofmeister or lyotropic series: $Cs^+ > Rb^+ > NH_4^+ \approx K^+ > H_3O^+ > Na^+ > Li^+$.

2.2.1. Caesium in UK soils

The deposition of radiocaesium within the UK originates from many sources, including atmospheric nuclear weapons testing, the Windscale and Chernobyl accidents (Eisenbud and Gesell, 1997) and routine releases from nuclear facilities (Food Standards Agency and Scottish Environment Protection Agency, 2000). Deposition may occur by wet or dry deposition. The largest single deposition of radionuclides within the UK was from the Chernobyl accident in 1986, and the most important of these radionuclides were ^{131}I, ^{134}Cs and ^{137}Cs (Coughtrey et al., 1989(b)). The Chernobyl accident increased the national environmental inventory of ^{137}Cs by an estimated 40 % (Cambray et al., 1987). The deposition of ^{137}Cs within the UK was largely attributed to wet deposition (Livens, Fowler and Horrill, 1992), with high levels of deposition occurring when a rainfall event coincided with the passage of the radioactive plume. In the UK, such areas were generally restricted to north-west England, north Wales and southern Scotland (Higget, Rowan and Walling, 1993).

The radiocaesium deposited in the UK has continued to cycle through the soil-plant-animal systems on upland soils many years after the Chernobyl accident (Jones, Paul and Mitchell, 1999) as it is more available for plant uptake on organic soils commonly found in upland areas compared to mainly mineral lowland soils (Graham and Killion, 1962). As a result, sheep grazing on upland pasture have accumulated radiocaesium at levels which continue to exceed the statutory level of 1000 Bq kg^{-1} live weight and restrictions on the movement, slaughter or livestock remain in place (Food Standards Agency and Scottish Environment Protection Agency, 2000).

2.2.2 Caesium-137 in the soil

Most of the Cs deposited directly onto plant surfaces will ultimately reach the soil either by being washed off by rainfall or by leaching from senescent plant material. Following the deposition of radiocaesium onto the surface of the soil, the ions (this assumes that caesium is always in ionic form but some will be in the form of particles which through weathering over time will release ionic caesium) become incorporated into the soil water. Cs-137 within the soil water is not easily leached as it is readily adsorbed onto the solid phase (Livens et al., 1996).

The soil water contains a range of cations, anions and organic molecules (Rowell, 1994). Soil particle surfaces react with soil water via the major processes of;

- Dissolution and precipitation of salts and minerals;
- Adsorption and desorption onto the surfaces and interlayer sites of clay minerals, sequioxides and humus (Rowell, 1994).

The clay fraction of the soil has silica tetrahedra units at its centre, which arrange themselves into sheets and, through the process of isomorphous substitution, K ions are introduced between two sheets. (See Figure 2.1 from Rowell, 1994.) Two types of clays dominate within soils the 1:1 single sheet clays or the non-expanding clays and the 2:1 multiple sheet clays or the expanding clays. The non-expanding clays as single sheets of tetrahedral units are only capable of holding ions of the surface of the clay particle (McLeish, 1992).

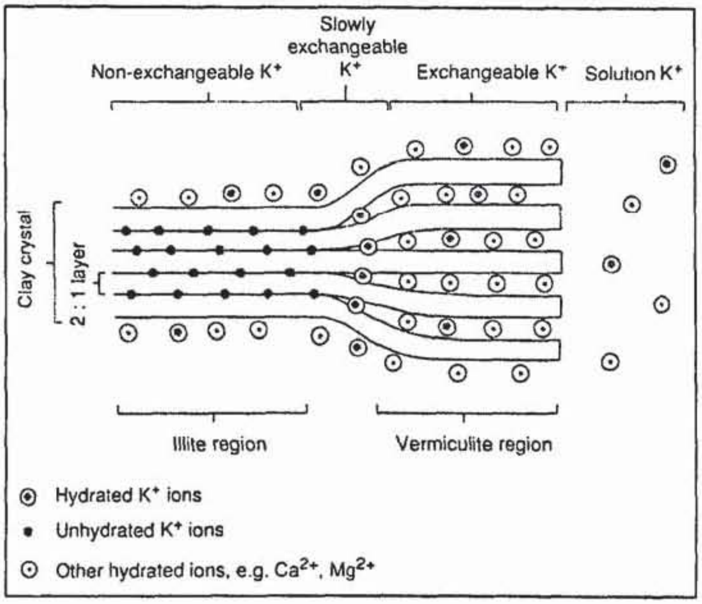


Figure 2.1 Clay structure (from Rowell, 1994)

Figure 2.1 shows expanding clay or 2.1 clay the mineral can retain charged ions on its surface (planar sites), however, as the mineral weathers the K ions become hydrated forcing the sheets apart (expanding the clay particle) and K is removed from between the silica sheets. This then allows other ions to become bound to the frayed edges (frayed edge sites) of the silica sheets. The loss of the K^+ leaves the sheets on each side with an overall negative charge and they repel each other further forcing the sheets apart allowing other ions to enter the space between the sheets (Read and Watson, 1982).

The Cs ion is a single positively charged ion that, like all ions, can be retained within the soil system through adsorption. The ion is electrostatically attracted to negatively charged sites within the soil where it can be retained or exchanged. In most lowland soils, the majority of these negatively charged sites are located on and within the clay minerals. There are at least three sites where the ions may absorb onto the clay mineral:

1) planar exchange sites on the crystalline surfaces

2) wedge or frayed edge sites (FES)

3) interlayer sites in which the ion may be permanently trapped

(Livens et al., 1996).

On the planar exchange sites (located on the edge of the vermiculite region in Figure 2.1) there is little selectivity for ions and the Cs^+ is readily desorbed, remaining easily available for plant uptake. However, if the ion enters a frayed edge site between silica tetrahedra sheets, desorption becomes more difficult, thus plant availability is reduced (Livens et al., 1996). For a Cs ion to be prevented from being available for plant uptake, fixation of the ion making it relatively unavailable is required. It is believed that fixation is dependent on the ion interacting with clay minerals within the soil, particularly those of illite and vermiculite (Hird, Rimmer and Livens, 1996). The Cs ion is slightly smaller than the K ion and this small radius allows the ion to move between the silica sheets and into the clay. As the Cs ion carries the same charge as the K ion, its entry causes the loss of charge repelling the two clay planes and they collapse fixing the Cs ion within the interlayer site. Any subsequent desorption of Cs^+ from these sites is slow (Goulding and Loveland, 1986). The larger more strongly hydrated ions are usually adsorbed onto external and expanded clay surfaces, as their size prevents them from sorbing onto sites in interlayer regions. Thus, 'sites in these zones (interlayer) are very specific for small weakly hydrated ions such as caesium' (Hird and Rimmer, 1995).

The high proportion of mineral matter and the associated clay content of UK lowland soils, result in a large number of potential interlayer sites for Cs^+. This explains the rapid immobilisation of Cs^+ in lowland soils (Pinder, Garten and Paine, 1980). By comparison, UK upland soils typically possess a higher organic matter content which was believed to be the reason for slow immobilisation of Cs^+ compared to lowland soils (Livens and Lowland, 1988). However, Shand et al., (1994), concluded that even in a highly organic peat, the eventual fixation of Cs was dependent on the clay minerals. Hird and Rimmer (1995) calculated that the total number of potential Cs^+ fixing sites in an acid organic soil was actually greater than the number present in a lowland mineral soil. They also determined that the fixation of Cs^+ through the collapse of the illite clay required a minimum Cs^+ concentration of 0.60 to 0.75mM. Such concentrations were unlikely to occur in any contaminated upland soil and required the presence of K^+, which could also induce interlayer collapse (Hird, Rimmer and Livens, 1996). However, heavy leaching of the K ion in upland soils results in a low concentration of K. Therefore, a rapid decline in Cs^+ availability through interlayer collapse is unlikely to occur.

The organic matter within the soil can have a significant impact on the availability of nutrients within the soil (Brady and Weil, 1999). Organic matter carries a weak charge on and within its surfaces and as such it is capable of retaining ions. However, if the organic matter is closely associated with the clay particle, the charge the clay particle can exert on the nutrient is lessened and as such the availability of nutrients increases.

Studies conducted by Dumat et al. (1997) and Maguire et al. (1992) showed that as the content of organic matter in a soil increases the actual affinity of a clay particle for Cs^+ decreases. Thus in more organic soils the Cs^+ remains more available for plant uptake and leaching from the soil than on mineral dominated soils.

Dumat and Staunton (1999) suggested that the presence of a humic substance can influence the affinity of the FES for Cs. When Cs^+ approaches the FES its low hydration energy forms a strong interaction with both clay surfaces closing the FES. The presence of a humic macromolecule at the FES impedes or limits the collapse of the FES preventing the ion associating with the clay particle (Staunton and Levacic, 1999; Dumat et al. 1997). In 1999, Dumat and Staunton demonstrated that the addition of organic matter reduced the affinity of illite for ^{137}Cs though there was no change in the separation of particles or reduction in the number of fixation sites available. Dumat et al. (1997) suggested that the presence of organic matter may affect the regular exchange sites on the clay surface but not specific sites of Cs^+ absorption. Shand et al. (1994) suggested that some Cs^+ retained by the organic matter which was closely associated with the clay surface might act as an intermediate between the exchangeable and interlayer mineral sites.

Regardless of the actual effect of organic matter on the adsorption of Cs within the soil, the availability of Chernobyl-derived Cs for plant uptake on organic soils of upland UK has continued to exceed that of mineral lowland soils many years after deposition (Dumat et al., 1997; Coughtrey, Kirkton and Mitchell, 1989(a); Hird and Rimmer, 1995; Jackson, 1990; Howard and Beresford, 1994).

2.2.3 Caesium-137 plant uptake

Following the aerial deposition of radionuclides it is expected that in the first growing season surface contamination will be important but in subsequent years vegetation contamination will occur mainly through the soil-root pathways (Sawidis, 1988). Ions may be incorporated into the roots by diffusion or active transport. Diffusion will facilitate the passage of many ions and other polar molecules including Cs and K (Robb and Pierpoint, 1983). Active transport utilises transport proteins within the cell wall to facilitate ion entry. Whilst transport proteins are specific for one type of ion, they will also transport any chemical congener in the uptake process (Eisenbud and Gesell, 1997). For example, the K^+ transporter will transport K^+, Rb^+, Na^+ or Cs^+, but K^+ is preferred (Taiz and Zeiger, 1991). Soil micro-organisms (e.g. mycorrihiza) can facilitate absorption of Cs^+ into the plant (Kirchman, 1993).

Two processes determine the caesium content of vegetation: caesium absorption by the root which reflects the availability of Cs in the soil and translocation of Cs from the root to other parts of the plant. 'The main factor affecting the latter process is the xylem transport of caesium' (Buysse, Brande and Merckx, 1996). Radiocaesium activity concentrations vary widely between plant species (Howard and Beresford, 1994; Broadley et al., 1999; McGee, Synnott and Colgan, 1993) and show a seasonal pattern (Salt and Mayes, 1991) which may reflect plant growth (Smolders and Shaw, 1995), generally indicating lower uptake in autumn and winter and greater uptake in spring and summer periods. However, Rafferty, Dawson and Colgan, (1994) observed highest activity concentration of ^{137}Cs in the winter months in pasture grass dominated by *Lolium perenne*, *Agrostis stolonifera* and *Festuca rubra*. A study by Salt et al., (1997) also observed that within *Agrostis capillaris* the highest activity concentrations of ^{137}Cs were present in mature leaves from October until December possibly due to a lack of re-translocation into younger tissue when plant growth slows down. Increases in ^{137}Cs concentration in the winter periods are often believed to be the result of soil adhesion onto plant surfaces by animal trampling (Sumerling, Dodd and Green, 1994). A study by Beresford and Howard (1991) calculated that within an upland site up to 62 % of the ^{137}Cs present in vegetation samples could be attributed to soil adhesion in the winter months. A similar study by Green and Dodd (1988) found that by dry weight 7 % of herbage from a sheep's paddock was soil which contributed 74 % of the total ^{137}Cs activity. The importance of soil adhesion is likely to depend on vegetation density and grazing pressure.

2.2.4 Characterisation of soil-plant transfer of ^{137}Cs

The concentration of ^{137}Cs ions in plant tissue can be easily measured by the gamma emission of its ^{137m}Ba daughter using a gamma spectrometer (Eisenbud and Gesell, 1997). The activity concentration in the vegetation is often expressed as Bq per unit mass and the transfer between soil and vegetation is typically defined as the concentration ratio, CR:

$$\boxed{CR = \frac{activity\text{ concentration in above ground vegetation }(Bq\ kg^{-1}d.w.)}{activity\text{ concentration in the soil }(Bq\ kg^{-1}d.w.)}}$$

Concentration ratios are widely used to compare the degree of radionuclide transfer from soil to plant for different soil types and different plant species and varieties (International Atomic Energy Agency, 1994). However, comparisons between soil types are limited because the concentration ratio does not take account of the bulk density of the soil which can vary by an order of magnitude between peats and heavy textured mineral soils (Salt and Mayes, 1991). The concentration is a ratio of concentration within the soil compared to the vegetation and there is no uniform depth to which soil samples are taken, although generally it encompasses the rooting depth (0-15 cm). Furthermore, CR's do not consider variations in plant biomass. The aggregated transfer coefficient (Tag) has been proposed as an alternative measure which overcomes the bulk density limitations of CR's by being based on the ^{137}Cs activity in soil per unit area rather than per unit mass (Howard et al., 1995) using the equation:

$$\boxed{Tag = \frac{activity\ concentration\ in\ the\ food\ product\ (Bq\ kg^{-1}\ d.w.\ )}{activity\ of\ deposit\ per\ unit\ area\ (Bq\ m^{-2}\ )}}$$

From Howard et al. 1995

Tag values are not dependent on soil bulk density and have an advantage of being more easily calculable from the literature than CR's since deposition measurements are more widely available than soil activity concentrations. Once again no uniform depth of soil is given to determine total deposition though 30 cm is generally adopted. However, neither Tag or CR's are suitable for quantifying the total proportion of Cs translocated from soil into the plant tissue. If the transfer of an ion from the soil to the above-ground biomass is considered on an ecosystem basis its transfer must reflect site specific factors such as climate, soil bulk density and plant biomass and the depth distribution of radionuclides (Salt and Kay, 1999). The use of a total flux approach allows sites with differing biomass production and soil concentrations to be directly compared. The flux value is derived by determining the total activity in the soil per unit area and relating that value to the total activity present in the above-ground biomass.

$$\boxed{\text{Total Flux} = \frac{\text{Total biomass (kg m}^{-2}\text{) x activity concentration within biomass (Bq kg}^{-1}\text{)}}{\text{Total deposition (Bq m}^{-2}\text{)}}}$$

All three methods of assessing the transfer of ^{137}Cs from soil to plant are subject to systematic errors since none of the values directly relate plant uptake to the concentration of Cs in the rhizosphere. In shallow rooting plants the transfer of ^{137}Cs into the biomass may be greater than in deeper rooting plants as the roots are concentrated in the upper soil layers where the soil activity concentration it typically at its greatest. Concentration ratios may generate the best estimate of the available ^{137}Cs within the soil provided the methodology involves sampling of soil from the rooting depth.

2.3 Potassium

Potassium in the soil exists in four forms: mineral, non-exchangeable, exchangeable and solution (Read and Watson, 1982). Clays and organic matter can hold K in the soil. Clay minerals of the 1:1 type e.g. kaolinite, and organic matter cannot fix K but hold it in an easily exchangeable form (Cooke, 1967). It is the 2:1 layered aluminosilicates e.g. mica which control the release and fixation of K (Read and Watson, 1982). In UK soils, most of the K in the clay fraction is in micas and hydrous micas – illites (Cooke, 1967; Eagle, 1963). Potassium within the soil is absorbed by the roots either passively, together with water, or actively transported into the cells as a K^+ ion. Plants generally maintain a certain level of K within their cells, however, during senescence of plant material the plant may translocate K from these areas to actively growing regions within the plant (Pritchard, Pigden and Folkins, 1964).

The availability of K^+ within the soil for plant uptake is determined by 'the quantity of K^+ that the solid particles are capable of releasing into the liquid phase of the soil, the K^+ concentration in the soil solution and the mobility of K^{+}' (McLean, 1978). The K^+ concentration in the soil solution is not directly related to the exchangeable K^+ in the soil but to other cations within the soil and is generally defined as:

$$\boxed{\frac{concentration\ of\ K^{+}}{\sqrt{concentration\ of\ Ca^{2+} and\ Mg^{2+}}}}$$

Relative availability of K^+ in soil solution (taken from McLean, 1978)

2.3.1. Potassium as a Countermeasure for ^{137}Cs transfer

The transfer of Cs into vegetation has been linked to a relative deficiency of plant available K within the soil (Coughtrey et al., 1989(b); Papastefanou et al., 1999). Smolders et al., (1996) demonstrated that ^{137}Cs activity concentration in spring wheat was reduced as the supply of K increased. The effects of a supplementary application of K on reducing the transfer of ^{137}Cs from soil to plant has been well documented by many authors (Jones et al., 1991; Shaw and Bell, 1991; Smolders and Shaw, 1995; Rafferty, Dawson and Synnott, 1998; Staunton, 1994). The transfer of ^{137}Cs from soil to plant has been so closely linked with the relative availability of K^+ in the soil that models have been developed which predict the transfer of radiocaesium in relation to the concentration of K in the soil solution and exchangeable K within the soil (Absalom et al., 1999 (a and b)).

K^+ is believed to reduce the uptake of ^{137}Cs from the soil to the plant by three possible methods:

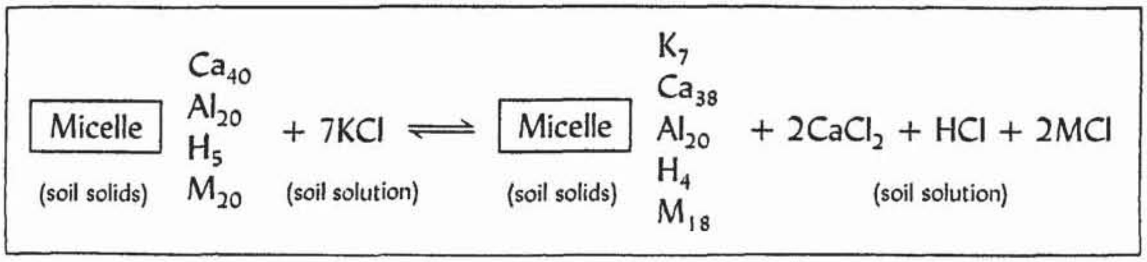
1) Ionic dilution
2) Competitive exclusion, and
3) Selective competitive exclusion

Sandalls (1989) suggested that ionic dilution could bring about the decrease in ^{137}Cs transfer from soil to plant as a result of K application. However, Shaw (1993) re-examined Sandalls data and concluded that the data could reasonably fit a competitive exclusion model where K^+ could effectively 'block' the uptake of Cs^+. If competitive exclusion were solely responsible for the exclusion of Cs^+, then a linear decline in Cs^+ would occur as K values rose. However, it has been observed that the effectiveness of K application at reducing ^{137}Cs transfer decreases as the K^+ concentration within the soil rises (Absalom, Young and Crout, 1995). As such, when the concentration of K^+ in the soil is high, any further application of K will have a negligible effect on ^{137}Cs transfer. Shaw (1993) suggested that any reduction in the suppression of ^{137}Cs uptake was likely to be due to direct competition between analogue ions and radioactive ions for uptake sites specifically adapted for the acquisition of nutrient elements.

Significant reductions in the transfer of ^{137}Cs following an application of K have been observed both in pot and in field trials. Paul and Jones (1995) reported a highly variable reduction of ^{137}Cs transfer from soil to plant, ten to twelve months after KCl application on a blanket bog with dominant species of *Erica tetralix* and *Eriophorum vaginatum*. At a site in Cumbria the reduction in transfer to bulk vegetation was between 33 and 45 % whilst on a site in Wales the reduction achieved was lower - between 6 and 16 %. Rafferty et al., 1996 (TEMAS project) reported that on blanket bog the ^{137}Cs activity concentration in vegetation was reduced by 75 % five months after K application. Rafferty also reported that the application of KCl affected the concentration of other ions in the vegetation, noticeably reducing the concentration of Mn in the biomass.

The application of K can result in changes in the availability of other nutrients for plant uptake. John and Vimpany, (1999) determined that although an application of KCl had no significant effects on the ionic composition of banana plants, it did cause 'a substantial portion of exchangeable Ca, Mg and Na to be displaced into the soil solution'.

The application of KCl may disrupt the availability of other ions in the soil solution either by ionic dilution or by complementary or antagonistic effects. As indicated in Figure 2.2, increases of K in solution will most likely lead to a decrease in the availability of Ca and Mg for plant uptake (Tinker, 1963). An application of KCl to a soil was illustrated by Brady and Weil (1999), (Figure 2.2) to result in the displacement of Ca from the exchangeable soil colloids.



$$\underset{\text{(soil solids)}}{\boxed{\text{Micelle}}}\begin{matrix}Ca_{40}\\Al_{20}\\H_{5}\\M_{20}\end{matrix} + \underset{\text{(soil solution)}}{7KCl} \rightleftharpoons \underset{\text{(soil solids)}}{\boxed{\text{Micelle}}}\begin{matrix}K_{7}\\Ca_{38}\\Al_{20}\\H_{4}\\M_{18}\end{matrix} + \underset{\text{(soil solution)}}{2CaCl_2 + HCl + 2MCl}$$

Figure 2.2 Effect of KCl addition to the soil, M represents other cations (taken from Brady and Weil, 1999)

The rapid dissociation of K^+ from the chloride may have been responsible for recorded losses of Ca. Cooke (1967) stated that the removal of chloride from the soil necessitates the loss of a cation and 'it is likely that large K dressings increase the loss of Ca'.

Frontenot, Wise and Webb (1973) recognised that the occurrence of Mg deficiency (grass tetany) was higher on pastures that had been fertilised with K. Tinker (1963) also demonstrated in field trials that any application of potassium in the form of KCl would lead to a loss of available Ca and Mg for root uptake by 'causing an increase' in the amount of Mg lost from the soil in drainage water'. This antagonism is greater the more acid the soil (Welte, 1963). Knoblauch and Odland (in Jacob, 1958) found that on acid soils a supply of Mg free fertiliser (KCl) caused Mg deficiency, resulting in the Mg in the soil being displaced by the K and subsequently being washed out. Hovland and Caldwell (1960) proposed three main mechanisms by which K may interfere with Mg uptake:

1) Adding K increases the loss of Mg from the soil system and thus makes it less available for plant uptake.
2) K 'out-competes' Mg for exchange sites on the plant roots.
3) High levels of K in the plant prevents Mg from functioning correctly.

The effect of KCl on the Mg status of a soil and its herbage may not be readily identifiable for a long period of time after application. In 1962, Salmond and Arnold showed that on a range of soils from organic to mineral-dominated a KCl application caused a reduction in the Mg status of grassland vegetation but this was only induced after 11 months of cropping. This was despite several of the soils already having been identified as 'deficient' in Mg.

A reduction in the availability of Mg within the soil may also have consequences for other trace elements within the plant. Jacob (1958) found that increasing the availability of Mg reduced the uptake of Mn.

Stewart and Holmes (1953) demonstrated that an application of KCl could depress the uptake of Molybdenum (Mo) from the soil to plants. Mo is an essential element in the nutrition of grazing animals, however the absolute concentration required by animals is very low and it is generally not deficient, but may be associated with toxic effects induced by excess concentrations (Bondi, 1987). The uptake of Cu from ingested plant matter by ruminants is inhibited by the presence of large concentrations (20-100 p.p.m.) of Mo in the plant matter (Ammerman, Barker and Lewis, 1995; Humphries et al. 1983 Bondi, 1987). The reduction of Cu absorption can lead to deficiency in animals, of which cattle and sheep are the most sensitive. Kreshtapova (1993) also found that when a range of inorganic fertilisers were applied to 'Timothy' grass growing on peat the K affected the supply of B, Zn, Cu and Mo to the plant. Cooke (1967) suggested the availability of phosphate and nitrate within the soil may be affected by an application of KCl through ion antagonism with the Cl ion.

Chapter 2 summary

Chapter 2 has demonstrated that a considerable amount of research has been undertaken to establish if an application of potassium to a soil will reduce the transfer of ^{137}Cs from soil to plant. However, few studies have been conducted to establish whether the effects of laboratory based experiments can be reproduced in a field environment. Before any consideration can be made to use K as a countermeasure for ^{137}Cs it is require that data be collected to determine any potential negative effects of the countermeasure on the ecosystem. Only one study was identified which had attempted to identify any side effects of a K application to an organic soil. The research presented in this thesis aims to provide more evidence regarding the performance of K application in the field and its potential effects.

Chapter 3

Study sites and experimental design

3.1 Introduction

One of the principle aims within this thesis was to examine whether the countermeasure was effective in a range of organic upland soils, thus a range of soil types had to be selected. To test whether the effects of potassium depended on the depth of the organic layer or the underlying geology these selected sites had to differ in this respect. The study was also required to be designed to generate data which could be statistically tested thus replicate samples were required from each site.

This chapter explains the criteria for study site selection, the design of the field experiment and the types of data collected from the field plots to test the eight hypotheses.

3.2 The experimental study sites

Four study sites were chosen for the study: Thornholme East, Thornholme West, Corney Fell North and Corney Fell South. All four sites are located in Cumbria, England, in a region that had been subjected to Chernobyl deposition. A previous field trial of K by Paul and Jones (1995) had also been conducted on Corney Fell and as such the selection of the Corney Fell sites allowed direct comparisons between the two studies. The four sites were chosen for their differing underlying geology, soil type, vegetation communities and grazing pressures. Where the sites underlying geology differed this would allow the effect of the application on differing soils and vegetation species, together with soils with different nutrient status to be directly compared.

The sites' geographical locations were identified using standard ordinance survey grid references and the soil profiles at each site were described according to Hodgson (1978). The flora were keyed using Stace (1991).

Figure 3.1. Map location of experimental study sites in Cumbria

3.2.1 Thornholme East

The site is located on Swainson Knott at an altitude of 310 m. NY 30785088, 1.2 km at 125^0 from Thornholme farm and 3 km at 62^0 from Prior Scales farm.

Aspect: 300^0 North north-west
Slope: 11^0
Soil Type: Peaty Podzol.
Solid geology: Granite
Soil Profile:

Horizon	Depth (cm)	Description
Litter	0-3	Reddish brown (5YR 2.5/2); litter; massive; abundant very fine roots; no stones; smooth clear boundary
O2	6-10	Dark brown (10YR 3/3); humus; massive; no stones; smooth clear boundary
O3	10-23	Black (5YR 2.5/1); loamy peat; massive; few small stones; smooth clear boundary
Ah	23-30	Dark brown (7.5YR 3/2); sandy silt loam; weak medium sub-angular blocky; clear wavy boundary
Bf	30	Iron Pan
Bs	30-30	Yellowish red (5YR 5/8); fine, sandy silt loam; weak medium, sub angular blocky tending to massive with depth; few fine fibrous roots; clear wavy boundary
C	60-80 (base)	Yellowish red (5YR 4/6); clay loam; massive; no roots; few medium large sub angular granite stones

Vegetation:

The vegetation is dominated by *Carex nigra* with *Molinia caerulea* becoming abundant in localised patches.

Species List	Common Name
Carex nigra L.	Common Sedge
Deschampsia flexuosa L.	Wavy Hair-grass
Festuca ovina L.	Sheep's-fescue
Juncus squarrosus L.	Heath Rush
Molinia caerulea L.	Purple Moor-grass
Polytrichum commune	
Vaccinium myrtillus L.	Bilberry

3.2.2 Thornholme West

The site is located on Wheel Fell at an altitude of 185 m. NY 30685078 2 km at 178^0 from Thornholme farm and 1.05 km at 56^0 from Prior Scales farm. The site has been previously drained and cleared of large stones, probably in the Victorian period.

Aspect: 290^0 North north-west
Slope: 7^0
Soil Type: Peaty Gley.
Solid geology: Calcic Sandstone
Soil Profile:

Horizon	Depth (cm)	Description
Litter	0-2	Litter
O	2-20	Dark brown (7.5YR 3/2); loamy peat > 50 % organic; fine; very fine fibrous roots; very few stones; clear wavy boundary
Bg	20-52	Matrix brown (10YR 5/3) ochreous mottles yellowish red (5YR 4/6); sandy clay loam; weak medium; sub-angular blocky tending to platy with depth; few roots; few small stones; smooth wavy boundary; humus staining in upper region
Bcg	52-80 (base)	Matrix brown (7.5YR 5/4) ochreous mottles yellowish red specks (5YR 5/6); sandy clay loam; massive; no roots; few large angular granite stones

Vegetation:

Poa annua, Anthoxanthum odoratum and *Deschampsia flexuosa* domiate the site.

Rumex acetosella and *Juncus squarrosus* encroach in the northern region of the site.

Species List	Common name
Agrostis capillaris L.	Bent
Anthoxanthum odoratum L.	Sweet Vernal grass
Deschampsia flexuosa L.	Wavy Hair-grass
Holcus mollis L.	Creeping soft-grass
Juncus squarrosus L.	Heath Rush
Rumex acetosella L.	Sheep's Sorrel
Poa annua L.	Annual Meadow-grass

3.2.3 Corney Fell North

The site is located on Corney Fell at an altitude of 230 m. NY 31294914, 1.15 km at 112^0 from Foldgate farm and 1.25 km at 83^0 from Myreground farm.

Aspect 276^0 North-west
Slope 7^0
Soil Type: Deep Peat (Flush Site)
Solid geology: Basalt
Soil Profile:

Horizon	Depth (cm)	Description
O1	0-11	Yellowish red (5YR 3/4); fibrous; abundant very fine roots; no stones;
O2	11-25	Black (5YR 2.5/1); semi fibrous; massive; no stones; smooth clear boundary
O3	25-60 (base)	Black (5YR 2.5/1); humified; massive; no stones;
IIC		Greyish brown (10YR 4/3); silty clay loam; massive; few small stones

Vegetation:

This flush site is dominated by *Trichophorum caespitosum, Molina caerulea* with periodic patches of *Juncus squarrosus.*

Species List	Common Name
Carex lepidocarpa L.	
Inidophorum caespitosum Spp	
Juncus squarrosus L.	Heath Rush
Molinia caerulea L.	Purple Moor-grass
Polygala Spp.	Milkwort
Potentilla erecta L.	Tomentil
Sphagnum Spp.	
Trichophorum caespitosum L.	Deergrass

3.2.4 Corney Fell South

Located on Thwaites Fell at an altitude of 230 m. NY 31754901, 0.8 km at 258^0 from Beckstones farm and 0.6 km 48^0 from Mere Crags.

Aspect: 168^0 South south-west
Slope: 12^0
Soil Type: Peaty Gley
Solid geology: Basalt
Soil Profile:

Horizon	Depth (cm)	Description
Litter	0-4	
O	4-20	Brown (5YR 2); humified; massive; no stones; smooth clear boundary
Bg	20-44 (base)	Dark brown (7.5YR ¾); sandy silt loam; humified; weak medium, sub-angular blocky; roots common fibrous; contains weathered granites

Vegetation:

Nardus stricta almost exclusively dominated this site with only the occasional presence of other species.

Vegetation Species	Common Name
Juncus squarrosus L.	Heath Rush
Molinia caerulea L.	Purple Moor-grass
Nardus stricta L.	Mat-grass
Sphagnum Spp.	
Trichophorum caespitosum L.	Deergrass
Vaccinium myrtillus L.	Bilberry

3.3 Field experimental design

The natural inputs and losses of nutrients to and from the soil system needed to be fully characterised prior to any consideration of the effect of a supplementary K application. Within upland soils, the total input of nutrients is almost exclusively through precipitation, which can be quantified through the collection and analysis of rainfall. The experimental design included control plots which would allow a 'background' level of nutrient changes in the soil and vegetation to be determined.

At each of the four sites, nine 15 x 15 m plots were established in June 1997, across the gradient of the slope to prevent interaction between treatments. A 2.5 m border zone was placed around each of the plots to avoid the possibility of edge effects during sampling. Thus, the effective plot size was 10 x 10 m. At each site plots were located in areas with similar vegetation composition.

At Thornholme East and Thornholme West, horizontal zero tension lysimeters (Figure 3.2) were installed at the base of each plot to retain the gravitational soil water moving through the soil system. These were placed at a depth of 25 cm from the soil surface and approximately parallel to the gradient of the slope, collecting the water in a container from where it could be recovered and analysed.

To estimate the residence time of the applied K in the soil system, the total output of K was quantified. Within an upland soil the vast majority of the water moves though the soil profile as soil water. There are three major types of soil water: (i) macropore or gravitational soil water which flows through the soil in response to gravity (10 to 20 kPa suction), (ii) soil pore or capillary water which is held within the soil (10 to 3100 kPa suction), and (iii) hygroscopic water which is held within the soil at tensions greater than 3100 kPa (Titus and Mahendrappa, 1996).

Within the soil, up to 90% of the water moves through preferential flow (Shaffer, Fritton and Baker, 1979) following root cracks and soil structure. This preferential flow is generally driven by gravitational forces and, as such, is macropore soil water. Zero tension lysimeters were used in this study since they are reported to be the best type of lysimeter to collect preferential flow water (Titus and Mahendrappa, 1996) and therefore should be most suited for estimating nutrient loss from the soil system. Zero tension lysimeters are also able to give some indication of the volume of soil from which the water originated and, as such, the loss of nutrients from a given soil volume.

The amount of added K remaining in the soil can be estimated by sampling the soil itself. Interstitial soil water can be extracted from the soil using centrifugation, which allows an assessment of the nutrients present in the capillary water fraction (Titus and Mahendrappa, 1996). Drying and subsequent analysis of the remaining soil permits an estimation of the nutrients available for plant uptake.

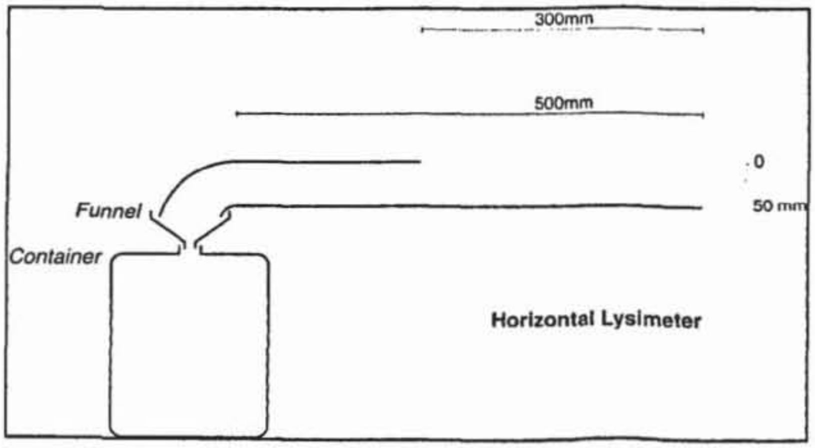


Figure 3.2 Zero tension horizontal lysimeters

The addition of nutrients from rainfall, particularly that of K was determined by the collection and analysis of rain from two gauges (Figure 3.3), one was located on Corney Fell and the second located at Thornholme.

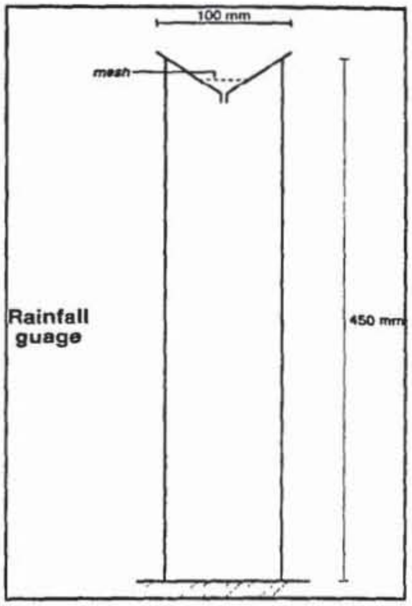


Figure 3.3 Rainfall gauges installed at Thornholme and Corney Fell

3.4 Potassium application

3.4.1 Selection of suitable form of K

Potassium occurs in several forms throughout the agro-chemical industry. The most common and frequent form of K application is within a general fertiliser which also contains nitrogen and phosphorus. However, the addition of a fertiliser containing nitrogen would have the potential to increase the side effects of the treatment and as such, a source of K was required which was devoid of nitrogen.

The K in synthetic fertilisers is derived from potash salts, originating from the evaporation of saline lakes e.g. the Trias deposits in England, Tertiary deposits in Poland, and Permian deposits in Germany. The major K minerals occurring in these deposits are sylvine [sylivite] (KCl), carnallite ($KCl.MgCl_2.6H_2O$), kainite ($KCl.MgSO_4.3H_2O$) and polyhalite ($K_2SO_4.MgSO_4.2CaSO_4.2H_2O$) (Read and Watson, 1982).

The field application of K in this study was designed to mimic potential future, large-scale application of the countermeasure. The form of K used would depend upon availability and costs. The latter would include the cost of the K itself, transportation and application. The cheapest form of K available is that which is directly extracted, namely potash. Potash is typically composed of 95 % KCL (Potash, Cleveland Ltd, pers comm. 1998). Economically, the costs of obtaining a K source with a greater KCL concentration would far outweigh the costs of increasing application mass by 5.3 %. It was therefore concluded that the form of K which would be most likely to be used in any large-scale application would be that of potash. Following extraction, potash can be granulated into various grain sizes from 0 to 4 mm (Potash, Cleveland Ltd, pers comm. 1998).

The potash may be applied either as a solid (powder or granular) or with the addition of water. Possible advantages of adding water prior to application are that the salt would begin to move into solution. If applied in such a form, the potash would be able to move rapidly through the soil to the rooting zone and thereby become available for root uptake relatively quickly. In comparison, by applying the potash without water, would incur a time delay between application and when sufficient moisture was available to begin dissolving the salt. However, the time costs of adding water to the salt during application in any large-scale event would be prohibitively large. It was therefore concluded that a 'completely dry' form of potash should be used for the application in this study.

The potash salt should be able to dissolve rapidly into the soil solution. However, the salt should preferably not dissolve at such a high rate that all the potash could be lost through run-off in a single heavy downpour event. Furthermore, the salt granules needed to be capable of diffusing evenly over the entire application area. From these considerations, a 2 mm size granule of potash was chosen as the appropriate size for application.

3.4.2 Application of K

The granular potash was applied to the soil as a surface dressing to minimise disturbance to the ecosystem. A rotatory spreader was used which was calibrated to evenly distribute the potash over the experimental plots. The application was made on all experimental sites on 15th June 1997 and was repeated at Thornholme East on 15th June 1998.

Three levels of K treatment were initially applied to each of the study sites at rates of 0, 100 and 200 kg K ha^{-1}, following the dose rates used by Paul and Jones (1995). The 200 kg K ha^{-1} dose rate (also used by Rafferty, Dawson and Synnott, 1998) was used to examine if increasing the application rate would result in a greater reduction in ^{137}Cs transfer. There were three replicates of each treatment at each site to permit statistical analysis of the data.

Following the first year of sampling, a further three plots were established at Thornholme East. At this time all plots establish at Thornholme East had their initial treatment re-applied and the three 'new' experimental plots were treated with a single application of potash at 200 kg ha^{-1}. The establishment of these three new plots and the repetition of the K application would permit the effect of yearly changes in the effectiveness of the application and repeated applications to be considered.

3.5 Limitations of study

The study aimed to statistically test a series of hypothesis with regard to the effect of a K application on organic soils. Due to the logistical constraints of time the number of sites was restricted to four which the author considered represented a broad range of organic upland soil and vegetation types. Due to the number of samples that had to be collected to test the hypotheses, the study was unable to examine any single study site in great detail. This study does not attempt to examine the specific effects of the countermeasure at any single site, but to develop knowledge into how the effects of the countermeasure may vary between sites and what type of sites may be most sensitive to a K application and require further research.

Chapter 4

Monitoring methods

4.1 Introduction

Prior to potash application, it was difficult to predict when a reduction in the transfer of ^{137}Cs from soil to plant would occur and the extent or duration of any reduction. The only relevant study by Paul and Jones (1995) demonstrated that there was a delay in time between the application and the effect of the countermeasure and that the countermeasure may remain effective for at least one year.

To determine the longevity of the application, a long-term monitoring programme was undertaken; this allowed the duration of any side effects of the treatment to be measured which was important since persistent side effects were more likely to deleteriously affect the ecosystem. The response of the sites to the treatment was likely to vary with time such that regular sampling was required. The number of samples that would be generated from each site, together with the associated processing and analysis time, determined that a monthly sampling programme would be appropriate (see Table 3.1).

Samples taken from rainfall gauges and lysimeters allowed the total inputs and losses of nutrients into and from the soil system to be quantified. Soil samples were taken to identify any change in the availability of nutrients. Vegetation samples enabled possible changes in the nutrient and ^{137}Cs availability to be measured, furthermore, analysis of vegetation gave information on the nutritional value of the foliage to grazing animals.

Table 4.1 Details of Sample Collection

Sampling Date	**Sites Sampled**				**Samples Taken**			
	Thornholme East	Thornholme West	Corney Fell North	Corney Fell South	Soil	Vegetation	Lysimeter	Rainfall
15th Jul '97	√	√	√	√	√	√	√	√
15th Aug '97	√	√	√	√	√	√	√	√
15th Sep '97	√	√	√	√	√	√	√	√
15th Oct '97	√	√	√	√	√	√	√	√
15th Nov '97	√	√	√	√	√	√	√	√
15th Jan '98	√	√	√	√	√	√	√	√
15th Feb '98	√	√		√	√	√	√	√
15th Mar '98	√	√		√	√	√	√	√
15th Apr '98	√	√		√	√	√	√	√
15th May '98	√	√		√	√	√	√	√
15th Jun '98	√	√		√	√	√	√	√
15th Jul '98	√				√	√	√	√
15th Aug '98	√				√	√	√	√
15th Sep '98	√				√	√	√	√
15th Oct '98	√				√	√	√	√

4.2 Field sampling methods

4.2.1 Vegetation sampling

Vegetation was sampled by removing all the above-ground biomass from a 40 x 40 cm quadrat, which had been randomly located within each experimental plot using random number tables. The vegetation was cut with stainless steel shears to within 7-10 mm of the soil surface. Occasionally, local obstacles prevented the shears from cutting to this height, however, the loss in sample biomass was determined to be less than 1 % of the sampled biomass.

4.2.2 Soil sampling

Following vegetation sampling, soil samples were removed from the same 40 x 40 cm quadrat. Five soil samples were taken with an auger from each quadrat, one from each corner and a fifth from the centre and bulked. The auger sampled the upper 15 cm of the soil profile which contained the majority of the plant roots.

4.2.3 Water samples

The volume of water collected in the rainfall gauges and lysimeters was noted on each sampling occasion and a sample of each was taken for later chemical analysis. Potential contamination by particulate matter was minimised by taking a mid-flow sub-sample from each container, as particulates would tend to congregate either on the surface or at the base of the sample.

All samples were returned to the laboratory within 12 hours. Soil and water samples were stored at 2 to 4^0C. Vegetation samples were removed from their packaging and placed in open trays to air-dry.

4.2.4 Total ^{137}Cs deposition and bulk density

Sampling to determine total ^{137}Cs deposition was undertaken on a single sampling occasion in March 1998 at all four experimental sites.

To determine the transfer of ^{137}Cs from soil to plant in terms of aggregated transfer coefficients (Tag values) the total ^{137}Cs deposition on each site had to be quantified. The amount of ^{137}Cs in the soil is generally far greater than that which is present in the above ground biomass. In this study the effect of adding the ^{137}Cs in the above-ground vegetation to the total soil deposition made no difference to the deposition value due to the comparatively small above-ground biomass. To sample the soil either a spade or a modified golf hole corer can be used to extract undisturbed soil of a given volume from a specific depth. Permanently high moisture content at one of the sites resulted in the corer being unable to sample, therefore a spade was used to sample at all the sites. It was assumed that the majority of ^{137}Cs in the soil would be located in the upper 0-15 cm of the soil profile (Smith and Elder, 1999; Horrill and Howard, 1991). The maximum rooting depth at each site was 15-20 cm; as a result the soil was sampled to 25 cm. Once the whole soil block had been extracted and its dimensions measured, it was bagged for later analysis. Typical extracted volumes of soil were 0.015 m^3. Variation in deposition was determined by analysing five samples from each site.

The bulk density of the soil at each site was also calculated from these samples using the standard method outlined by Rowell (1994) by recording the field moist volume and oven-dry mass (at 105 ^{0}C).

4.2.5 Cs-137 Profiling and Bulk Density

To permit a detailed interpretation of how the four sites responded to the experimental treatments the depth distribution of ^{137}Cs activity concentration within the soil profile needed to be known. Soil blocks were again used to sample to a depth of 25 cm within the soil (following the method outlined in section 4.2.4). These blocks were divided into five sections, each of which represented a five centimetre depth interval, these sections were then labelled and double bagged for later analysis. Eight replicate blocks were sampled at each site in May 1998.

Changes in bulk density with depth were also derived from these samples by using the standard methodology outlined in section 4.2.4.

4.3 Chemical laboratory analyses

4.3.1 Processing of soil samples

Time and storage constraints meant that only extraction of interstitial water and the measurement of pH could be undertaken on fresh soil samples prior to the remaining soil sample being air dried. Recording the mass of the sample in a field moist, and again once in an air-dry state, allowed the calculation of moisture content. The soils were then sieved to less than 2 mm grain size.

4.3.2 Extraction of interstitial water

Centrifugation is a reliable method of extracting a soil solution, provided that solutions are extracted as quickly as possible after sampling (Jones and Edwards, 1993). The method involves the extraction of a solution from the soil through force rather than through chemical release. As the process is not a passive one, it can be assumed that the solution extracted will contain a greater proportion of elements than retained in a zero tension lysimeter. The solution obtained is from the soil rather than an added liquid so it can be assumed, provided the soil samples were not freely draining water, that the water extracted by centrifugation is that which is retained by the soil, namely the interstitial water (Kinniburgh, and Miles, 1983).

The centrifuge tubes used for the extraction were constructed in two interlocking parts following Grieve (1996) (Figure 3.1). At the base of the upper region of the tube a 0.5 mm diameter hole allowed liquid to drain into the lower section of the tube. This lower region of the centrifuge tube could retain approximately 12 ml of liquid.

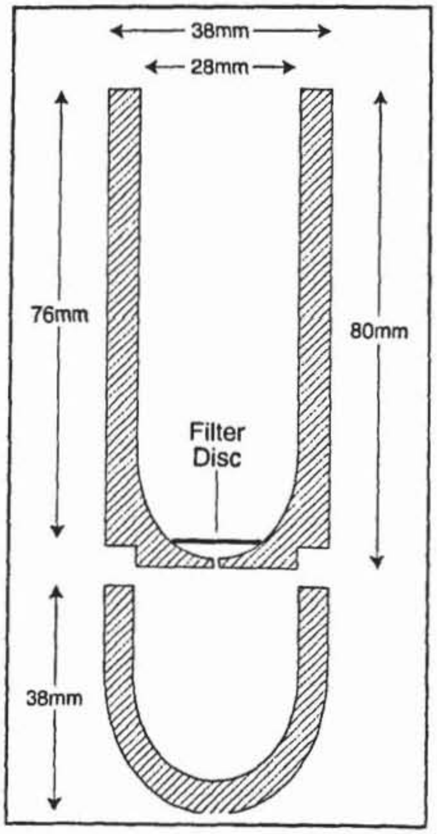


Figure 4.1
Diagram of the
two-part centrifuge tubes.

The tube was made of 'white nylon 66' a polyamide (Adipic acid - hexamethylenediamine) which has a crystalline structure and potentially can absorb 10% of its mass on prolonged immersion (Plasticsusa, 1999). Due to the relatively short time period that the soil is exposed to the nylon, it was reasonable to assume that no interaction between the soil/solution and the nylon would occur.

The centrifuge tubes were soaked overnight in 20 % nitric acid, then washed in warm water, rinsed in double-distilled water and dried at 80 ^{0}C. The soil samples were thoroughly mixed and root matter greater than five millimetres was removed. The procedure was only carried out on fresh soil samples which had been stored at 2 to 4 ^{0}C in a refrigerator for between one and four days following sampling.

A cellulose nitrate membrane filter disc (0.8 μm nominal particle retention) was placed at the base of the upper section of the centrifuge tube to prevent soil particles passing directly into the lower region of the centrifuge tube (Figure 4.1). The mass of the upper section of the tube and filter was measured. The centrifuge tubes were packed with approximately 40 g of the field moist soil, weighed, and centrifuged at –59 kPa for 30 minutes.

Centrifugation 'drove' the liquid from within the soil sample to the base of the upper tube, where it moved through the 0.5 mm hole into the lower section via the filter. The volume of this solution was approximated by the decrease in mass from the upper section of the tube. The low recovery of the interstitial water, which was typically around 2 to 3 ml from each of the sub-samples but varied from below 1 to 8 ml, required 4 sub-samples of soil to be centrifuged to generate sufficient sample for analysis. All four extracted soil solutions were bulked into acid washed bottles before being frozen.

4.3.3 Soil *pH*

The pH of the soil samples was measured in distilled water and in a 0.01 M $CaCl_2$ solution (Rowell, 1994).

4.3.4 Ammonium Acetate Extraction

Extraction with 1 M ammonium acetate is recommended for the determination of available K, Mg and Ca in neutral or acidic soils (Allen, 1989). Five grams of air dry soil was mixed with 100 ml of NH_4Ac and shaken for one hour on a rotary shaker. The solution was then filtered through a Whatman No.44 filter into acid washed bottles. As the total moisture content of each sample had been established, it was possible to determine available cations in the soil as per kg air dry soil, or per kg field moist soil. The impurities in the ammonium acetate used are listed in Table 4.2, these impurities were negligible in comparison to the concentrations of ions extracted from the soil.

Table 4.2. Composition of ammonium acetate for extraction.
(Fisher Scientific, 1998; 1999).

Element		**Concentration per unit mass**	**Concentration in extracting solution**
Assay		>99%	>99%
Reaction	(5% soln.)	PH 6.5-7.5	pH 7.00
Calcium	(Ca)	<2p.p.m.	<0.15p.p.m.
Iron	(Fe)	<1p.p.m.	<0.1p.p.m.
Magnesium	(Mg)	<1p.p.m.	<0.1p.p.m.
Potassium	(K)	<0.001%	<0.0001%

4.3.5. Ethylene diamine tetra-acetic acid (EDTA) Extraction.

Ethylene diamine tetra-acetic acid (EDTA) was chosen as a suitable extractant to complex with the copper (Allen, 1989). Fifty millilitres of 0.05 M EDTA solution was added to 5 grams of air dry soil which was then mixed using a rotary shaker for 40 minutes prior to being filtered through a Whatman 542 filter. The impurities within the extractant used are displayed in Table 4.3.

Table 4.3 Composition of EDTA used for extraction
Fisher Scientific 1998 and 1999.

Element		**Concentration per unit mass**	**Concentration in extracting solution.**
Assay		99.15%	>99%
Calcium	(Ca)	0.320p.p.m.	<0.01p.p.m.
Copper	(Cu)	<0.200p.p.m.	<0.01p.p.m.
Iron	(Fe)	<0.200p.p.m.	<0.01p.p.m.
Potassium	(K)	<2.000p.p.m.	<0.04p.p.m.

4.3.6 Soil organic matter

Organic matter was determined by loss on ignition (Allen, 1989). This method is suitable for estimating the organic content since the soils were of low clay and low carbonate content (Rowell, 1994). Soil samples of approximately 10 grams in mass were dried in a furnace at 550^{0}C for at least four hours to ensure complete loss of organic matter.

4.3.7. Water samples

The water samples that had been taken from the lysimeters and rainfall gauges were initially stored at 2 to 4 ^{0}C. Within 24 hours of sampling, these samples were then filtered through No.44 Whatman filter paper and the filtrate collected and frozen for later analysis.

4.3.8. Vegetation

Prior to digestion and analysis of the vegetation samples each sample was allowed to air-dry. Following air-drying, the samples were mixed and dried at 80 ^{0}C before a sub-sample of approximately 20-25 % of the vegetation mass was removed for digestion. The remaining sample was retained to determine ^{137}Cs activity concentration within the vegetation.

The vegetation was ground into a fine powder using a Glen Creston agate grinding dish, which minimised risk of contamination to the sample. The digestion with sulphuric acid and hydrogen peroxide (Allen, 1989) allowed the concentrations of K, Mg, Ca and Cu to be determined from a single solution. However, the method was modified (from Quarmby and Grimshaw, 1967) to allow the solution to be analysed for Mn and Fe. One gram of vegetation was digested with sulphuric acid with a selenium catalyst for 45 minutes before 15 ml of hydrogen peroxide solution was added whilst the solution was being heated. Heating of the solution continued until it became translucent. The digest mix was then made up to 50 ml with distilled water before the solution was allowed to cool prior to analysis.

The sulphuric acid and hydrogen peroxide digestion methodology was not a suitable method to determine the concentration of Co in the biomass. The methodology did not allow high recovery rates of Co from the sample or low detection limits to allow samples to be differentiated on an inductively coupled plasma mass spectrometer

(ICP-MS). As there was no other suitable technique to determine Co concentration whilst retaining a method for determining the concentration of other elements in the biomass Co was measured using the sulphuric acid and hydrogen peroxide digestion methodology.

4.3.9 Instrumentation

Sample solutions were analysed for Ca, Cu, Fe, K, Mg and Mn to determine ion concentration on either an inductively coupled plasma mass spectrometer (ICP-MS) or atomic absorption spectrometer (AAS) instrument. Vegetation samples were analysed on the ICP-MS, whilst the remaining solutions were analysed on AAS.

The nutrient analysis of the vegetation digests was undertaken on a Jobin-Yvon JY 38 Plus ICP-MS, a sequential spectrometer capable of multi-element analysis (Jobin-Yvon, Instruments S.A., 1989). The instrument was calibrated with six standards and random repeat analysis of samples ensuring that precision was maintained.

Nutrients in soil extractions and lysimeter water were analysed on two Atomic Absorption Spectrometer (AAS) instruments, the Pye Unicam SP9 using the Unicam 919 Atomic Absorption software and data station version 1.7 and the Unicam Solaar 989 spectrometer using Solaar 32 software and data station 9178. Both instruments were calibrated using five standards.

4.3.10 Accuracy and Precision

When analysing element concentrations in sample solutions by ICP-MS and AAS precautions had to be taken to avoid false positive measurements of the analyte. This was achieved by determining the detection limit which shows the background variability encountered in blank samples. The detection limit for each element analysed by ICP-MS or AAS was calculated using equation 3.1:

$$\boxed{\text{Limit of Detection} = 4.65 \times \text{Standard Deviation of ten blank samples}}$$

Equation 4.1.

The multiplication factor of 4.65 ensures 99.9 % confidence in determining that a sample value is greater than the background concentration in the blank sample. Although it was possible to identify the analyte in a sample below this detection limit, there was little confidence in the accuracy of the results and such results are reported as below the detection limits.

The accuracy and precision of the results was checked by repeat analysis of certified standard reference materials. Two standard reference materials were used, a vegetation sample (hay) and a water sample. Both standards were treated as samples and the analytical results are shown in Tables 4.4 and 4.5. During the analysis of the standards the results were only accepted if the values for the standard fell within the published ranges, otherwise, the instrument was re-calibrated and the sample batch was re-run.

For the soil extraction using EDTA and NH_4Ac a single soil sample was used as an internal standard since no certified standard was available. The single soil sample was repeatedly analysed to give a measure of the mean and variability of nutrient availability within the sample (Table 4.6). This internal standard was analysed with all subsequent extractions to ensure that the methodology remained precise. Analysis results were rejected if the value for the internal standard was greater than one standard deviation of the mean and the extraction procedure was repeated.

4.3.11 Grain size analysis

The relative proportions of clay, silt and sand within the mineral component of the soil influence the availability of nutrients and ^{137}Cs for plant uptake. The composition of this mineral fraction was determined by Coulter counter analysis of the soil. Initially, the organic matter was removed by loss on ignition (see section 4.3.6). The remaining ash was then suspended in a distilled water and analysed on a LS 230 Coulter counter capable of measuring the size and abundance of particles between 0.04 and 2000 μm (Coulter Electronics Limited, 1994). Each sample was analysed three times and a mean calculated. The output of the analysis can either be displayed in terms of the proportion within each grain size, the area of the grains or total volume of the grains within the sample.

Table 4.4. Certified composition of vegetation standard reference material (International Atomic Energy Agency, Vienna, Austria. IAEA/V-10 HAY) and values obtained from analysis.

Standard Vegetation Type	Values	Concentration (%)											
		Potassium (K)		Magnesium (Mg) (10^{-2})		Iron (Fe) (10^{-3})		Manganese (Mn) (10^{-3})		Copper (Cu) (10^{-4})		Calcium (Ca) (10^{-1})	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Hay	Expected	1.90-2.30	2.10	13.3-14.5	13.6	17.7-19.0	18.5	3.2-5.2	4.7	8.8-9.7	9.4	21.0-22.2	21.6
	Obtained (n=16)	2.08-2.30	2.21	13.0-14.7	14.0	16.0-28.0	19.0	4.9-5.6	5.13	9.5-13.1	10.2	20.8-21.7	21.3

Table 4.5 Composition of aqueous standard reference material (U.S. Department of Commerce. National Institute of Standards and Technology) and accepted values obtained during analysis.

* Denotes that the data set was accepted after repeated checks and that the result was judged to be sufficiently close to be accepted.

Element	Concentration (mg l^{-1})	Range (mg l^{-1})	Lysimeter Water Samples (n = 15)		Interstitial Water Samples (n = 12)	
			Accepted Analysis Mean (mg l^{-1})	Accepted Analysis Range (mg l^{-1})	Accepted Analysis Mean (mg l^{-1})	Accepted Analysis Range (mg l^{-1})
Magnesium Mg	7.989	7.9 - 8.0	8.00	7.95 – 8.10*	8.01	7.96 - 8.21*
Potassium K	2.356	2.32 - 2.39	2.36	2.32 – 2.42	2.37	2.32 - 2.39
Manganese Mn	37.66	36.8 - 38.5	37.5	36.7 – 38.5*		

Table 4.6 Element concentration of the internal standard.

Ammonium acetate (A.Acetate), Ethylene diamine tetra-acetic acid disodium salt (EDTA).

Element		Extractant	Absolute Range (mg kg^{-1})	Mean (mg kg^{-1}) (n=24)	Standard Deviation	Accepted Analysis Range (mg kg^{-1})	Analysis Mean (mg kg^{-1}) (n=45)	Analysis Standard Deviation
Potassium	**K**	A.Acetate	130 – 169	158.9	16.0	142.9 – 174.9	162.1	7.2
Magnesium	**Mg**	A.Acetate	96 – 145	120.2	11.4	108.8 – 131.6	121.7	4.6
Calcium	**Ca**	A.Acetate	101 – 142	126.1	11.0	115.1 – 137.1	126.3	5.5
Iron	**Fe**	A.Acetate	16 – 54	35.2	12.4	22.8 – 47.6	34.1	5.1
Copper	**Cu**	EDTA	0.95 – 1.07	1.01	0.03	0.98 – 1.04	1.01	0.02

4.4 Cs-137 sample preparation and analysis

4.4.1 Sample Preparation

Soils

Soil samples were sub-divided where necessary and ground in batches using a steel grinding set of a Creston Gy-Ro mill; each sample was then bulked and homogenised. A cylindrical polypropylene container of fixed geometry of typically 150 ml was weighed and filled with sample tapping frequently to encourage settling. The container was then sealed and re-weighed.

Vegetation

After a representative sub-sample of vegetation had been taken for digestion, the remaining sample was dried at 85 ^{0}C and sub-samples were ground using a hardened alloy steel grinding dish. The sub-samples were homogenised before being placed into a cylindrical container using the same procedure as for soils. As the amount of vegetation collected from each plot varied through time, and across sites, five containers of differing volumes and geometries were used; 150, 75, 20, 10 and a petri dish of 25 ml.

4.4.2 Gamma Spectrometry

The detection of radionuclides by gamma spectrometry was undertaken on a semiconductor (solid state) detector. The semiconductor detector requires electrons in the valance band to become excited by ionization and cross the forbidden band.

Gamma rays interact with a semiconductor and result in electron excitement from the valance band into the conduction band. In the HPGe detector used this excitement results in an electronic pulse, which is collected via a large potential difference (c 3000 volts). The magnitude of the pulse is directly proportional to the magnitude of the gamma ray interaction. Thus a full interaction i.e. all the energy transferred to valance electrons, will be directly proportional to the electronic pulse.

The pulse is collected in a multi-channel analyser (MCA), via amplification. The MCA is calibrated in units of energy (keV), the gamma ray and thus the radionuclide are identified via these units of energy (Tyler, 1994). The HPGe detector used in this study used GammaVision software (version 2.02) with the necessary multi-channel analysing capacity to analyse a suite of radionuclides from one sample concurrently. The detector was calibrated using a National Physical Laboratory (NPL) mixed radionuclide spike (Table 3.7) which provided a range of photopeaks to spike blank soils. These blank soils contained no anthroprogenic radionuclides.

These spiked soils could then be used to determine the detection efficiency of the detector as a function of radionuclide energy. The detector was calibrated following standard procedures. However, the relative efficiency of the detector changes with the density of the material (Figure 3.2) and so the calibration was modified to account for these changes (Tyler, 1994).

The detector was calibrated for several geometeries and densities so that a valid calibration could be used for any sample. Having constructed a series of efficiency calibrations for each geometry, these were then tested against prepared International Atomic Energy Agency (IAEA) samples (Table. 3.8.). The principal detector gave values for the IAEA samples in agreement with the documentation provided. Samples of both soil and vegetation were 'counted' in the detector until the detectors estimate of the activity concentration of the radionuclides of interest was typically within a 5% error. This 5% error was a 'trade off' between time on the detector and the accuracy of the results. Occasionally, due to sample size and contamination levels, errors of less than 8% were accepted.

Table 4.7 Details of R08-03 Mixed Radionuclide Spike for Efficiency Calibration. 1st February 1998. National Physical Laboratory.

Nuclide	Gamma-ray Energy (Mev)	Gamma rays per second per gram of solution	Overall uncertainty (±)
Americium-241	0.060	7.8	4.3%
Cadmium-109	0.088	5.1	3.7%
Cobalt-57	0.122	10.1	2.0%
Cerium-139	0.166	6.6	5.5%
Mercury-203	0.279	8.5	4.7%
Tin-113 (via Indium – 113m)	0.392	18.4	3.4%
Strontium-85	0.514	51.8	3.8%
Caesium-137	0.662	42.1	2.1%
Yttrium-88	0.898	194	1.6%
Cobalt-60	1.173	48.7	2.2%
Cobalt-60	1.333	48.8	2.2%
Yttrium-88	1.836	205	1.6%

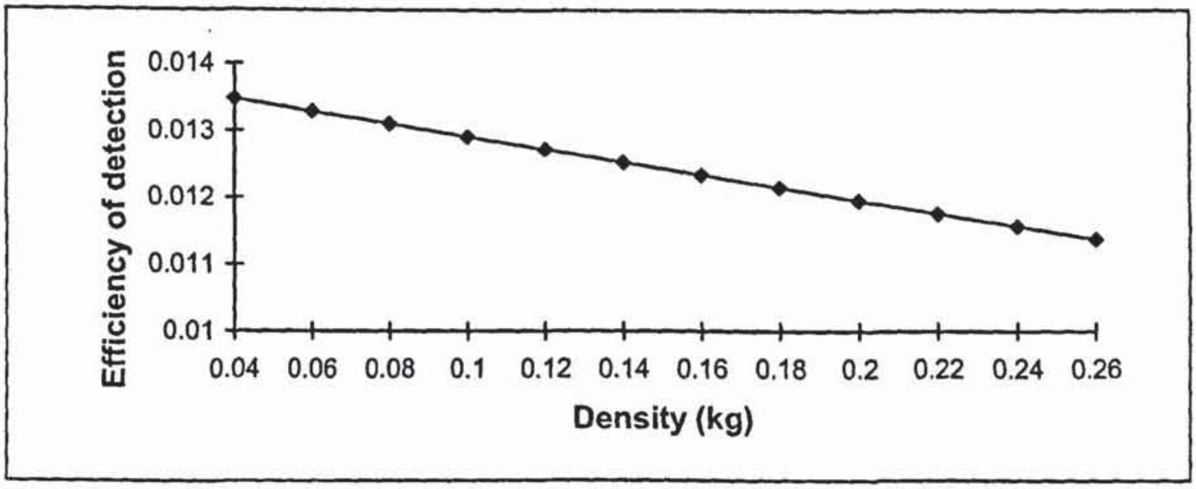


Figure.4.2 Plot of changes in the efficiency of ^{137}Cs detection with density (based on interpolation – not original data).

Table 4.8 Details of IAEA standards used to confirm calibration of the principle detector. Analytical Quality Control Services. International Atomic Energy. Vienna, Austria.

Radionuclide	Recommended Values (Bq kg^{-1}) dry weight	Confidence Interval (Bq kg^{-1})	Number of Analysis	Range of results obtained on Detector
IAEA 375 – Soil				
^{134}Cs	463	454 – 472	87	456 – 464
^{137}Cs	5280	5200 – 5360	91	5265 – 5312
^{40}K	424	417 – 432	84	419 – 424
IAEA 373 – Grass				
^{134}Cs	1167	1143 – 1191	80	1155 – 1182
^{137}Cs	12350	12130 – 12570	84	12228 – 12375
^{40}K	432	421 – 443	76	422 – 438
^{90}Sr	1312	1266 – 1358	37	

Reference Date: 31st December 1991

4.5 Statistical Analysis

Minitab 12 software (Minitab Inc, 1998) was used to statistically test all the data collected within this study at each of the four sites. Statistical analysis used a General Linear Model (GLM) which allows a series of direct comparisons to be performed on the data set without increasing the probability of obtaining an erroneous result by conducting multiple comparisons of the data through several tests (Dytham, 1999). The multiple comparisons option within the GLM permits an examination of which sample means are different with two or more datasets and to estimate the extent of the differences by displaying a probability that the datasets were from the same population.

The GLM allows uneven datasets to be compared and allows the variation in the data to be attributed to several factors in the data (Dytham, 1999). Thus several variables in the data can be tested. The GLM used within this study allowed three types of comparisons to be made between the data sets: 1) effects of treatments and time over the whole study period; 2) between treatment comparisons over the whole study period, and 3) between treatment comparisons on a single sampling occasion. To retain the validity of the data only one test was undertaken on each data set. As the principle area of investigation was related to the effect of the potassium treatment at each site compared to the control plots the test was undertaken to establish the differences within each site. It was theoretically possible to expand the GLM to include all the data from each of the sites, however, due to the high variability both within and between sites it is likely that such a test would have only found significant differences between sites and none would have been found between the treatments or over time. Thus to retain the power of the statistical testing of variables between sites was not undertaken unless the data was not to be used for further testing in the thesis.

The three variables included in this GLM model were treatment, time and plot. However, as plots were always associated with specific treatments, for the model each plot had to be tested with a treatment (Plot [Treatment]). The GLM model was:

Treatment + Plot [Treatment] + Time + Treatment*Time

Where Treatment was control, 100 or 200 kg K ha^{-1}, Plot was each replicate plot and Time was each monthly sample / analysis. Treatment*Time indicates that the model tested if there was a significant interaction between treatment and time.

A GLM model was also used to test if the mineral content of the soil increased with soil depth using the model:

Depth + Mineral content

Regression analysis was also undertaken with Minitab 12 software to investigate and model the relationship between K in the soil and in the plant. A fitted line plot analysis was used which allowed the generation of an equation of a line together with a correlation coefficient.

The use of standard methodologies and standard reference materials does allow much of the data to be directly compared to that of other studies. However, analysis of soil samples principally that of NH_4Ac and EDTA extraction may allow user operator error to effect the data. Nevertheless, the methodologies chosen were recommended methods and should allow the data to be compared with that of other studies.

If greater resources, both time and financial, had been available during this study further analysis techniques may have been used which would have permitted the effect on other ions notably that of Co to have occurred.

Chapter 5

Spatial and temporal variation in site characteristics

5.1 Introduction

To statically test many of the hypotheses listed in section 1.1 required control plots where no potassium treatment had been applied. These control sites allowed the natural variability in nutrient availability to be quantified which is caused by season, plant growth, grazing patterns and weathering. Chapter 5 attempts to characterise the four experimental sites by both the physical composition and fluctuations in the transfer of nutrients between soil and plant.

The first hypothesis within this thesis was that 'the countermeasure significantly reduces the transfer of ^{137}Cs from soil to plant in a range of organic upland soils'. To allow this hypothesis to be tested it must be statistically proven that plots treated with K have significantly lower transfer of ^{137}Cs from soil to plant than the control plots. The hypothesis also requires that the treatment be proven over a range of organic upland soils. Chapter 5 will aim to characterise the differences between the sites to determine if site selection was a success.

Hypothesis 2 in this thesis states the 'the reduction of ^{137}Cs concentration in the biomass as a result of potassium concentration is not affected by the depth of the organic horizon. As such within this chapter it will be demonstrated whether the four experimental sites do have differing organic horizons and as such stipulate whether this hypothesis can be tested.

Chapter 5 aims to identify the physical properties of the four experimental sites and any trends in the variables measured that are not caused by potassium treatments such that in subsequent chapters any differing effect between the treatments can be attributed to the K application.

On each sampling occasion only a single sample of soil, vegetation or water was taken from each of the plots. Thus it is impossible to identify if any significant differences occurred between the control plots.

5.2 Site Characterisation

5.2.1 Physical Properties of the Soils

The experimental sites were chosen to represent a diverse range of upland soil types and vegetation communities. The bulk density, mineral and clay content of the soil within each of the experimental sites were determined as it was expected that these variables would affect the transfer of ^{137}Cs and the response to the potash application. Natural fluctuations in the soil pH and the total above-ground standing biomass produced were also monitored over the study period.

Differences in the proportion of mineral matter with soil depth are shown in Figure 5.1. Five samples of soil were analysed at each depth interval. Statistical examination of this data using the General Linear Model showed that the mineral content of the soil significantly increased with depth at three of the four experimental sites ($p< 0.0001$), Thornholme East being the exception.

The composition of the soil is shown in Figures 5.3 to 5.5, which show the proportion of clay (<2 µm, Brady and Weil, 1999) in the soil. Soils at all four experimental sites had a similar number of particles of any given size. The surface area of different sized particles were also similar, but a proportion of larger particles at Corney Fell North and Thornholme West compared to Thornholme East and Corney Fell South. Figure 5.5 shows that particle volumes are more variable between sites. Thornholme East and Corney Fell South have particle distributions which are similar and are dominated by small volume particles of <100 µm size. At Corney Fell South particles of 100 µm occupy the largest volume, whilst at Thornholme West particles of 300 µm dominate the volume of the soil.

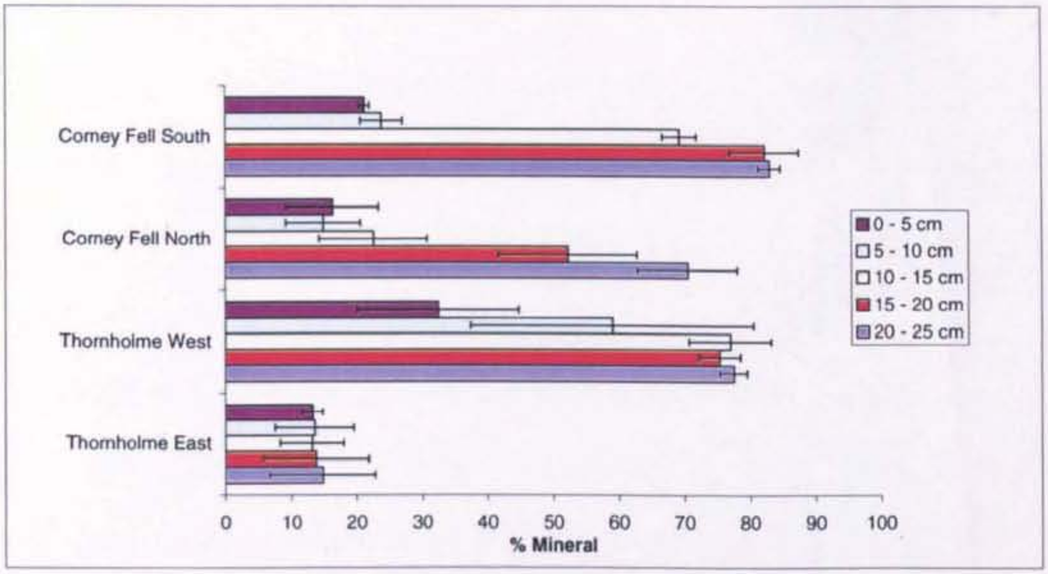


Figure. 5.1 The proportion of mineral matter at different soil depth.
(mean and one standard deviation)

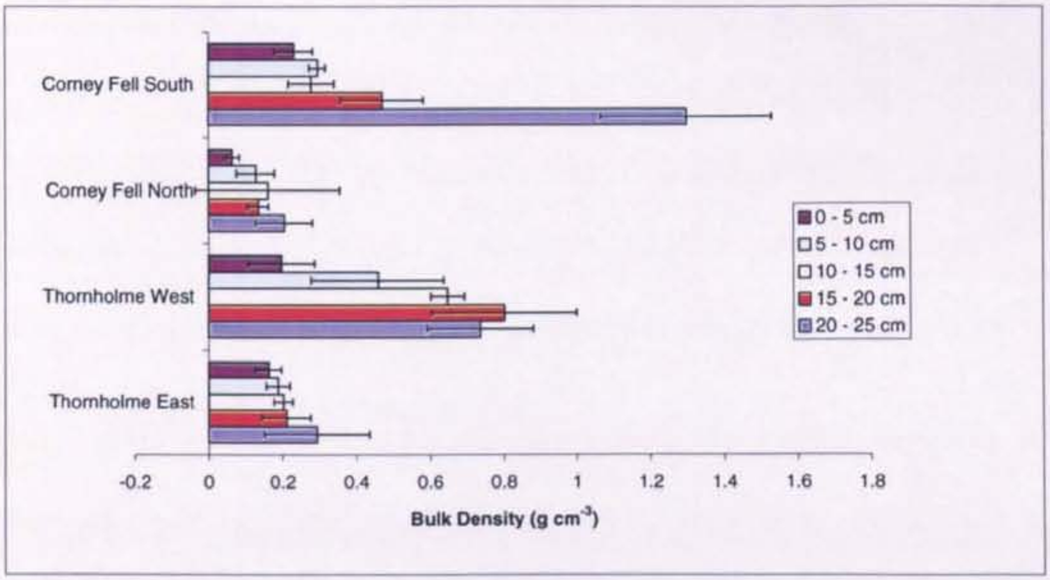


Figure 5.2 Bulk density at different soil depths.
(mean and one standard deviation)

5.2.2 Precipitation

The rainfall gauges installed at Thornholme and Corney Fell were periodically disrupted which led to missing data. On Corney Fell they had been disturbed by grazing animals and by people on almost every sampling occasion so that no chemical analysis of the precipitation was possible. To overcome this difficulty meteorological data was obtained from B.N.F.L. and the Meteorological Office. The two meteorological stations were located at B.N.F.L. Sellafield, and at Grizedale (National Grid Reference 337941, 22 km east of Corney Fell) in Cumbria. The meteorological site at Sellafield was located 6 km south-west of the two Thornholme sites and approximately 17 km north of the Corney Fell sites. Precipitation data from Sellafield was correlated against the available data at Thornholme and an R^2 value of 0.991 was obtained. Data from the Sellafield meteorological station was therefore used to approximate precipitation at the two Thornholme experimental sites when no record was available. As the Sellafield station was also the closer of the two meteorological stations to the Corney Fell experimental sites and in a similar coastal position, this data set was also used to characterise precipitation on Corney Fell.

Figure 5.6 shows the total input of potassium and magnesium via precipitation to the soil surface over each month.

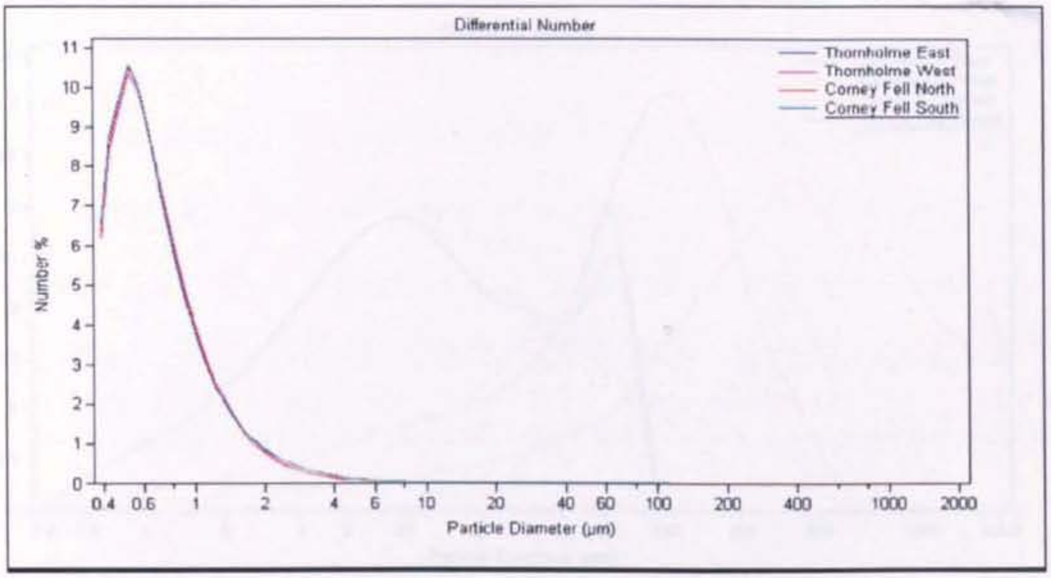


Figure 5.3 Number of different sized particles contained within the mineral fraction of each soil (as % of total).

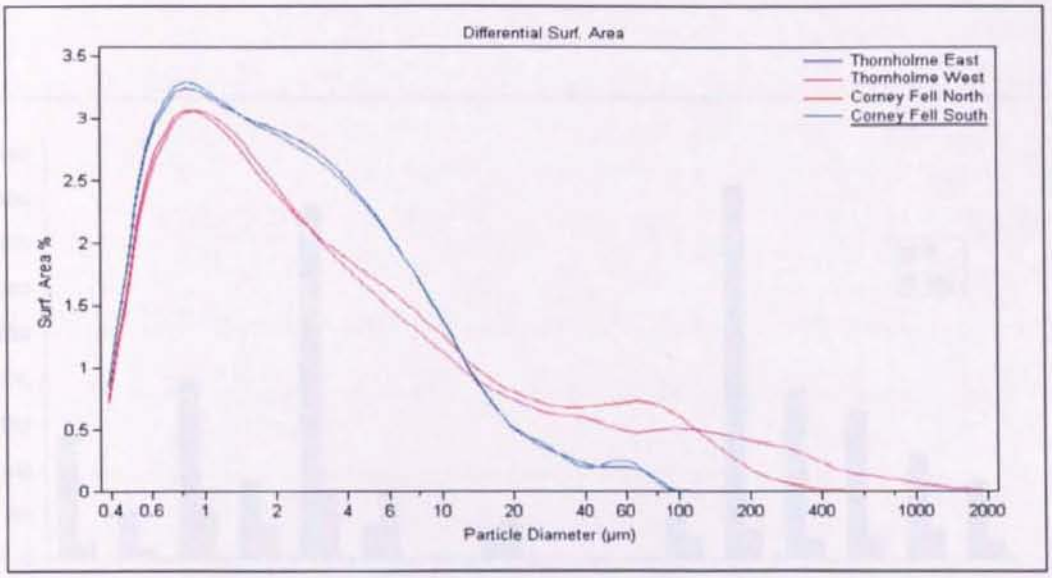


Figure 5.4 Surface area of different sized particles contained within the mineral fraction of each soil (as % of total).

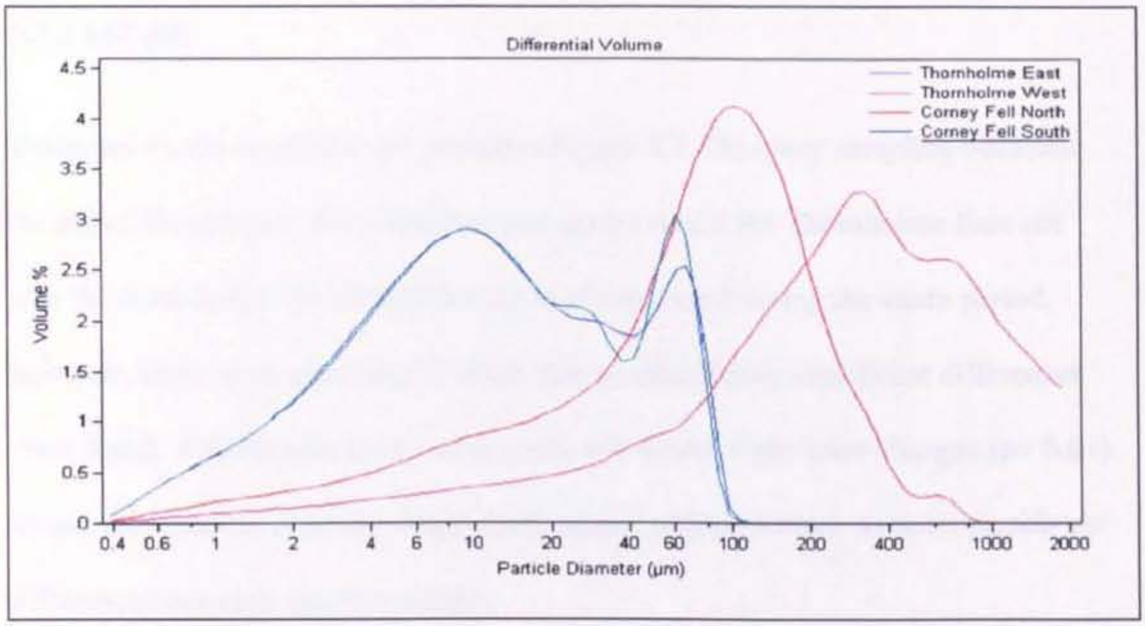


Figure 5.5 Volume of different sized particles contained within the mineral fraction of the soil (as % of total).

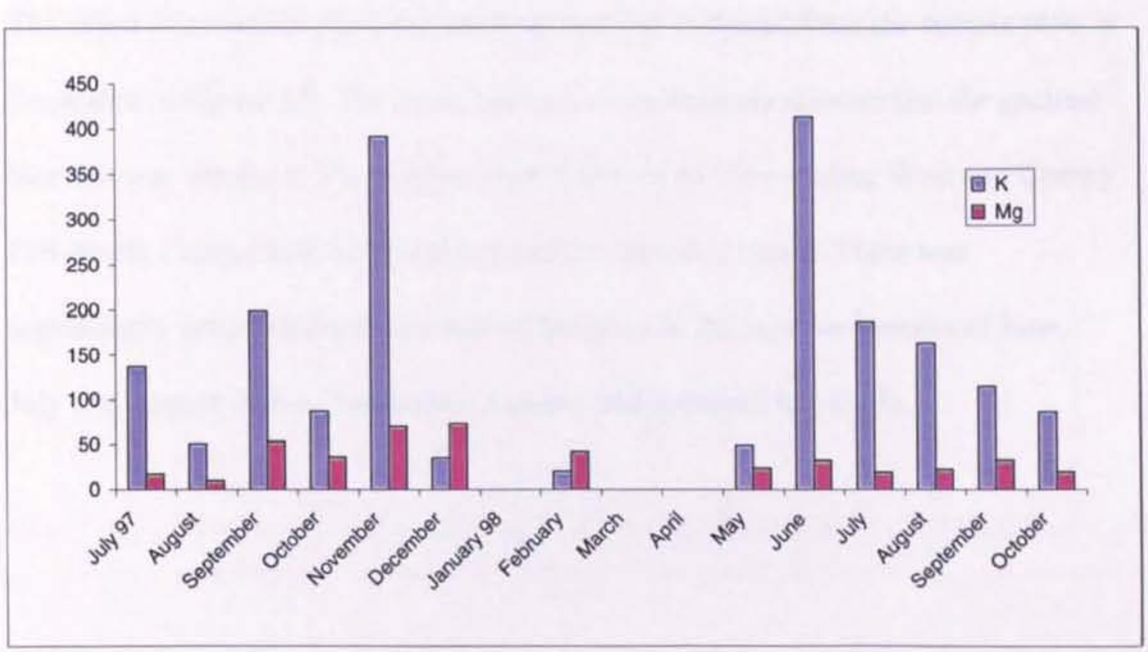


Figure 5.6 Total input of K and Mg through precipitation (mg m^{-2})

5.2.3 Soil pH

Temporal trends in soil pH are plotted in Figure 5.7. On every sampling occasion the pH at Thornholme West was the least acidic whilst the Thornholme East site was the most acidic. Small fluctuations in pH occurred during the study period, however, these were generally so small that no statistically significant differences were found. Thornholme East was the only site where significant changes ($p< 0.01$) in soil pH occurred over the whole study period, although there were no significant differences between any two months.

5.2.4 Standing biomass production

The effect of season on the total standing biomass collected from the sample plots is illustrated in Figure 5.8. The mean biomass measurements showed that the greatest biomass was always at Thornholme East followed by Thornholme West and Corney Fell North, Corney Fell South always had the lowest biomass. There was significantly greater biomass present on the plots in the summer months of June, July and August than in November, January and February ($p< 0.05$).

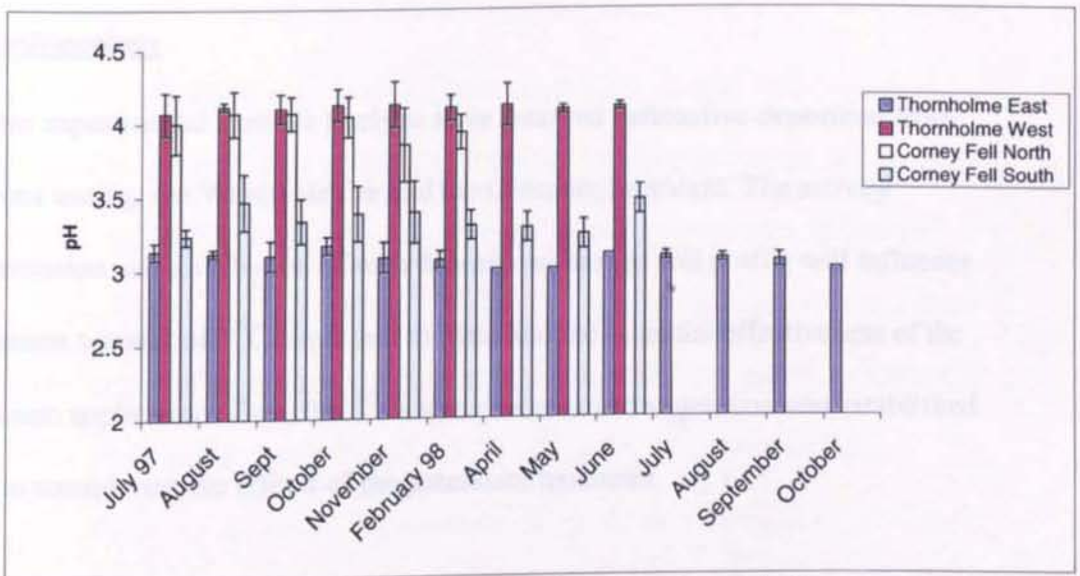


Figure 5.7 Soil pH at the four experimental sites.
(mean and one standard deviation).

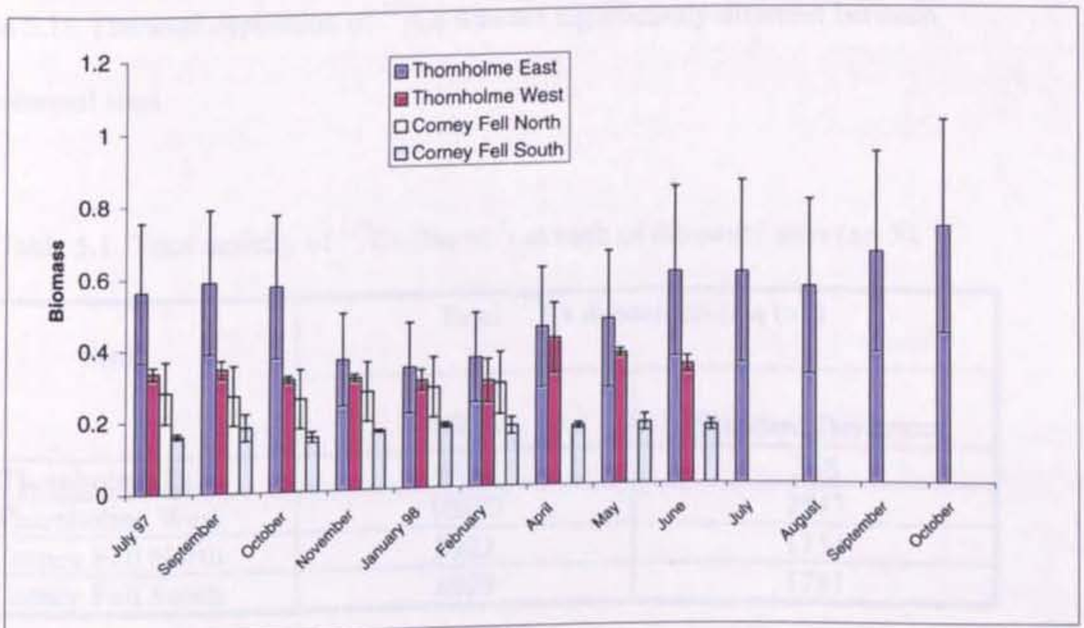


Figure 5.8 Total above ground biomass (kg m^{-2})
(mean and one standard deviation)

5.3 Radioecology

All four experimental sites are likely to have received radioactive deposition from weapons testing, the Windscale fire and the Chernobyl accident. The activity concentration and distribution of such deposits within the soil profile will influence the current transfer of ^{137}Cs from soil to plant and the potential effectiveness of the potassium application. Thus, the ^{137}Cs status in soils and vegetation was established prior to considering the effects of the potassium treatment.

5.3.1 Cs-137 Deposition

The total deposition of ^{137}Cs was calculated at five locations within each experimental site to estimate the variability in deposition within and between site (Table 5.1). The total deposition of ^{137}Cs was not significantly different between experimental sites.

Table 5.1. Total activity of ^{137}Cs (Bq m^{-2}) at each of the study sites (n= 5).

Site	Total ^{137}Cs deposition (Bq m^{-2})	
	Mean	Standard Deviation
Thornholme East	9457	368
Thornholme West	10677	2847
Corney Fell North	8922	1154
Corney Fell South	8929	1781

5.3.2 Depth distribution of ^{137}Cs activity concentration

Characterisation of the activity concentration of radiocaesium at different soil depths was undertaken following the methodology outlined in Chapter 3.2.5. Figure 5.9 indicates that the greatest ^{137}Cs activity concentration was always within the upper 10 cm of the soil. To allow the ^{137}Cs profiles between the experimental sites to be directly compared, the activity concentration was also expressed in relation to the soil volume, by calculating Bq cm^{-3} of soil. Figure 5.10 shows that this generally reduces the apparent differences in ^{137}Cs activity concentration with depth intervals compared to Figure 5.9.

5.3.3 Cs-137 activity in the vegetation

5.3.3.1 Activity concentrations

Figure 4.11 shows that the activity concentration of ^{137}Cs in the above-ground biomass significantly changed over the study period at three of the experimental sites; Thornholme East ($p< 0.0001$), Thornholme West ($p< 0.0001$) and Corney Fell South ($p< 0.001$). Cs-137 activity concentrations were significantly greater in May, June, July, September and October at the Thornholme East site than on any other sampling date. At Thornholme West the activity concentration was greater in January compared to any other sampling dates. There were no significant differences between sample dates for the Corney Fell sites. Activity concentrations were generally lower at Thornholme West compared to the other sites.

5.3.3.2 Total ^{137}Cs transferred

The effect of time on the total amount of ^{137}Cs contained within the above-ground standing biomass is shown in Figure 5.12. Significant reductions in the content of

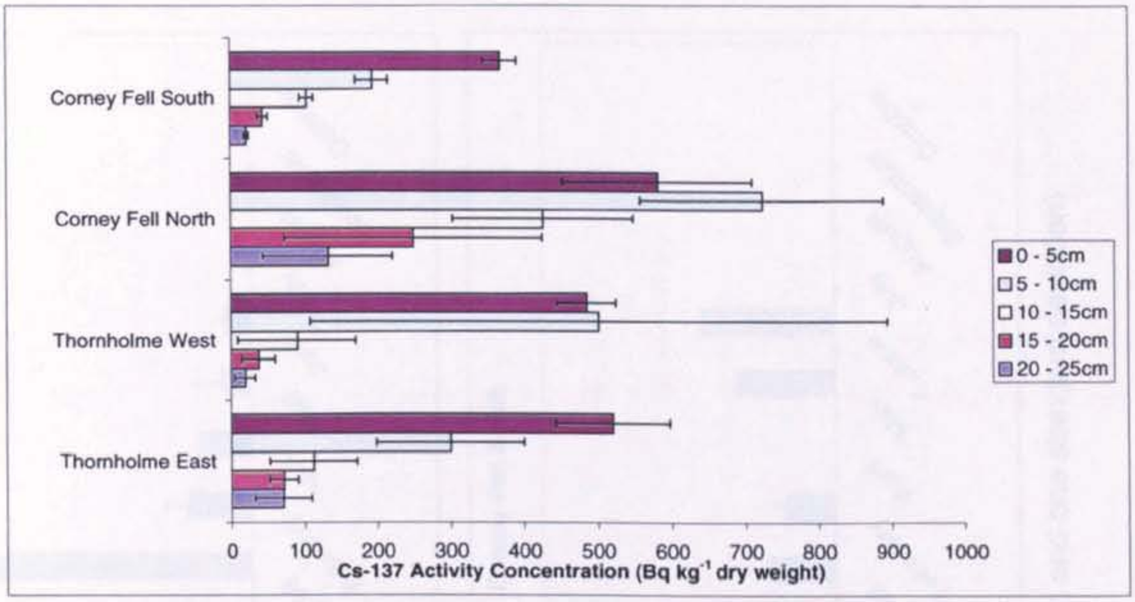


Figure 5.9 Profile of ^{137}Cs activity concentration with depth at the four experimental sites (mean and one standard deviation).

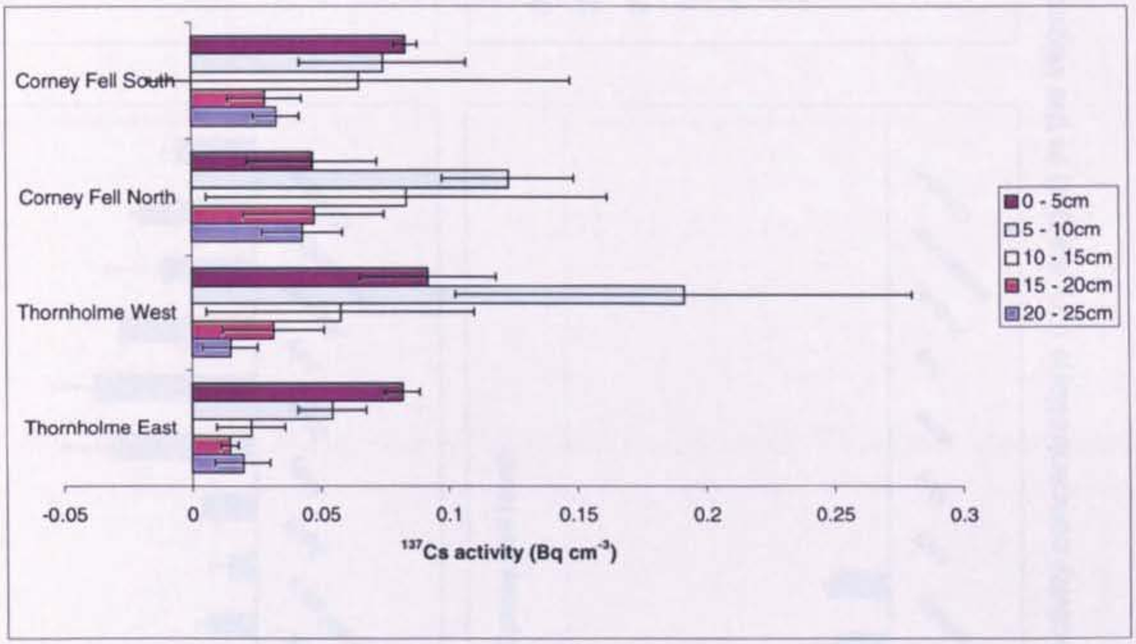


Figure 5.10 Profile of ^{137}Cs activity with depth corrected for changes in bulk density (mean and one standard deviation).

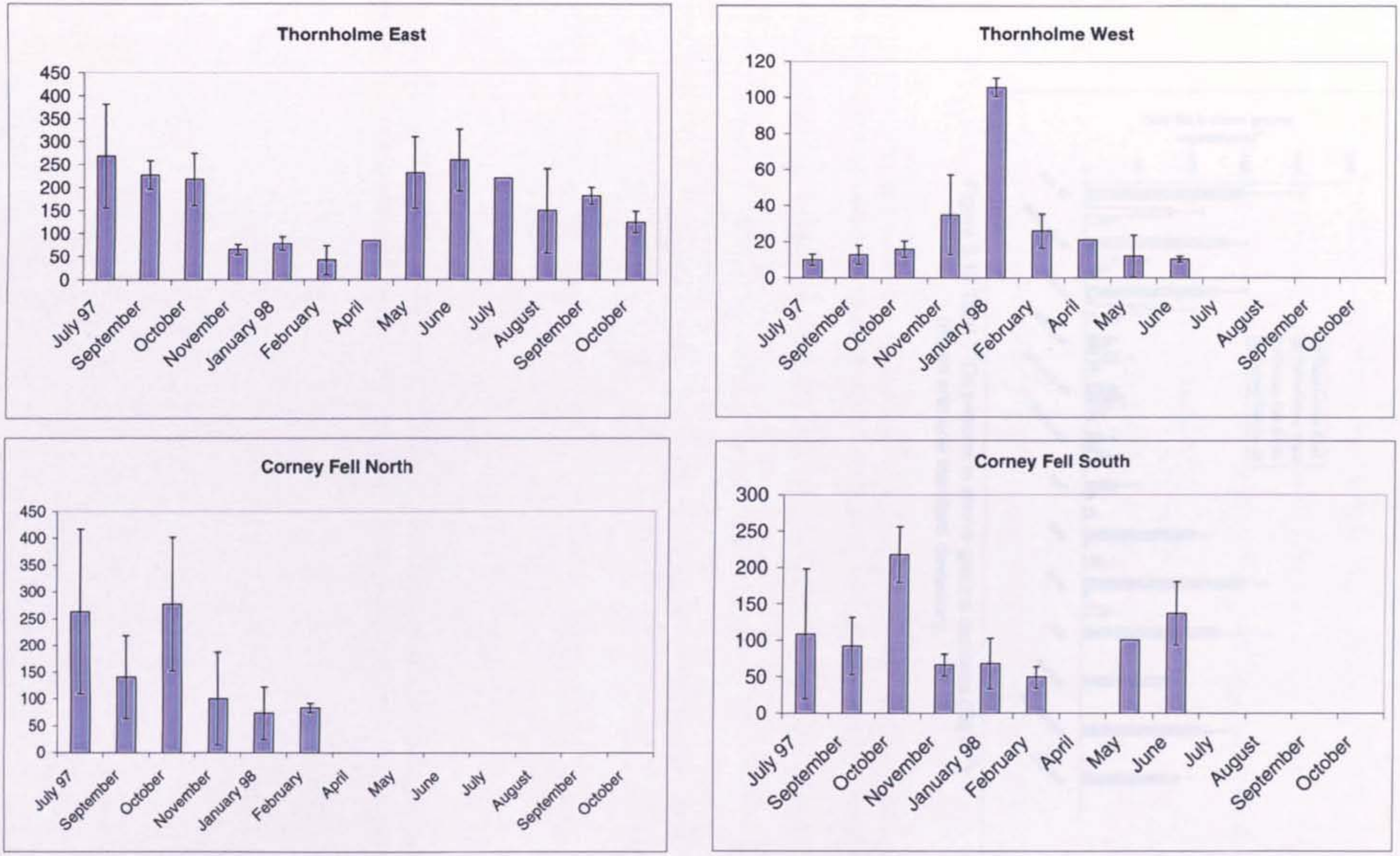


Figure 5.11. Cs-137 activity concentrations (dry weight) in the vegetation over time (mean and one standard deviation).

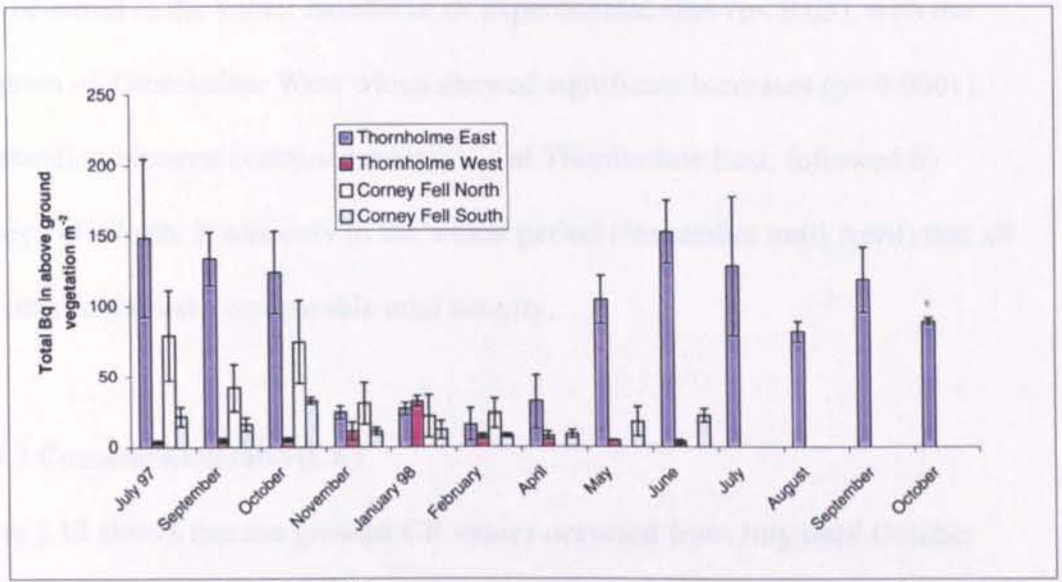


Figure 5.12 Total ^{137}Cs present in above-ground biomass (Bq m^{-2}) (mean and one standard deviation).

^{137}Cs occurred in the winter months at all experimental sites ($p < 0.05$), with the exception of Thornholme West which showed significant increases ($p < 0.0001$). The standing biomass contained most ^{137}Cs at Thornholme East, followed by Corney Fell North. It was only in the winter period (November until April) that all four sites contained a comparable total activity.

5.3.3.3 Concentration ratio (CR)

Figure 5.13 shows that the greatest CR values occurred from July until October 1997 at both Corney Fell sites and the Thornholme East site, however, at Thornholme West the CR was at its highest in November 1997 and at its lowest in May and June 1998. The ratios changed considerably over the sampling period, but due to the high variability within sites, significant differences only occurred at the Thornholme East and Corney Fell south experimental sites ($p < 0.001$).

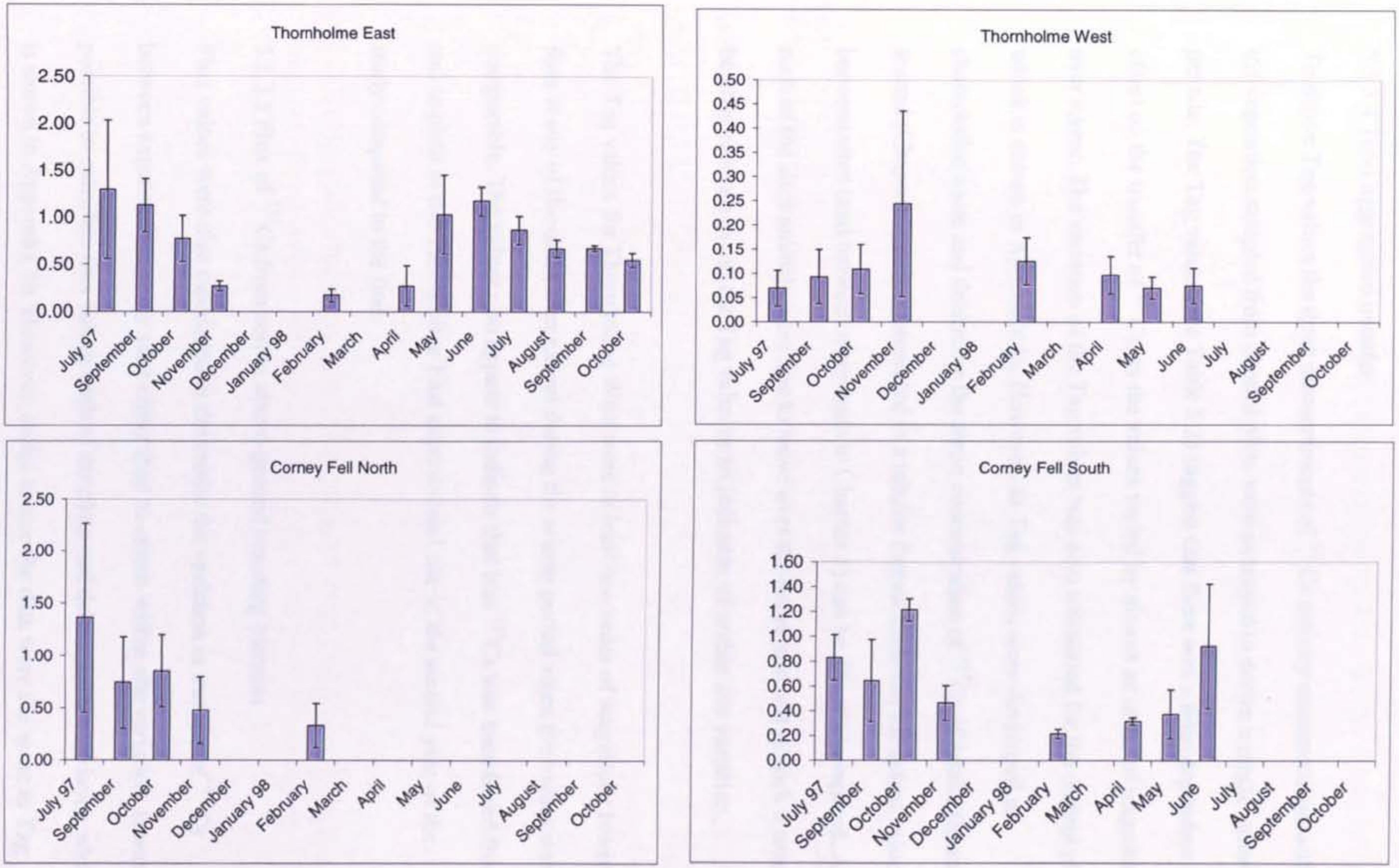


Figure 5.13 Soil:plant concentration ratio of ^{137}Cs (mean and one standard deviation).

5.3.3.4 Total aggregated transfer

To derive Tag values the three measurements of ^{137}Cs activity concentration within the vegetation sampled from control plots were averaged to derive a single value per site. The Tag values (see Table 5.2) suggest that there was a time-dependent effect on the transfer of ^{137}Cs, as the values varied by almost an order of magnitude over a year. The variation of the Tag values was also calculated for the control plots which is shown in Appendix 1a. However, as Tag values were developed to characterise a site and determine the mean concentration of ^{137}Cs of intake for an animal (Chapter 2) data is presented in a tabular format such that the actual values between sites (and between treatments in Chapter 6) can be directly compared. At each of the sites animals were free to move over the entire site and as such it would be inappropriate to use the Tag value as an indicator of within site variation.

The Tag values for Thornholme West were at least one order of magnitude lower than at any of the other sites except during the winter period when the values were comparable. The values also appear to indicate that less ^{137}Cs was transferred from soil to plant at the Thornholme East experimental site in the second year of the study compared to the first.

5.3.3.5 Flux of ^{137}Cs from soil to above-ground standing biomass

Flux values were also calculated to determine the variation in transfer of ^{137}Cs between experimental study sites rather than to assess within site variation. It was possible to calculate flux values each of the plots and determine the variation which is shown in Appendix 1b. However, as the source the data were the same as Tag values the effect of calculating these errors only reflected the between plot variability of biomass production shown in Figure 5.8. Like the Tag values the flux data is calculated in this study to drawn comparisons between treatments and sites rather than with plots thus to allow direct comparison of the values the flux data for ^{137}Cs is displayed in Table 5.3.

Table 5.3 shows that the percentage of ^{137}Cs transferred from soil to plant ranges from a maximum of 1.6 % at Thornholme East site to a minimum of 0.03 % at the Thornholme West site. There are marked temporal changes in the flux of ^{137}Cs with higher transfer in the summer months within the Thornholme East and both Corney Fell sites. However, the Thornholme West site shows a greater flux of ^{137}Cs from soil to plant in the winter months. During November, January and February all four experimental sites show a similar flux value of between 0.1 and 0.3 %.

Table 5.2 Tag values for each sampling date and site.

Tag (m^2/kg)	Thornholme East	Thornholme West	Corney Fell North	Corney Fell South
July 97	0.0284	0.0009	0.0295	0.0122
September 97	0.0240	0.0012	0.0157	0.0103
October 97	0.0231	0.0015	0.0310	0.0244
November 97	0.0069	0.0033	0.0112	0.0074
January 98	0.0083	0.0099	0.0082	0.0076
February 98	0.0045	0.0024	0.0092	0.0055
April 98	0.0091	0.0020		0.0061
May 98	0.0247	0.0011		0.0113
June 98	0.0275	0.0010		0.0153
July 98	0.0233			
August 98	0.0159			
September 98	0.0194			
October 98	0.0133			

Table 5.3 Percentage flux of ^{137}Cs from soil to above-ground biomass

% Flux from soil to plant	Thornholme East	Thornholme West	Corney Fell North	Corney Fell South
July 97	1.570	0.031	0.886	0.236
September	1.413	0.041	0.469	0.176
October	1.311	0.046	0.834	0.362
November	0.251	0.101	0.342	0.120
January 98	0.277	0.297	0.240	0.133
February	0.163	0.069	0.264	0.090
April	0.336	0.074		0.100
May	1.106	0.041		0.200
June	1.615	0.031		0.247
July	1.359			
August	0.864			
September	1.251			
October	0.942			

5.4 Nutrient Cycles – Potassium

5.4.1 Additions and losses

Potassium ions may be added to the soil system through rainfall or weathering of the mineral fraction of the soil (Read and Watson, 1982). However, due to the slow and almost constant rate of release of the potassium ions from the mineral fraction the only source of K that could vary over the study period was that from precipitation. Figure 5.6 (page 60) shows that the input of K from aerial deposits was highly variable. It also shows that the greatest input occurred between October and November in 1997 and between May and June in 1998, which is a reflection of the total rainfall.

The zero tension horizontal lysimeters at Thornholme East and West were installed to record the amount of K removed from the soil via vertical migration of soil water. At both sites there were no significant changes between any two months in the total amount of K present in the lysimeter water (See Figure 5.14). From July until October 1998 at the Thornholme East significantly more K was found in the lysimeter water than over the same period in 1997 ($p< 0.05$). There were no significant differences between months in 1998.

The total input of K to the Thornholme sites from June until October in 1997 represented 63 % of the total K present in the lysimeter water (Thornholme East) and 65 % Thornholme West in 1997 whilst in the same period in 1998 the rainfall contained 311 % more K than was being lost from the lysimeters.

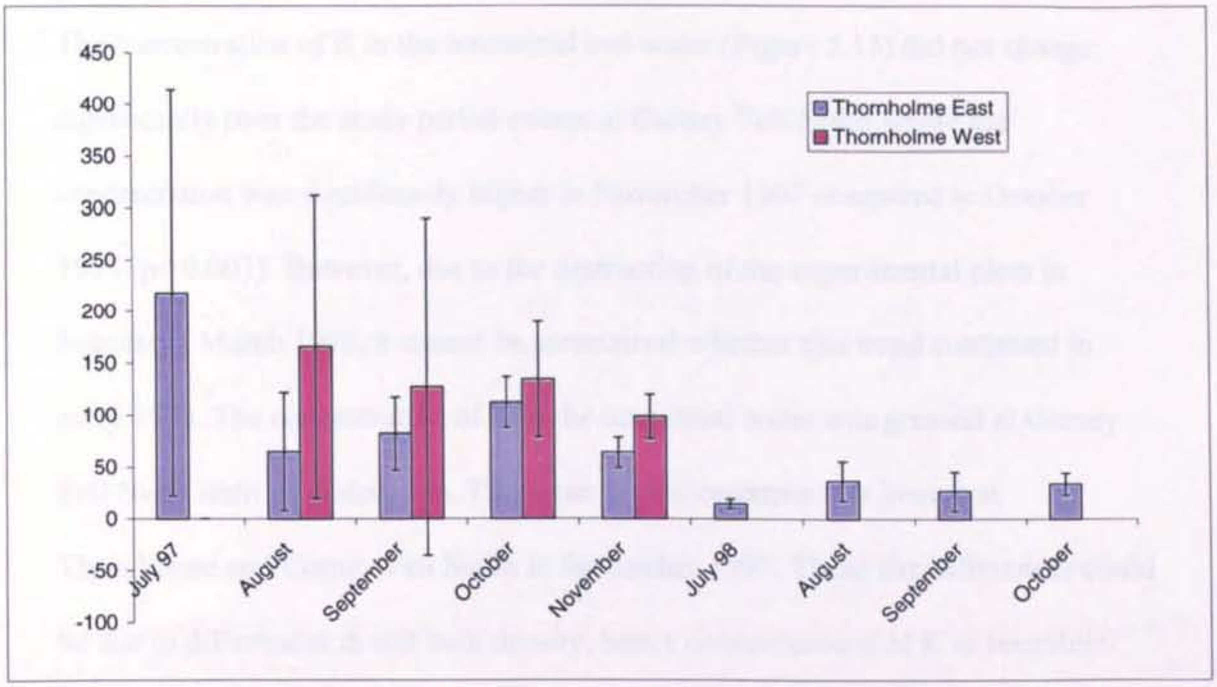


Figure 5.14 Total K present in lysimeter (mg m^{-2}) mean and one standard deviation

5.4.2 Interstitial soil water

The concentration of K in the interstitial soil water (Figure 5.15) did not change significantly over the study period except at Corney Fell North where the concentration was significantly higher in November 1997 compared to October 1997 ($p < 0.001$). However, due to the destruction of the experimental plots in February / March 1998, it cannot be ascertained whether this trend continued in early 1998. The concentration of K in the interstitial water was greatest at Corney Fell North until its destruction. The mean K concentration was lowest at Thornholme and Corney Fell South in September 1997. These site differences could be due to differences in soil bulk density, hence concentrations of K in interstitial water were also expressed per unit volume of field moist soil (See Figure 5.16). When K in the interstitial soil water is presented per unit volume rather than unit dry soil mass the two experimental sites located on Corney Fell had more potassium in solution than either of the Thornholme sites. During October the Thornholme West experimental site had the lowest concentration of K in the interstitial water (per unit volume). As the values have been calculated with a single bulk density value within each site the trends of changes in K concentration are the same as for dry soil. However, between sites the magnitude of the difference in K concentration is reduced and the similarity between the two Corney Fell sites becomes apparent. Such similarities may also occur between the two Thornholme sites, however, these would be obscured by the high variability within each site.

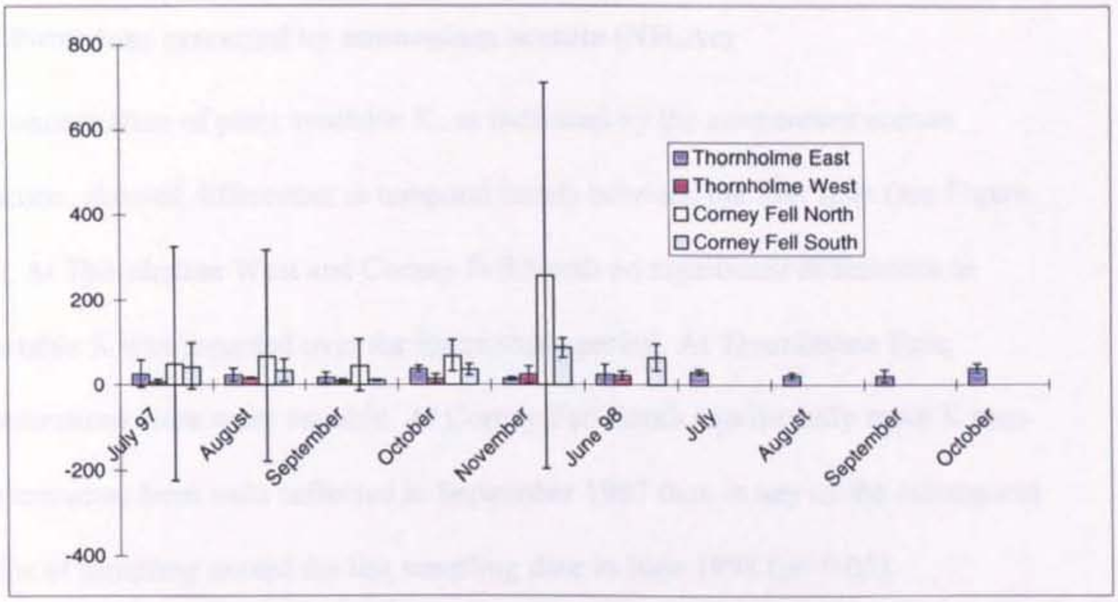


Figure 5.15 Concentration of K in interstitial water (mg kg^{-1} dry soil) (mean and one standard deviation).

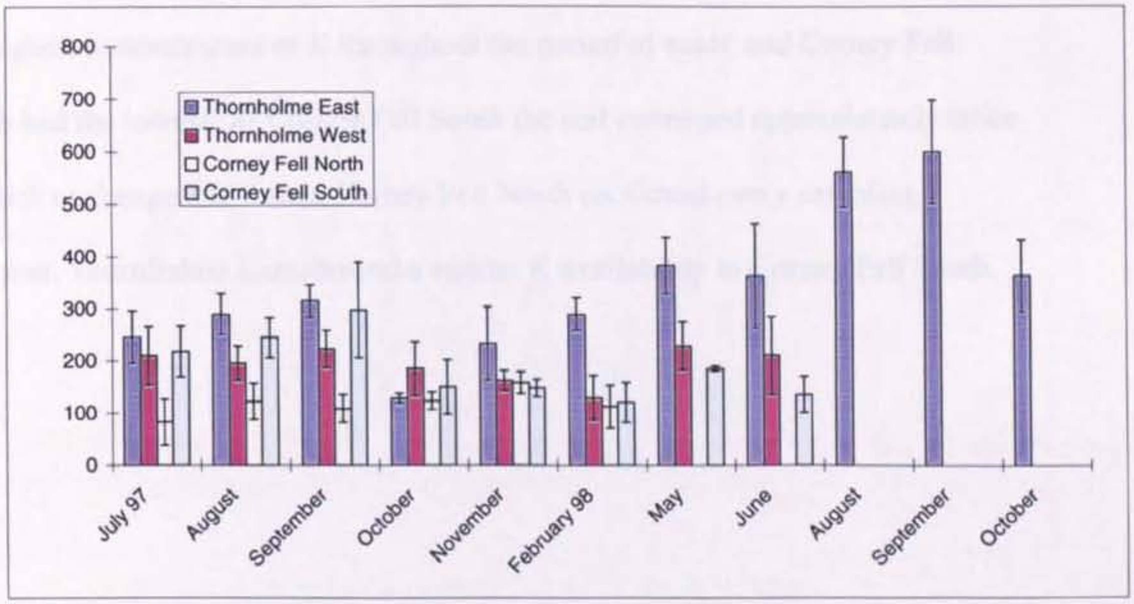


Figure 5.16 Extracted K in soil (NH_4Ac) (mg kg^{-1} dry soil) (mean and one standard deviation)

5.4.3 Potassium extracted by ammonium acetate (NH_4Ac)

The concentration of plant available K, as indicated by the ammonium acetate extraction, showed differences in temporal trends between the four sites (see Figure 5.17). At Thornholme West and Corney Fell North no significant differences in extractable K was recorded over the entire study period. At Thornholme East, concentrations were more variable. At Corney Fell South significantly more K ions were extracted from soils collected in September 1997 than in any of the subsequent months of sampling except the last sampling date in June 1998 ($p< 0.05$).

When the K extracted by ammonium acetate is expressed as a function of unit volume of soil (see Figure 5.18) several differences between sites occurred which had not previously been identified. The experimental site at Thornholme West had the highest concentration of K throughout the period of study and Corney Fell North had the lowest. At Corney Fell South the soil contained approximately twice as much exchangeable K than Corney Fell North on almost every sampling occasion. Thornholme East showed a similar K availability to Corney Fell South.

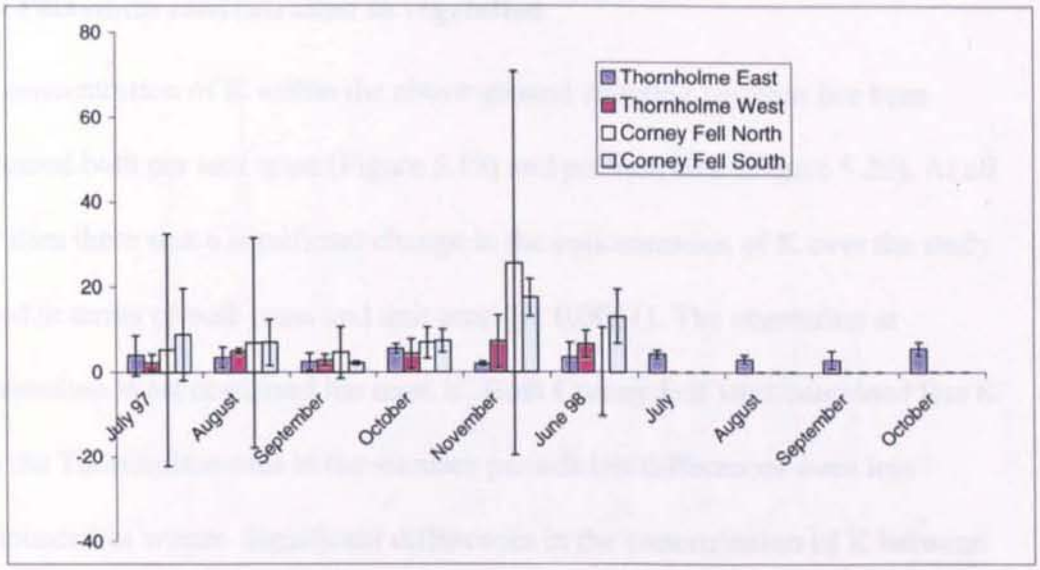


Figure 5.17 K in interstital water (mg l^{-1} field moist soil).
(mean and one standard deviation).

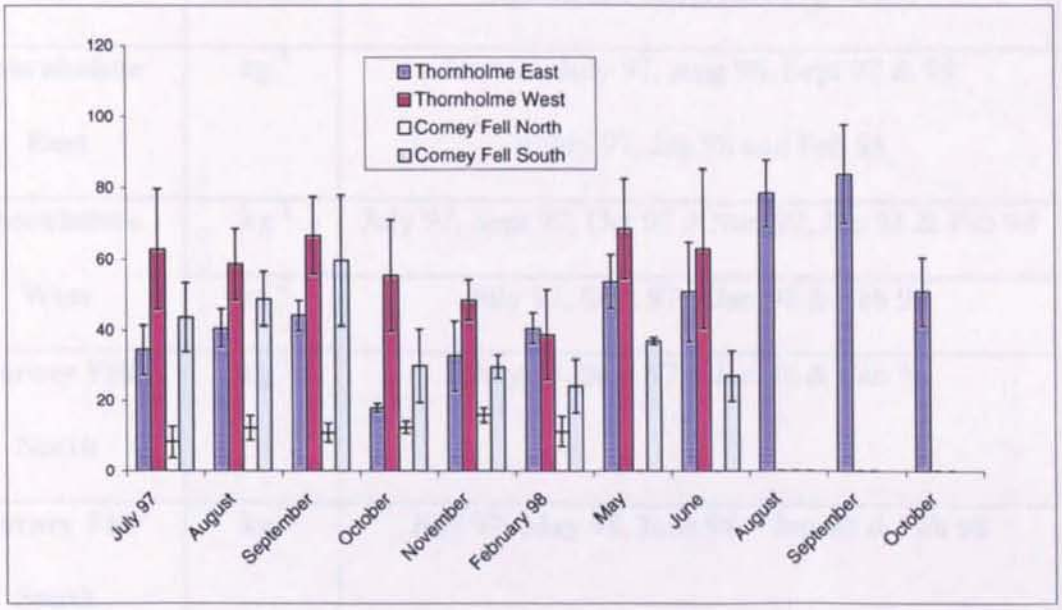


Figure 5.18 Extracted K (mg l^{-1} field moist soil).
(mean and one standard deviation).

5.4.4 Potassium concentration in vegetation

The concentration of K within the above-ground standing biomass has been expressed both per unit mass (Figure 5.19) and per unit area (Figure 5.20). At all four sites there was a significant change in the concentration of K over the study period in terms of both mass and unit area ($p < 0.0001$). The vegetation at Thornholme West contained the most K. Both Corney Fell sites contained less K than the Thornholme sites in the summer periods but differences were less pronounced in winter. Significant differences in the concentration of K between sample months are displayed in Table 5.4.

Table 5.4 Significant differences between K concentration ($p<0.05$)

Site	Variable	Significant differences ($p<0.05$)
Thornholme East	kg^{-1}	June 97, July 97, Aug 98, Sept 97 & 98 > Nov 97, Jan 98 and Feb 98
Thornholme West	kg^{-1}	July 97, Sept 97, Oct 97 > Nov 97, Jan 98 & Feb 98
	m^{-2}	July 97, Sept 97 > Jan 98 & Feb 98
Corney Fell North	kg^{-1}	July 97, Sept 97 > Jan 98 & Feb 98
Corney Fell South	kg^{-1}	July 97, May 98, June 98 > Jan 98 & Feb 98

When the concentration of K was expressed as per unit area there was no significant change over the sampling period at Corney Fell North. A decline in K concentration

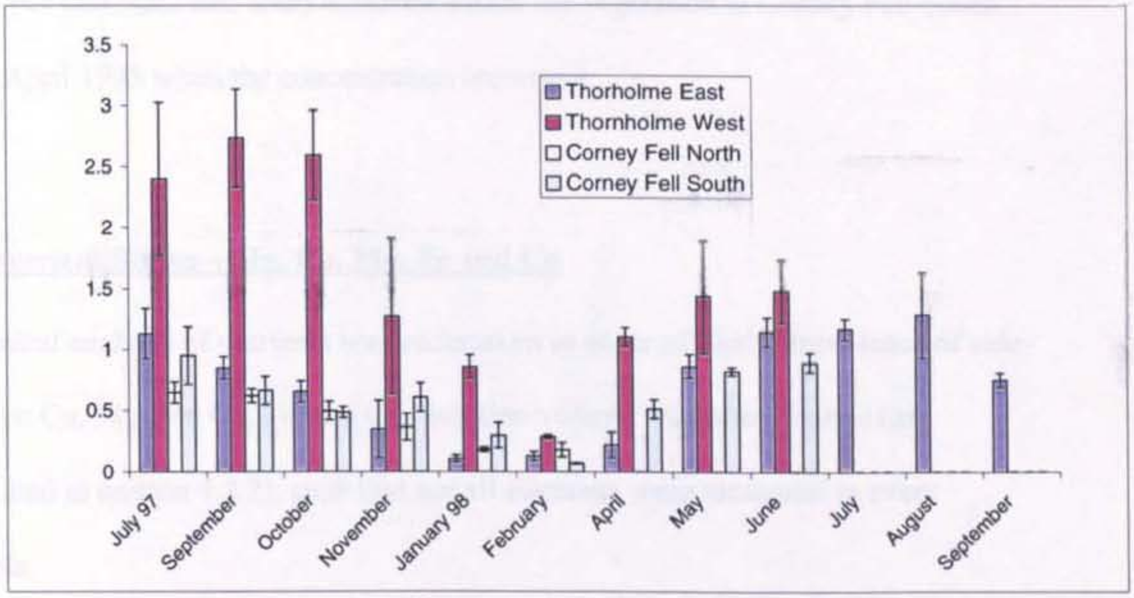


Figure 5.19 Concentration of K in vegetation (%)
(mean and one standard deviation)

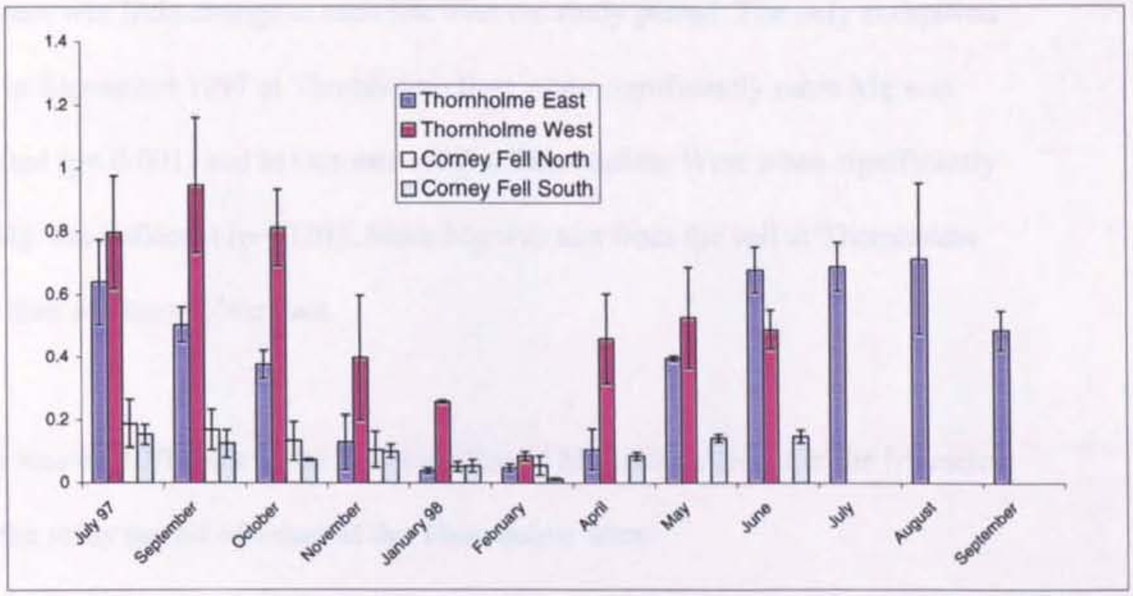


Figure 5.20 K in above-ground biomass per unit area (g m^{-2})
(mean and one standard deviation)

(both per unit mass and area) occurred within the vegetation at Corney Fell South until April 1998 when the concentration increased.

5.5 Nutrient Status – Mg, Cu, Mn, Fe and Co

Chemical analysis of nutrients was undertaken in order of likely importance of side-effects: Cu, Mg, Mn Ca, Fe, and Co. Solution volume was often limited (as indicated in section 4.3.2), such that not all elements were measured in every sample.

5.5.1 Nutrients lost from the soil

The amount of dissolved Mg collected in the lysimeter water (Figure 5.21) shows that there was little change at each site over the study period. The only exceptions were in September 1997 at Thornholme East when significantly more Mg was collected ($p < 0.001$) and in October 1997 at Thornholme West when significantly less Mg was collected ($p < 0.01$). More Mg was lost from the soil at Thornholme West than at Thornholme East.

There was no difference in the concentration of Mn ions collected in the lysimeters over the study period of either of the Thornholme sites.

The dissolved Ca collected in the lysimeters was measured at Thornholme East from July until October 1998. Although not statistically significant, Figure 5.22 shows that the mean concentration of Ca reached a maximum of 55 mg m^{-2} in August before falling to 27 mg m^{-2} in October.

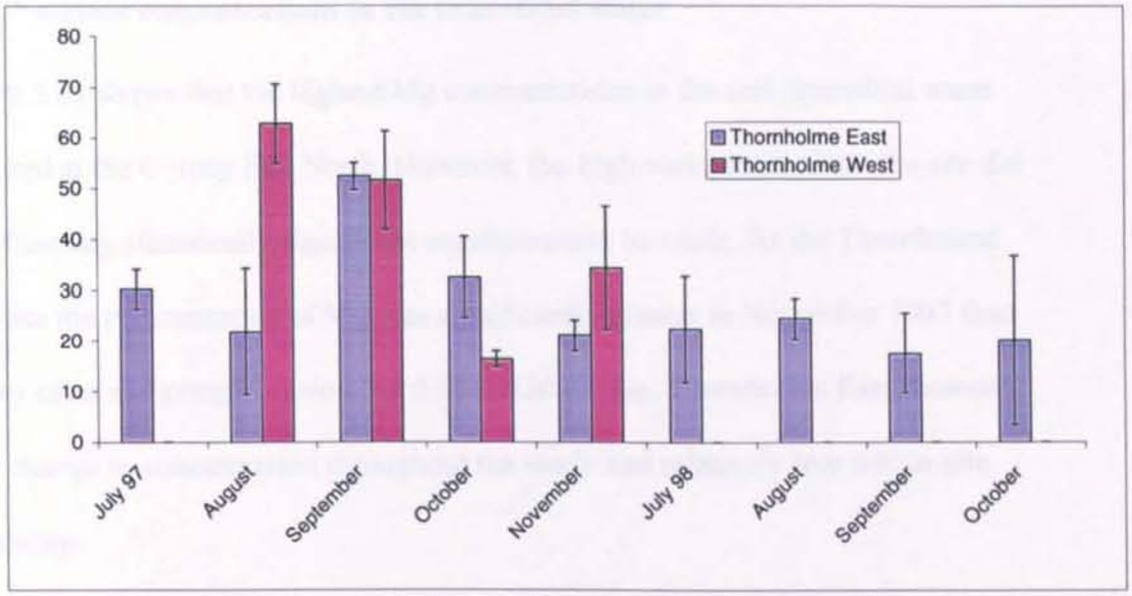


Figure 5.21 Total Mg in lysimeter water (mg m^{-2})
(mean and one standard deviation)

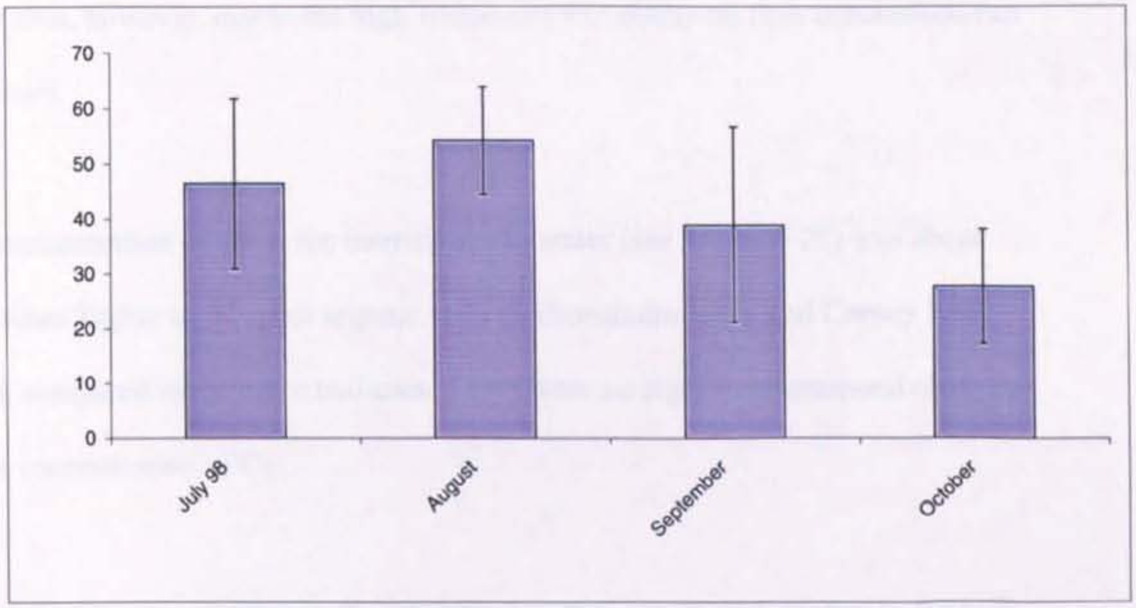


Figure 5.22. Total Ca in lysimeter water at Thornholme East (mg m^{-2})
(mean and one standard deviation).

5.5.2 Nutrient concentrations in the interstitial water

Figure 5.23 shows that the highest Mg concentrations in the soil interstitial water occurred at the Corney Fell North. However, the high variability within the site did not allow any statistically significant conclusions to be made. At the Thornholme East site the concentration of Mg was significantly greater in November 1997 than on any other sampling occasion ($p < 0.001$). Otherwise, Thornholme East showed little change in concentration throughout the study and relatively low within-site variability.

When the Mg concentration in the interstitial water is expressed relative to the soil volume (Figure 5.24) the magnitude of the differences between sites is reduced. Again Corney Fell North showed a mean Mg concentration greater than any of the other sites, however, due to the high within-site variability no firm conclusions can be drawn.

The concentration of Cu in the interstitial soil water (see Figure 5.25) was about four times higher in the most organic soils of Thornholme East and Corney Fell North compared to the other two sites. There were no significant temporal changes in the concentration of Cu.

When the Cu concentration in the interstitial water is expressed relative to the soil volume (Figure 5.26) the magnitude of the differences between sites are reduced.

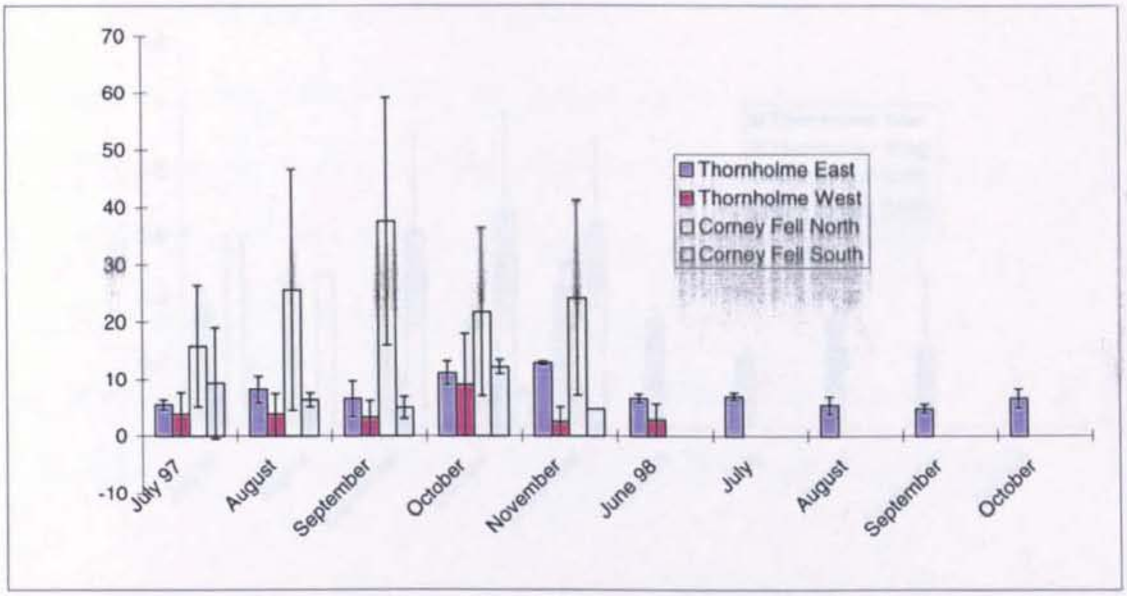


Figure 5.23 Concentration of Mg in interstitial soil water (mg kg^{-1} dry soil) (mean and one standard deviation).

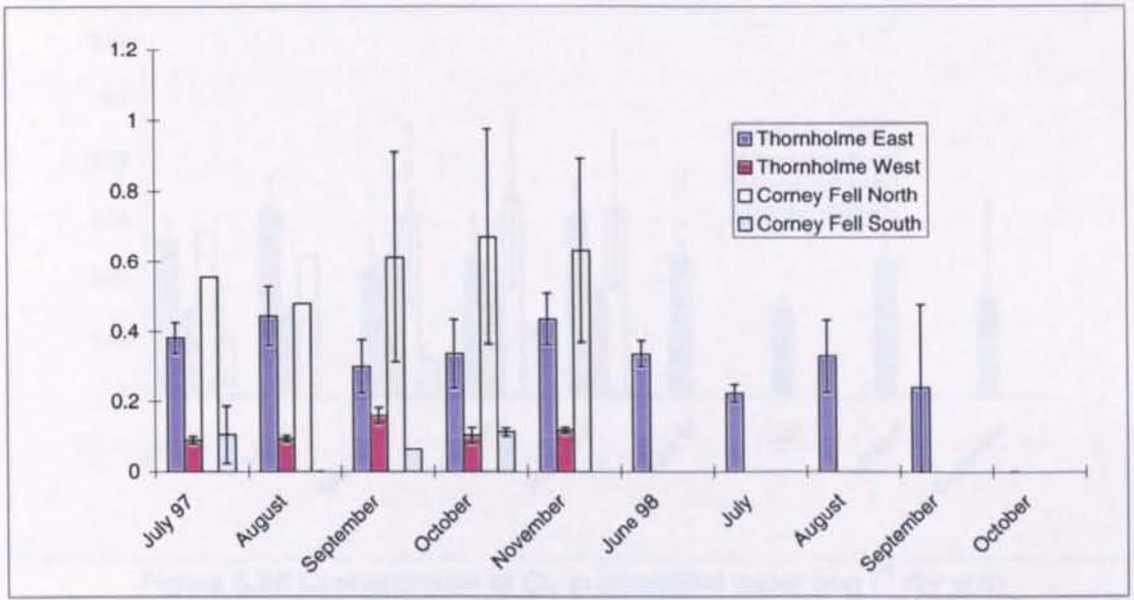


Figure 5.24 Concentration of Mg in interstitial soil water (mg l^{-1} dry soil) (mean and one standard deviation)

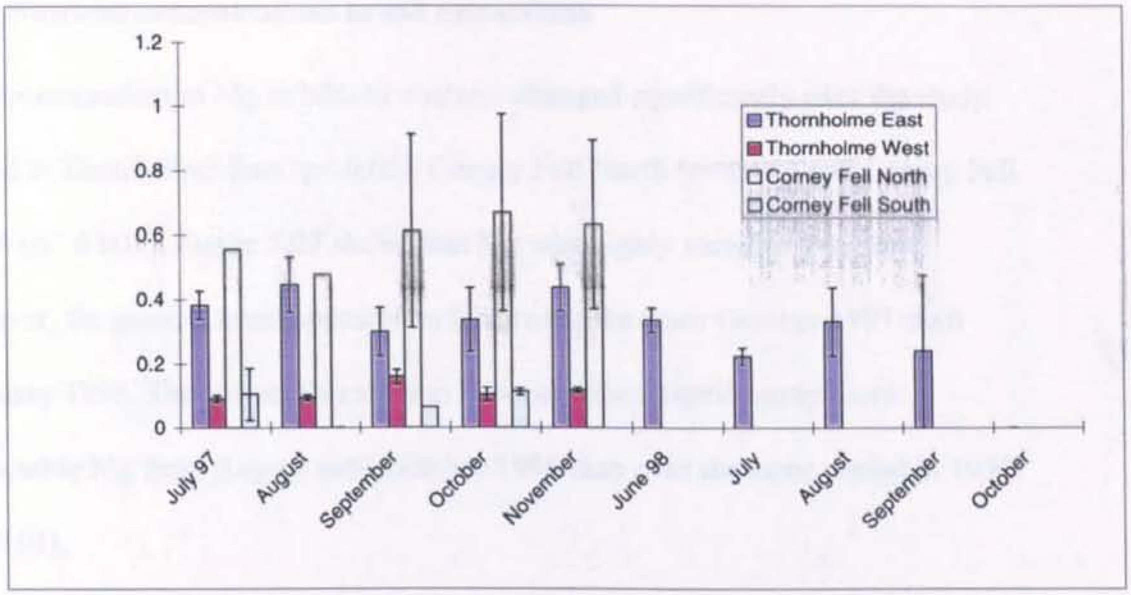


Figure 5.25 Concentration of Cu in interstital water (mg kg^{-1} dry soil) (mean and one standard deviation)

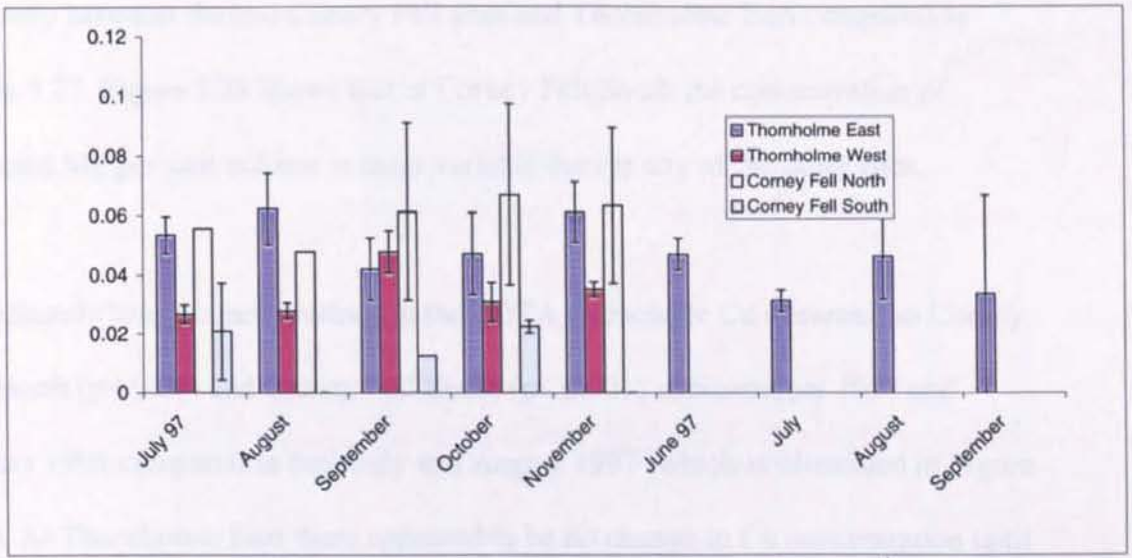


Figure 5.26 Concentration of Cu in interstitial water (mg l^{-1} dry soil) (mean and one standard deviation).

5.5.3 Nutrient concentrations in soil extractions

The concentration of Mg in NH_4Ac extracts changed significantly over the study period at Thornholme East ($p < 0.05$), Corney Fell North ($p < 0.01$) and Corney Fell South ($p < 0.001$). Figure 5.27 shows that Mg was highly variable over time, however, the general trend appeared to be a reduction from October 1997 until February 1998. The soil at Thornholme East contained significantly more extractable Mg from August until October 1998 than over the same period in 1997 ($p < 0.01$).

Temporal trends in extractable Mg per unit soil volume are shown in Figure 5.28. In general Thornholme West had the greatest concentration of Mg. The main effect of expressing the Mg extractability as a function of soil volume was to reduce the similarity between the two Corney Fell sites and Thornholme East compared to Figure 5.27. Figure 5.28 shows that at Corney Fell South the concentration of extracted Mg per unit volume is more variable than at any of the other sites.

Significantly lower concentrations in the EDTA extractable Cu occurred on Corney Fell North ($p < 0.05$) and Corney Fell South ($p < 0.001$) in November 1997 and January 1998 compared to both July and August 1997 (which is illustrated in Figure 5.29). At Thornholme East there appeared to be no change in Cu concentration until September 1998, when the extracted Cu increased significantly ($p < 0.001$). Figure 5.29 shows that the concentration of Cu expressed per unit mass is lowest at Thornholme West.

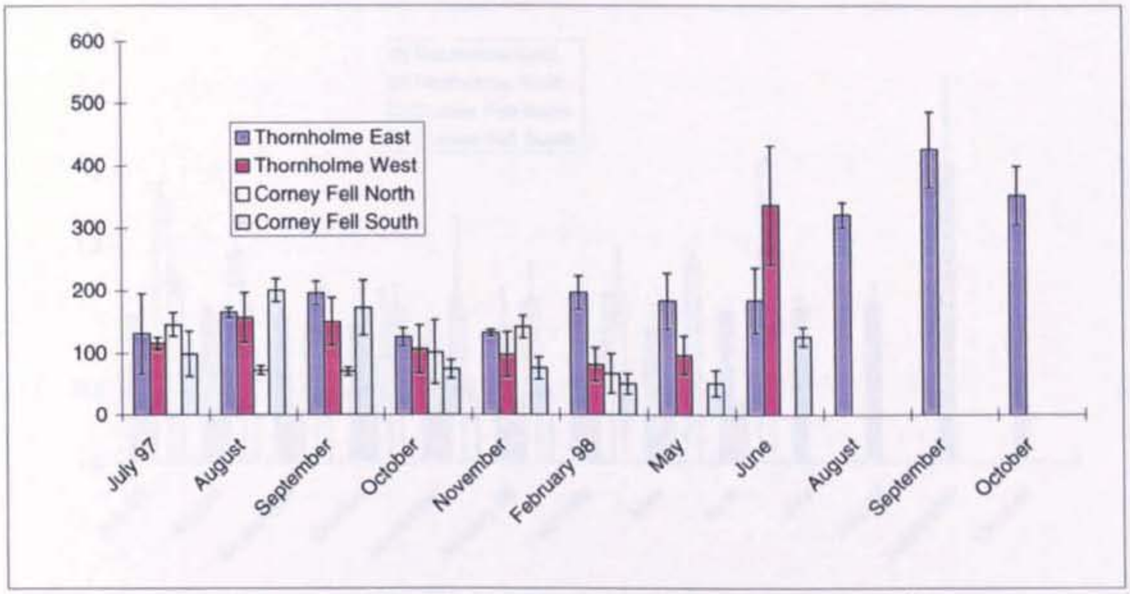


Figure 5.27 Extractable Mg in the soil (mg dry soil kg^{-1})
(mean and one standard deviation)

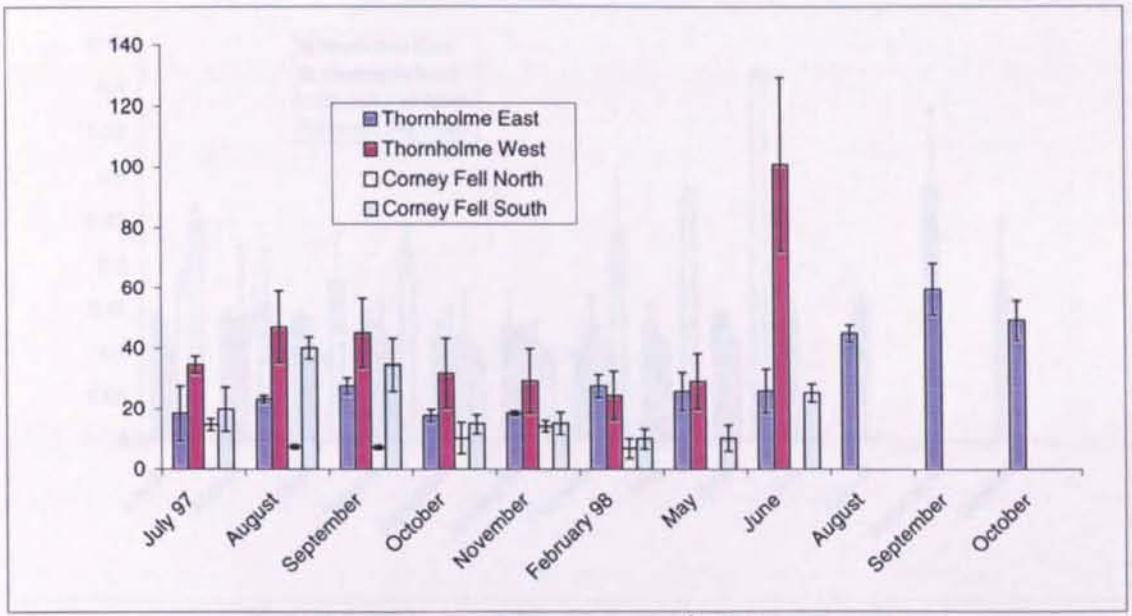


Figure 5.28 Extractable Mg (mg l^{-1}field moist soil)
(mean and one standard deviation).

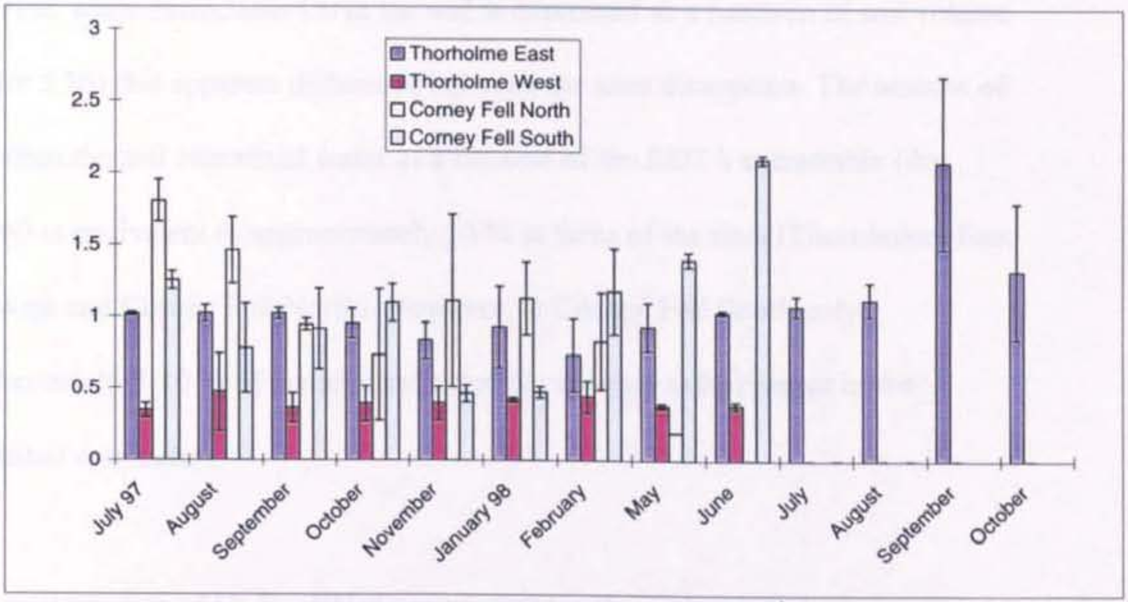


Figure 5.29 Extractable Cu in soil (mg kg^{-1} dry soil)
(mean and one standard deviation)

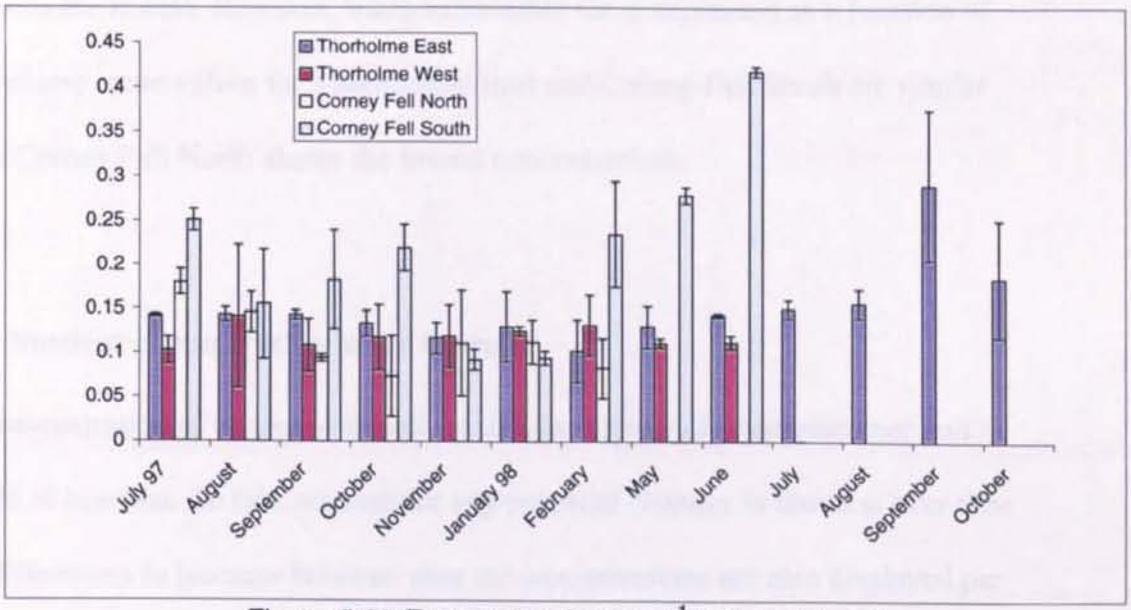


Figure 5.30 Extractable Cu (mg l^{-1} field moist soil)
(mean and one standard deviation).

However, when extractable Cu in the soil is expressed as a function of soil volume (Figure 5.30) this apparent difference between the sites disappears. The amount of Cu within the soil interstitial water as a fraction of the EDTA extractable (dry weight) is equivalent to approximately 50 % at three of the sites (Thornholme East and West and Corney Fell North). However, at Corney Fell South only approximately 5-10 % of the total extracted Cu appears to be present in the interstitial soil water.

The concentration of Ca (by NH_4Ac extraction) in the soil significantly increased in November from October 1997 at the Thornholme West site ($p < 0.05$). There were no significant temporal changes in extractable Ca at other sites. Figure 5.31 shows that the Thornholme West soil had the highest concentration of Ca and the Corney Fell soils the lowest. However, when extractable Ca is expressed as a function of soil volume mean values for Thornholme East and Corney Fell South are similar while Corney Fell North shows the lowest concentrations.

5.5.4 Nutrient concentration in the biomass

The concentration of cations within plant tissues is generally expressed per unit weight of biomass. To take account for any potential changes in biomass over time and differences in biomass between sites the concentrations are also displayed per unit area (m^2).

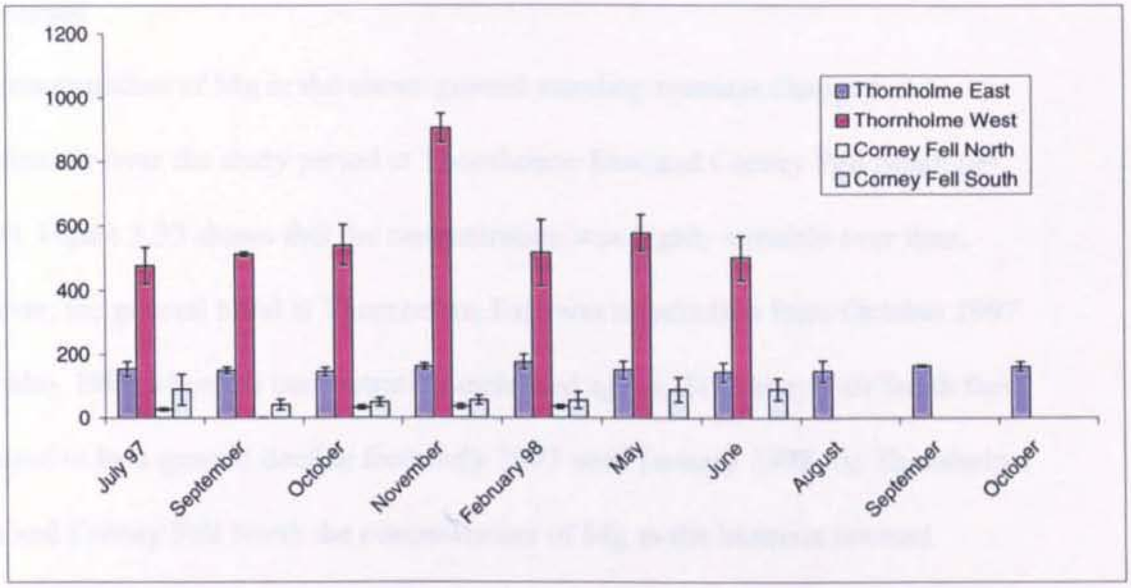


Figure 5.31 Extractable Ca in the soil (mg kg^{-1} dry soil) (mean and one standard deviation)

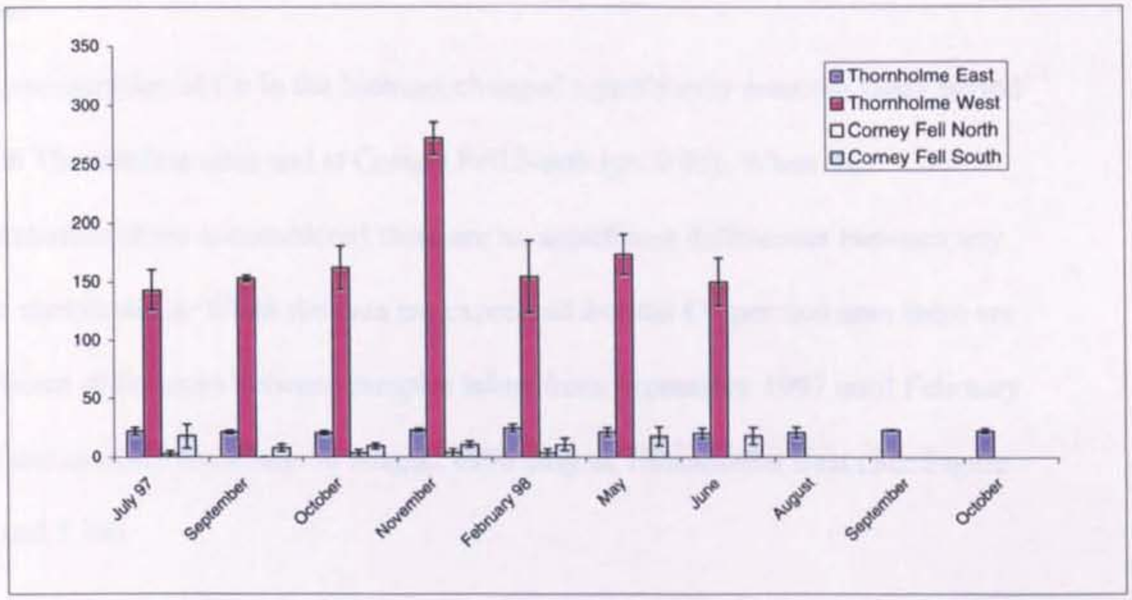


Figure 5.32 Extractable Ca in the soil (mg l^{-1} field moist soil) (mean and one standard deviation).

Magnesium

The concentration of Mg in the above-ground standing biomass changed significantly over the study period at Thornholme East and Corney Fell South ($p < 0.001$). Figure 5.33 shows that the concentration was highly variable over time, however, the general trend at Thornholme East was a reduction from October 1997 until May 1998 when the concentration increased again. At Corney Fell South there appeared to be a general decline from July 1997 until January 1998. At Thornholme West and Corney Fell North the concentration of Mg in the biomass seemed constant over time though the lack of data does not allow any firm conclusions to be drawn. Figure 5.34 shows that the seasonal pattern identified at Corney Fell South in Figure 5.33 is not apparent when the data is expressed as content per unit area.

Copper

The concentration of Cu in the biomass changed significantly over the study period at both Thornholme sites and at Corney Fell North ($p < 0.05$). When the concentration alone is considered there are no significant differences between any of the sample dates. When the data are expressed as total Cu per unit area there are significant differences between samples taken from September 1997 until February 1998 and samples from June to August 1998 only at Thornholme East (See Figure 5.35 and 5.36).

Manganese

The concentration of Mn in the biomass changed significantly over the study period at Thornholme East and Corney Fell South ($p < 0.01$). However, at Corney Fell South this result was due to a series of three replicate low values in July 1997.

Figure 5.37 & 5.38 show that Mn in the biomass was highly variable within plots but there were no consistent values at Thornholme West or Corney Fell North.

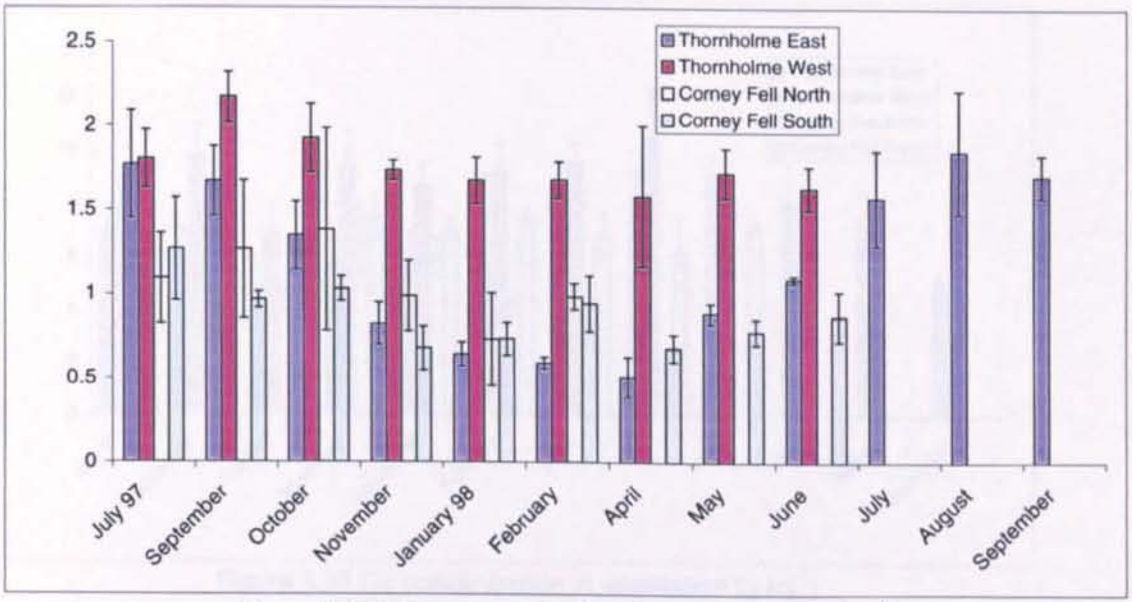


Figure 5.33 Mg concentration in vegetation (g kg^{-1})
(mean and one standard deviation)

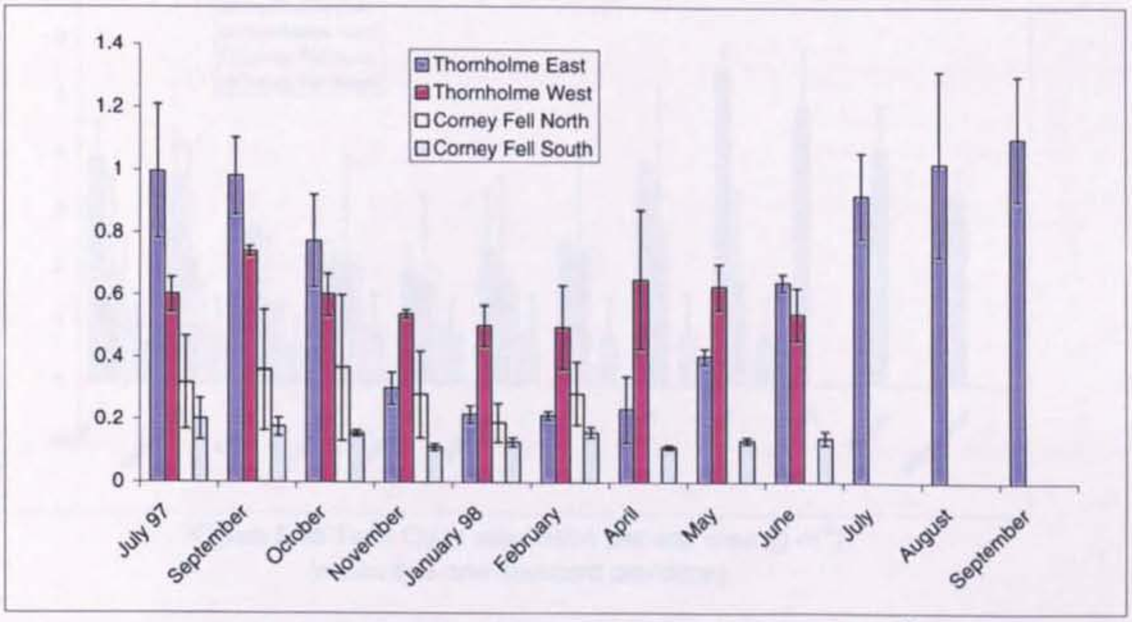


Figure 5.34 Total Mg in vegetation per unit area (g m^{-2})
(mean and one standard deviation

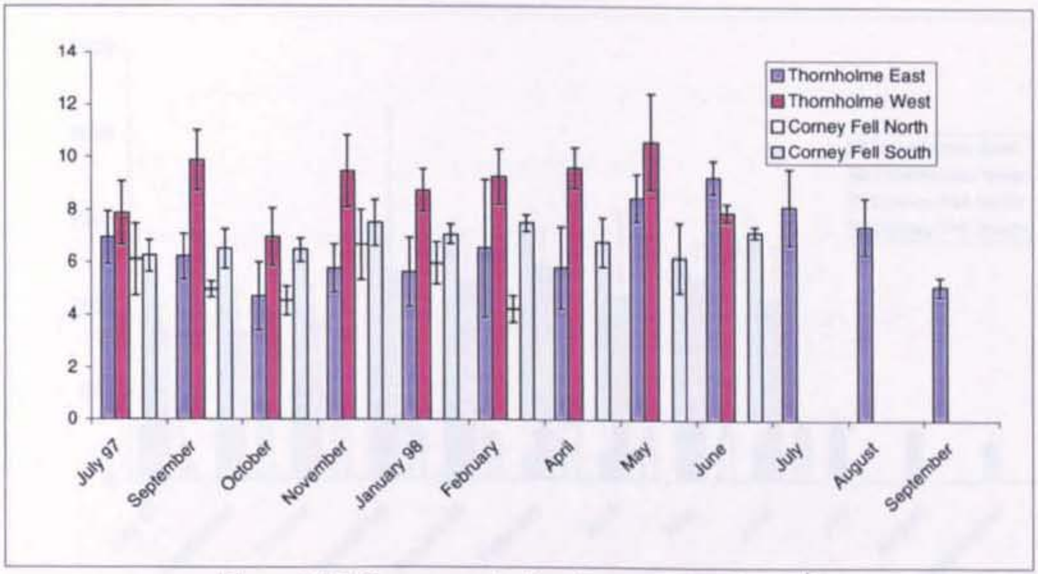


Figure 5.35 Cu concentration in vegetation (g kg^{-1})
(mean and one standard deviation)

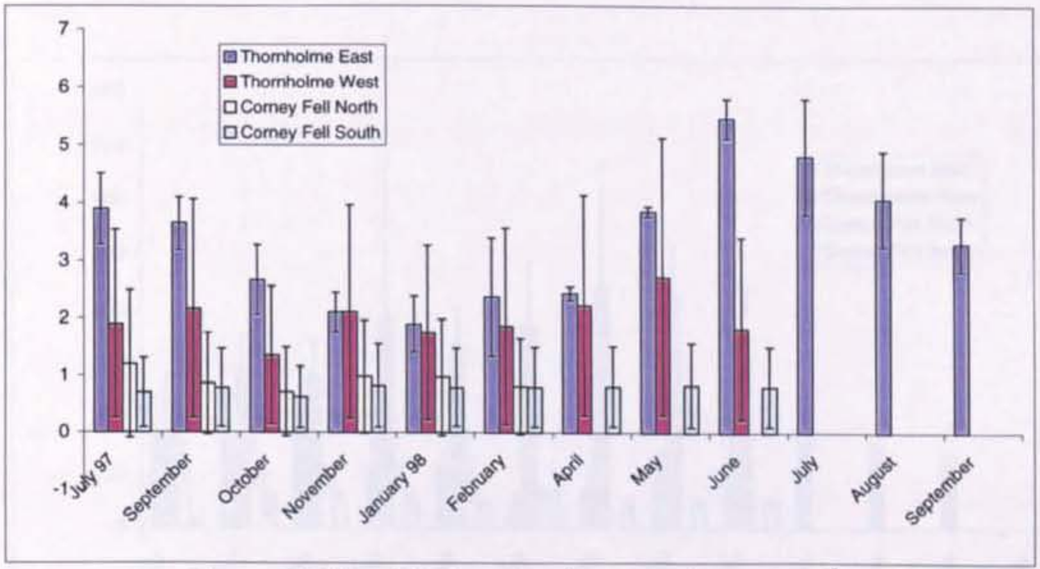


Figure 5.36 Total Cu in vegetation per unit area (g m^{-2})
(mean and one standard deviation)

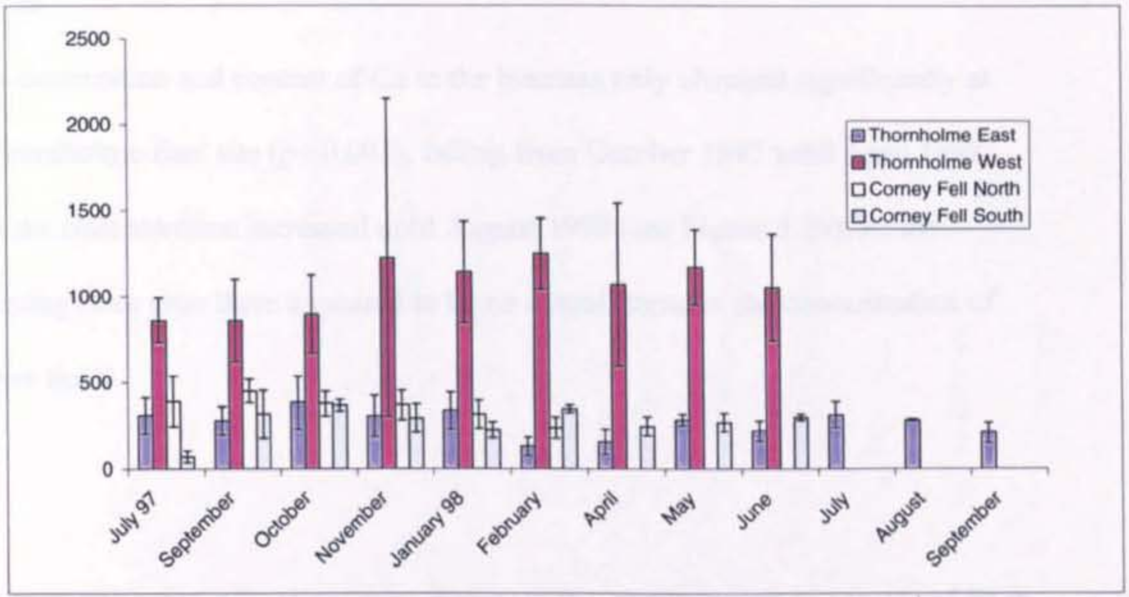


Figure 5.37 Concentration of Mn in vegetation (mg kg^{-1})
(mean and one standard deviation)

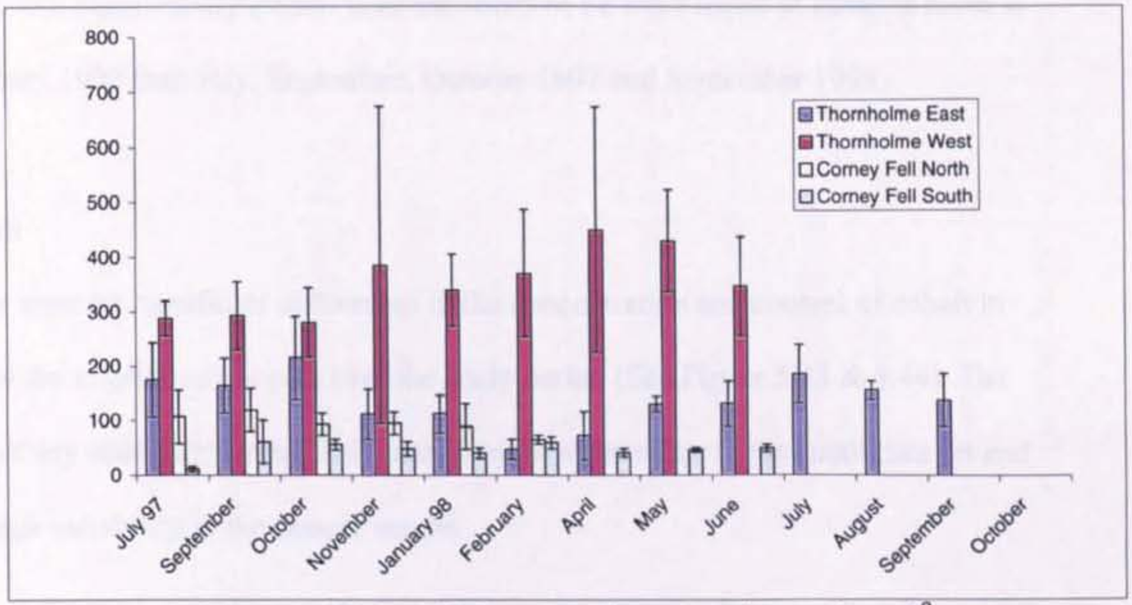


Figure 5.38 Total Mn in vegetation per unit area (mg m^{-2})
(mean and one standard deviation)

Calcium

The concentration and content of Ca in the biomass only changed significantly at the Thornholme East site ($p < 0.001$), falling from October 1997 until April 1998 when the concentration increased until August 1998 (see Figure 5.39). At the remaining three sites there appeared to be no overall trend in the concentration of Ca over time.

Iron

There was no statistically significant change in the concentration or content of Fe in the vegetation at both Thornholme sites and Corney Fell North. At Corney Fell South there was a significant change in Fe in the biomass over time ($p < 0.001$). The variability in the vegetation from Thornholme West was very large (see Figure 5.41 and 5.42). Significantly greater concentrations of Fe were found in samples taken in February 1998 than July, September, October 1997 and September 1998.

Cobalt

There were no significant differences in the concentration and content of cobalt in any of the vegetation samples over the study period (See Figure 5.43 & 5.44). The lack of any observable trend in the data may have been due to the small data set and the high variability in the sample results.

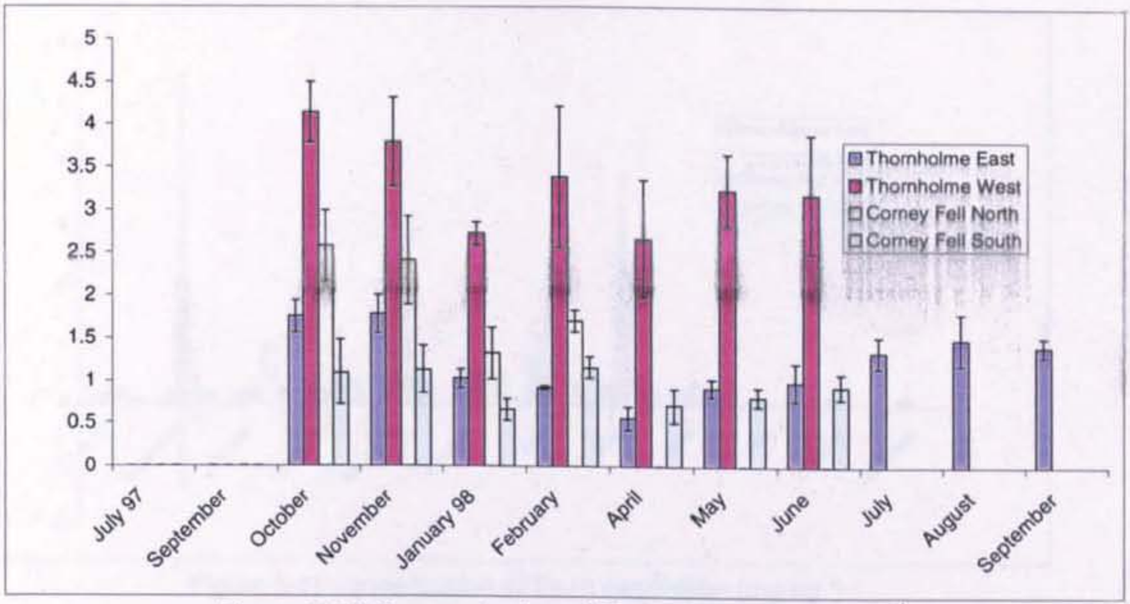


Figure 5.39 Concentration of Ca in vegetation (g kg^{-1})
(mean and one standard deviation)

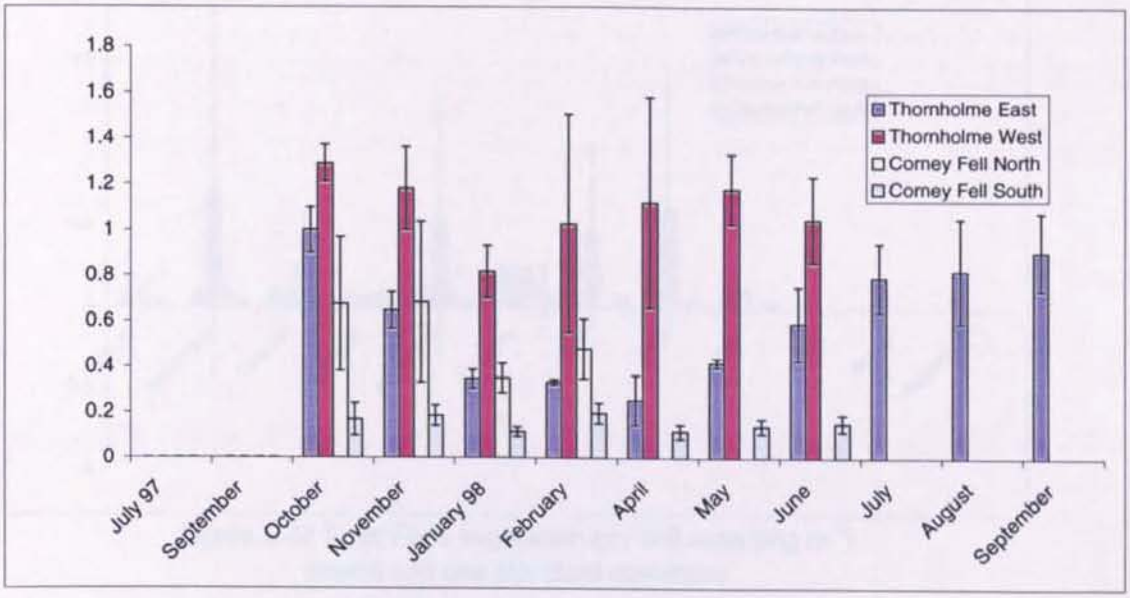


Figure 5.40 Total Ca in vegetation per unit area (g m^{-2})
(mean and one standard deviation)

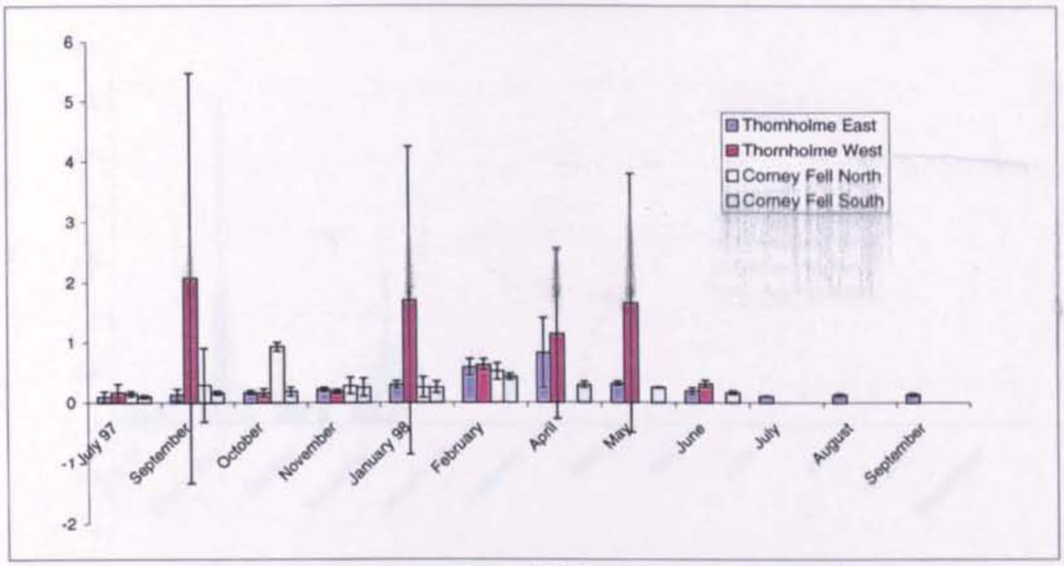


Figure 5.41 concentration of Fe in vegetation (mg kg^{-1})
(mean and one standard deviation)

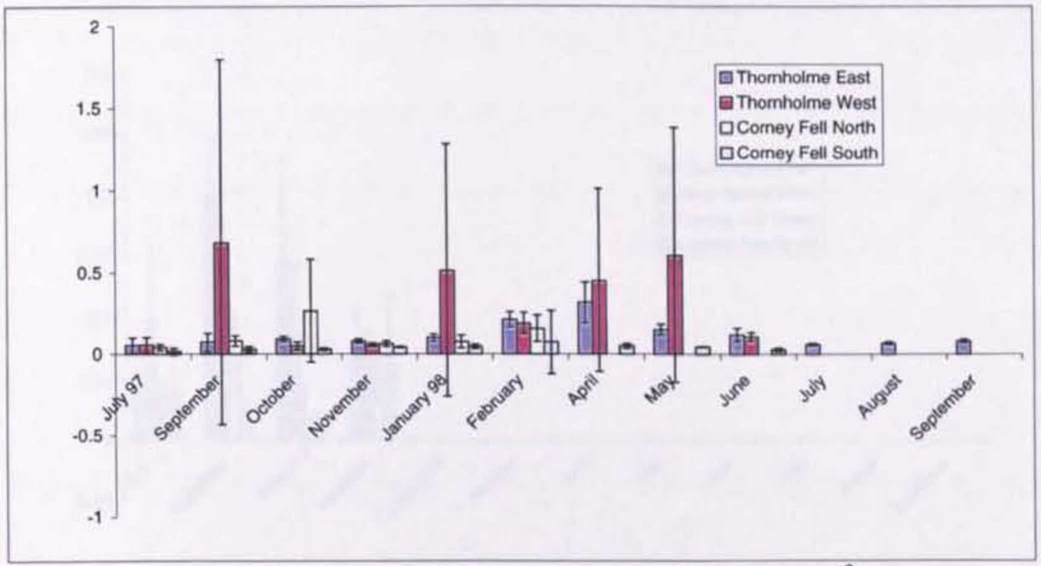


Figure 5.42 Total Fe in vegetation per unit area (mg m^{-2})
(mean and one standard deviation)

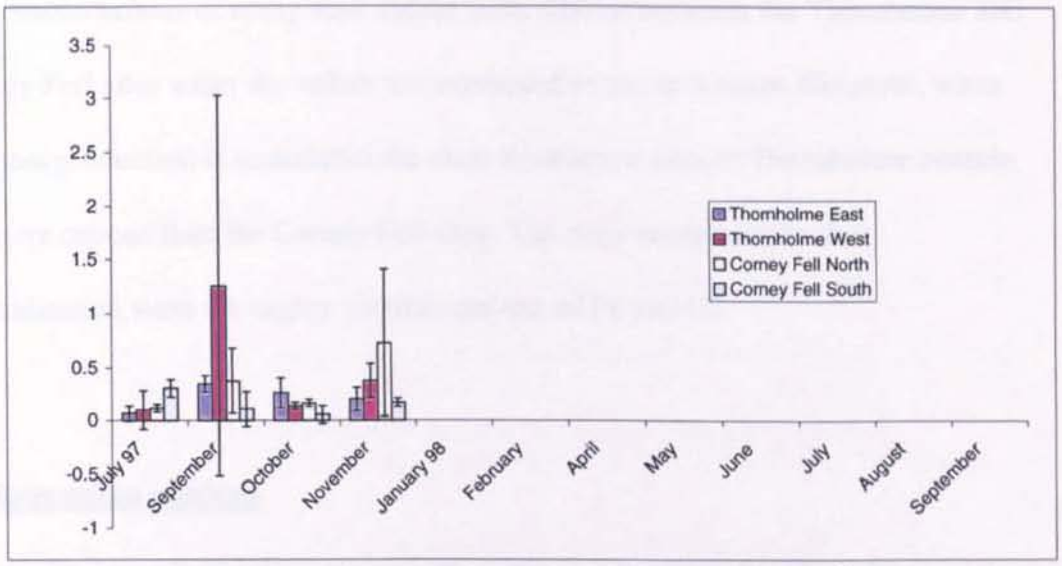


Figure 5.43 Concentration of Co in vegetation (mg kg^{-1})
(mean and one standard deviation)

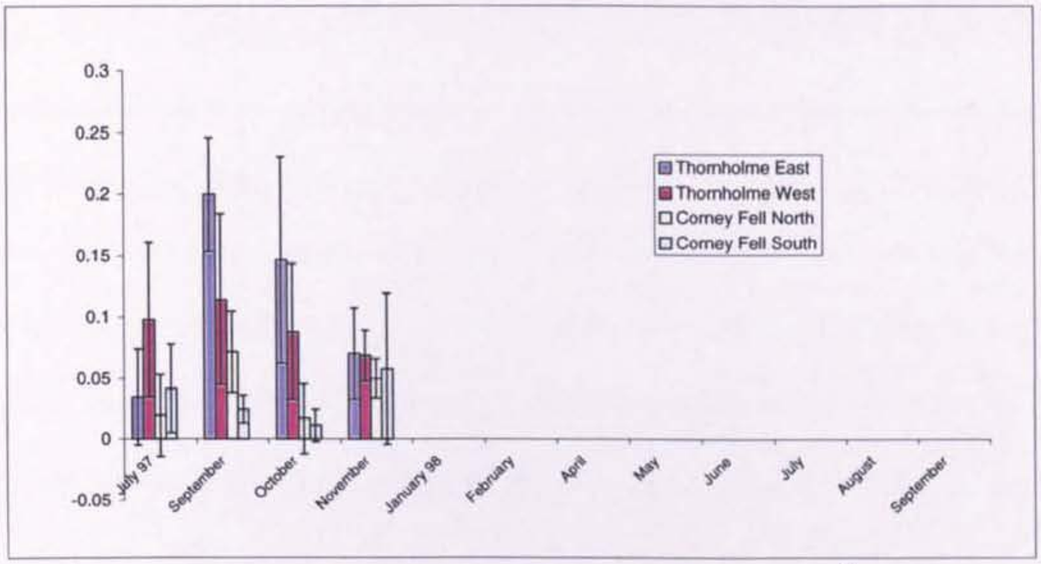


Figure 5.44 Total Co in vegetation per unit area (mg m^{-2})
(mean and one standard deviation)

The concentrations of many ions appear to be similar between the Thornholme and Corney Fell sites when the values are expressed as per unit mass. However, when biomass production is considered the most productive sites at Thornholme contain far more cations than the Corney Fell sites. The only exceptions to this generalisation were the highly variable cations of Fe and Co.

5.6 Regression analysis

To identify any relationships between K in the vegetation and in the soil regression analysis was undertaken by regressing the concentration of K in the biomass against both K measured in the interstitial soil water and K extracted from the soil by NH_4Ac. The regression analysis data is presented in Appendix 3.

5.7 Chapter 5 discussion

All four sites showed differing soil and vegetation properties, thus allowing the testing of the first hypothesis. Figure 5.1 shows that Corney Fell North had a deep organic layer whilst Thornholme West and Corney Fell South had relatively thin organic horizons which meant that sites had been selected with a range of organic horizon depths which would allow the testing of the second hypothesis.

Chapter 5 has also shown how temporal variations can effect the transfer of nutrients through the soil and from soil to plant. In each of the study sites many of the variables measured are co-dependent and as such must be considered together when discussing the effect of changes in one measured parameter. As Chapter 5 has presented an analysis of data for all the variables measured in the control plots it is possible to discuss at this point how these variables are inter-related. As Chapter 5 identifies trends in the data on plots where no application of potassium occurred subsequent chapters are able to determine whether the treatment did have an effect by comparing the treated plots to the control plots. Although not providing testing of any of the hypotheses, Chapter 5 has provided data which will allow testing of hypotheses 1,2,4,5,6,7 and 8 in later chapters.

Prior to considering how the application of K may have effected the soil and vegetation at each of the sites, it is necessary to consider the characteristics of the untreated soil and vegetation and how these are interrelated.

5.7.1 Soil properties

At each of the sites, many of the physical properties were inter-related, for example, at Thornholme West the underlying sandstone geology resulted in a high proportion of sand in the mineral component of the soil. In contrast, the soil underlain by the highly resistant igneous rocks (Read and Watson, 1982) at Thornholme East and Corney Fell South was dominated by particles < 100 μm. At Thornholme West, the proportion of clay particles within the mineral component was relatively small, however, the soil also contained relatively small amounts of organic matter. Therefore, as the mineral component was relatively large, the total number of clay particles in the soil at Thornholme West was far greater than at any of the other sites.

The flush site at Corney Fell North was almost permanently saturated with water, which was in direct contrast to the soil at Corney Fell South where it was comparatively dry. As both sites were underlain by the same basic geology, it was expected that they would have a similar particle size distribution, however, this did not occur. It is likely that the higher soil moisture at Corney Fell North permitted greater weathering of the underlying bedrock and that in-washing of sediment to the site caused the site to accumulate particles of 100 to 1000 μm.

Differences in the pH of the soil between the four sites can be linked to the underlying geology. The acidic parental rocks underlying Thornholme East were associated with the most acidic soil. Thornholme West, which was underlain by a calcic sedimentary rock, had the least acidic soil. Corney Fell South had a more acidic soil than Corney Fell North, despite being underlain by the same basic geology, this may be due to the greater soil depth together with the higher organic and moisture content of the Corney Fell North site.

The pH of the soil was not expected to change significantly over the relatively brief study period. The observed change at Thornholme East was probably due to a low buffering capacity. As buffering capacity is dependent on soil texture and organic matter at pH values between 4 and 7 (Rowell, 1994), the high organic content of the soil throughout its profile may have resulted in a low buffering capacity allowing the pH of the soil to change. The actual cause of this change is unclear, though the low buffering capacity of the soil would have allowed the addition of a relatively small number of ions to raise the soil pH as the soil does not retain sufficient hydrogen ions to neutralise the effect of the added K (Brady and Weil, 1999)

5.7.2 Cs-137 within the soil

The activity concentration profile of ^{137}Cs with soil depth is a function of many environmental factors including climatic conditions, the soil moisture content at the time of fallout and the soils structure and infiltration rate (Smith and Elder, 1999). At the time of sampling all four experimental sites recorded similar amounts of total ^{137}Cs deposition which was approximately 10 kBq m^{-2} which would relate to a deposition of approximately 12 kBq m^{-2} in 1986.

At Corney Fell, a similar study conducted by Paul and Jones (1995) reported activity concentrations in the soil of 2100 Bq kg^{-1} in the upper 10 cm of the soil compared to 300 to 900 Bq kg^{-1} measured in this study. Such high variation in ^{137}Cs activity concentrations within a small geographical area is consistent with previous reports that the deposition of ^{137}Cs was highly spatially variable (Smith and Elder, 1999). Sandalls and Bennett (1992) sampled a range of soils in and around Corney Fell in 1987 that showed that total deposition values of ^{137}Cs ranged between 19 to 25 k Bq m^{-2}. Horrill and Howard (1991) determined a deposition of 16 kBq m^{-2} at a site on Corney Fell. Jackson (1990) also showed that total deposition of ^{137}Cs at both Corney Fell and Thornholme sites was similar in 1987 with values of 14.3 and 12.8 k Bq m^{-2}.

Although the four sites displayed a similar total deposition of ^{137}Cs, the vertical distribution of ^{137}Cs within the soil profile varied between the sites. Such differences are probably due to differences in the soil moisture regime and soil composition. There are no known studies of the distribution of ^{137}Cs within the soil at the Thornholme sites. Work by Paul and Jones (1995) on Corney Fell showed that over 90 % of the total ^{137}Cs was within the upper 5 cm of the soil, while in this present study the maximum proportion on either of the Corney Fell sites was 50 %. Livens, Fowler and Horrill (1992) showed that at a range of sites in Cumbria almost 90 % of the total ^{137}Cs was present within the upper 10 cm of the soil surface (per unit mass) which is consistent with observations of the ^{137}Cs concentrations at both Thornholme sites and Corney Fell South. This would suggest that the bulk of the ^{137}Cs remained in the near-surface horizon. However, correction of the data presented in this study for changes in soil density indicates that there has been greater migration of ^{137}Cs down the soil profile at all sites than initial concentration-based measurements suggest. Rosen, Oborn and Lonsjo (1999) reported that the rate of downward ^{137}Cs migration was greatest in the most highly organic soils and that the distribution changed significantly over time. They stated that the rate of migration in the most organic soils could reach 0.9 to 1.0 cm yr^{-1}. In the peaty soil at Corney Fell North the bulk of the ^{137}Cs was at a depth of 15 cm which is in good agreement with Rosen, Oborn and Lonsjo's migration rate. Smith and Elder (1999) tested a model of ^{137}Cs movement within an organic soil on Corney Fell and found that a downward rate of movement of 0.764 cm yr^{-1} had an associated R^2 value of 0.996. For mineral soils, Rosen, Oborn and Lonsjo (1999) estimated migration rates of 0.5 to 0.6 cm yr^{-1}. Such rates of movement in the organic and mineral horizons at Thornholme West would result in most of the ^{137}Cs being present at 5 - 10 cm depth which agreed with the observations of this study.

The vertical distribution of ^{137}Cs within a soil can be influenced by the soil moisture both at the time of deposition and following deposition (Smith and Elder, 1999). The influence of soil moisture was most apparent in the two Corney Fell sites. The soil at Corney Fell South retained less moisture than Corney Fell North which was almost permanently saturated, it is assumed that this was also the case at the time of deposition. Consequently, when the ^{137}Cs was deposited in association with rainfall, it may have moved quickly through the soil profile at Corney Fell North both vertically and laterally. The drier soil at Corney Fell South would have absorbed the water in the top soil and the associated ^{137}Cs remained in the upper 5 cm of soil, which is indicated by the high activity concentration at this depth. It is possible that peat growth may have contributed to the apparent downward movement of ^{137}Cs within these sites. However, local landowners have reported that no peat growth has occurred at any of the sites studied. Further as the bulk of ^{137}Cs was from the Chernobyl accident it is unlikely that peat growth could have caused the downward movement observed at Corney Fell North as peat growth is typically 0.2 to 0.8 mm yr^{-1} (Brady and Weil, 1999)

Most the ^{137}Cs deposited from Chernobyl occurred during precipitation (Jackson, 1990), rapid movement of the ^{137}Cs down the soil profile would have occurred in areas with high moisture and migration would have been slower in drier areas. At Corney Fell North, the spatial variability in ^{137}Cs activity concentration and moisture is greater than at any of the other sites. It is suggested that as the rate of water transmission through peat is greater as organic matter increases (Ryecroft, Williams and Ingram, 1974), the rate of infiltration of ^{137}Cs would have been greater in the wetter and more organic peat of Corney Fell North than Corney Fell South.

The relatively high variability in ^{137}Cs activity concentration in the 0-5 cm soil layer at Thornholme West could also have been a function of spatial variability of soil composition. In the upper 5-10 cm, the composition of the soil was relatively homogenous and as a consequence variability in ^{137}Cs activity concentration was low. The mineral content of the soil increases at approximately 4 to 12 cm. As the site was freely draining and the soil was moist for most of the year, ^{137}Cs deposited within a water droplet would be quickly able to penetrate the highly organic upper zones of the soil to become sorbed onto the clay particles within the soil. However, at the 5-10 cm depth interval where the mineral composition became spatially variable, (indicated by the high variability in the proportion of mineral matter at this depth) the associated activity concentration of ^{137}Cs was also highly spatially variable at this depth. This may be due the localised changes in the composition of the depth interval from being organic to mineral dominated. Below 10 cm, the variability in ^{137}Cs activity concentration continues since the total ^{137}Cs penetrating to this depth is dependent on the amount penetrating the overlying horizons. At Thornholme East, the consistent increase in the proportion of mineral matter with depth is reflected in the low spatial variability of the activity concentration of ^{137}Cs, as all the ^{137}Cs migrates at a similar rate. It appears that the ^{137}Cs activity concentration profiles within each of the four experimental sites are principally controlled by the relative proportions of mineral and organic matter and the moisture regime within the soil.

5.7.3 Cs-137 in above-ground biomass

The activity concentration of ^{137}Cs in the above-ground biomass was typically around 300 Bq kg^{-1} (dry weight) during the summer period at all the experimental sites, with the exception of Thornholme West. This value is two orders of magnitude lower than other studies conducted on similar vegetation communities on Corney Fell by Paul and Jones in 1995 and Sandalls and Bennett in 1987 but similar to those given by Coughtrey, Kirkton and Mitchell (1989(a)) for this site. The specific reasons for such differences are unclear, however, they may relate to the year of sampling, differences in the species composition of bulk samples of vegetation or greater localised deposition of ^{137}Cs. The lower activity concentrations of ^{137}Cs in the vegetation at Thornholme West (around 20 Bq kg^{-1}) were similar to values obtained by Howard and Beresford (1987) on a lowland soil in Cumbria. This may indicate that the plant roots at Thornholme West site are obtaining many of their nutrients from the more mineral horizon below the organic surface, though no evidence is presented within the research to support this and to establish the cause would require further research. Both Corney Fell and the Thornholme East sites contained a similar amount and proportion of the total ^{137}Cs deposition in the plant biomass, possibly because there was a similar amount of ^{137}Cs available in the rooting zone for plant uptake (per unit volume of soil). However this does assume that the vegetation species at both sites have a similar uptake of ^{137}Cs from the soil to the biomass. The activity concentration of ^{137}Cs in the vegetation at Thornholme East and both Corney Fell sites typically followed a seasonal pattern of being highest in late autumn and lowest in winter and early spring. Such a seasonal trend was also reported by Bunzl and Kracke (1989) for *Trichophorum caespitosum* and *Molinia caerulea.* In the spring high demand for K ions and relatively high availability is likely to result in low transportation of Cs^+ from the soil into the plant. Active transport mechanisms in the plant also enhance this preferential uptake of K rather than Cs (Taiz and Zeiger, 1991). Available K is depleted over the growing season, and as Cs availability is less affected and active transport of K lessens more Cs is able to move from the soil into the plant (Salt et al., 1997). In the winter, very low rates of plant growth result in little demand on the soil for K, possibly leading to reduced uptake of ^{137}Cs.

The ^{137}Cs activity concentration in the vegetation from Thornholme West increased from around 20 Bq kg^{-1} to a maximum of 100 Bq kg^{-1} in January 1998. Such an increase in ^{137}Cs activity concentration in the winter months was also reported by Rafferty, Dawson and Colgan, (1994) for a raised bog in Ireland. The relatively low transfer of ^{137}Cs during the summer at Thornholme West may have been due to a low concentration of ^{137}Cs in the soil solution though this could have only been conclusively demonstrated by further research. The significant increases in ^{137}Cs activity concentration in the winter period may be a direct effect of soil adhesion onto plant surfaces by animal activity (Sumerling, Dodd and Green, 1994). However, at Thornholme West, if soil adhesion was singularly responsible for the rise in ^{137}Cs activity concentration in the winter months, this would have required 16 % of the vegetation sample (by dry oven mass) to be composed of adhered soil (assuming mean ^{137}Cs vegetation and soil activity concentrations from the summer months). Therefore of the sixty grams of above ground biomass typically removed from the 40 x 40 cm sample plot on each occasion 9.6 g would have been soil. As the site was densely covered with vegetation, with only occasional exposures of open soil, this seems unlikely and would require very high levels of trampling. Changes in agricultural practice could also have caused this increase in ^{137}Cs activity concentration during October and November. During the winter periods a greater number of grazing animals were located on the Thornholme West site than during the spring and summer months. This increase in grazing intensity would have lead to a reduction in sward height, which was observed. As the standing biomass at Thornholme West did not significantly change over the study period this would suggest that the sward density increased compared to other sampling times. Alternatively, the green shoot to dead leaf ratio may have changed producing such an effect, however as this was not recorded it is impossible to confirm if this change did occur. A lower sward height was observed by Salt et al., (1997) to result in an increase in ^{137}Cs activity concentration within *Agrostis capillaris*. On the Thornholme West plots treated with potash, the winter increase in ^{137}Cs activity concentration was far lower than on the control plots. It therefore seems unlikely that changes in the stocking density could have produced an effect that was specifically restricted to the control plots. It is suggested as there is no data which could provides a likely explanation for this rise in ^{137}Cs concentration, data presented in later chapters which demonstrates the effect of the K application at this site may provide evidence of the potential cause of this increase.

At Corney Fell, a number of studies have been previously conducted to determine the activity concentration of ^{137}Cs in the vegetation and how this relates to the ^{137}Cs in the soil (Howard and Beresford, 1987 and 1994; Horrill and Howard, 1991; Coughtrey, Kirkton and Mitchell, 1989b and Green and Dodd, 1988). The present study has obtained comparable data for the activity concentration of ^{137}Cs (if temporal changes are considered) in the vegetation, the concentration ratio and Tag values. In contrast Jones, Paul and Mitchell, (1999) recorded concentration ratios from soil to plant an order of magnitude greater than this study. A number of possible reasons for such differences were discussed, however, Howard and Beresford (1987) identified that the concentration ratio within a paddock on an upland farm in Cumbria varied between 0.2 and 3.8 within a 0.7 ha area, thus one order of magnitude variation in the data may accurately reflect spatial variability.

In 1995 Howard et al., conducted a review of the Tag values of a range of soils and concluded that organic peaty soils generally had values between 0.018 and 0.083 m^2 kg^{-1} which would encompass values calculated for both Corney Fell sites and Thornholme East. In contrast, Thornholme West had a Tag value more typical of a mineral soil.

Salt and Mayes (1991) considered the soil to plant transfer of radioceasium and showed that in experiments involving the direct injection of ^{134}Cs into a peaty podzol the transfer between May and September was between 3.1 and 6.5 %. In this study flux values ranged from 0.03 to 1.1 between May and September, which are within the range reported by Coughtrey and Thorne (1983) of 0.003 to 14 % with a mean of 0.2 %. The differences in soil to plant transfer are related to differences in the soil at the four sites, the sandy soil at Thornholme West with a high clay content is a site where the availability of ^{137}Cs was low, in comparison the deep highly organic peat at Corney Fell North had a relatively high availability of ^{137}Cs in the soil. Thus site selection encompassed sites where the availability of ^{137}Cs was variable.

Appendix 1 shows that the total error in determining Tag values and similarly likewise total flux approach (if these errors were calculated) is large. However, as the intake to the animal is from a large spatial area, it is likely that the mean Tag value of each treatment would represent the average intake. Although the error in the Tag value may be important on a small spatial scale when the actual effects are considered on a larger scale the total error is of low importance. In presenting the mean data the author accepts that it is possible that some biomass may average Tag values which are greater than the mean value calculated.

5.7.4 Potassium in the soil

All four sites had different proportions of K in the interstitial and available (NH_4Ac extractable) fractions of the soil. At Corney Fell North, almost all the K was present in the interstitial soil water. In contrast, at the Thornholme East and Corney Fell South sites about 10 % of the available K was in the interstitial soil water. At Thornholme West only 1 to 2 % of the available K was in the interstitial soil water,

and analysed for its K concentration reflected the concentration of K at a time previous to the time of soil sample analysis. However, it is also possible that the samples collected were not sufficient in number to allow a direct relationship to be calculated. The results from the regression equations may change if the equations were to relate total flux of K per soil volume, rather than unit mass to that of K in the biomass and likewise it would be possible to relate total K per unit area rather than per unit mass.

The reason why concentrations of K extracted by NH_4Ac were not useful as an indicator of available K in the soil was that during extraction only the surface K on the planar clay sites is removed. The extraction makes no assessment of K present in the interlayer sites from which deep rooted plants can feed (Nair, 1996). Plants feed not only from K^+ on the surface of the clay particles but also K^+ trapped in the interlayer sites of non-expanded 2:1 clay minerals (Hoagland and Martin 1933; Read and Watson, 1982). However, plants generally obtain the greatest proportion of the K from the interstitial water. As such the concentration of K which is extracted from the clay sites using NH_4Ac represents a small proportion of the total uptake of K by the plant.

It can be assumed that the extraction techniques used within this study do not allow a direct relationship between any change in available soil K and that in the biomass to be drawn. Therefore any discussion of the effects of K application on the soil in Chapter 7 will be limited and the author cannot directly attribute changes of K in the soil to changes in the biomass.

5.7.6 Concentration of Ca, Co, Cu, Fe, Mg and Mn

Differences in the availability of ions for plant uptake as indicated by the concentration within the biomass, interstitial water and NH_4Ac extractions, can be partly explained by the mineralogy of the soil. On the basic parental bedrock at Corney Fell, the soil contained more available Cu than on the more acidic and sedimentary geology of the Thornholme sites. The high moisture and organic content on Corney Fell North would lead to a high proportion of the Cu being present in the interstitial soil water. Subsequent leaching has occurred, which has likely lead to the reduction in the concentration of EDTA extractable Cu. Leaching has also likely lead to the loss of Mg and Ca from the soil at Corney Fell North. The high concentration of Ca in the Thornholme West soil is due to the Ca rich parental material (Read and Watson, 1982). The effects of low availability of Ca at Corney Fell North on the availability of other elements within the soil is unclear from examination of the nutrient data alone. However, low Ca availability may have consequences for the availability of K in the soil. The K potential in the soil solution has been shown to be dependent on the concentration of Ca in the soil (Wild, 1988) as follows;

$$I = \frac{(K^{+})}{\sqrt{(Ca^{2+})}}$$

Where I denotes 'the intensity of K in solution', K and Ca are the concentrations of K and Ca in the soil solution. Wild considered that the effect Mg may have on the availability of K in comparison to Ca was minimal and did not consider it as McLean (1978) did in his calculations. From Wild one may infer that as the concentration of Ca at Corney Fell North dramatically increased in October, November 1997 and in February 1998, providing the concentration of K remained constant, the relative intensity of the K in the soil interstitial water for plant uptake would have decreased. As the concentrations of Ca within the soil at sites other than Thornholme West were low and showed no large changes in the availability of Ca, the changes in the Ca concentration within the soil would therefore have had a minimal effect on the 'intensity' of K.

5.7.7 Temporal changes in nutrient concentration in the plant biomass

Over the study period there were temporal changes in the concentration of other nutrients in addition to K in the standing above-ground biomass. Of the elements that were measured, temporal changes occurred in Ca, Cu, K, Mg and Mn concentrations. The underlying trend appeared to be climatically controlled, with decreases in ion concentration as the plants entered senescence in the autumn and winter. This agrees with observations for K, Ca and Mg reported by Pritchard, Pigden and Folkins (1964) in a study conducted on timothy (*Phleum pratense*) and bromegrass (*Bromus inermis*). The study identified that the greatest concentrations within the stems occurred in May and then reduced throughout the remainder of the growing season. Rafferty et al., in the TEMAS (1996) project also reported seasonal changes in the composition of the biomass in *Eriophorum vaginatum* with highest concentration of Mg in May and the lowest in October 1997. They also reported that the concentration of Cu and Mn reached a maximum in May and a minimum in October.

Thomas and Trinder (1947) analysed a range of upland grasses which showed the maximum concentrations of Cu, K and Mg occurred in May, Mn peaked in September and Fe reached a maximum in February. *Molina* was most prominent in the sward at Thornholme East and although the concentrations reported in Chapter 4 are lower than those of Thomas and Trinder, the general trends were similar.

Jacob (1958) quantified the nutrient content of several grasses including *Poa pratensis* and *Agrostis* spp. which dominated the bulk of the vegetation sampled at Thornholme West. For these two species Jacob reported concentrations typically between 1.6 - 2.4 and 1.2 - 2 % K respectively; 0.45 - 0.7 and 0.5 - 0.6 % Ca and; 0.13 - 0.16 and 0.15 - 0.17 % Mg within the biomass. A general average at Thornholme West from April to October was 2 % K, 0.35 % Ca and 0.16 % Mg. The low concentration of Ca may have been a consequence of low availability in the soil.

For deer-grass (*Scirpus caespitosus*) Thomas and Trinder (1947) reported peak concentrations of K, Mg and Fe of 0.85%, 0.18 % and 125 mg kg^{-1}, respectively in May. Slightly lower values were measured in the deer-grass dominated sward at Corney Fell North: 0.7 K %, 0.1 Mg % and 100 mg kg^{-1} Fe in July 1997.

At Corney Fell South, the sward was almost entirely dominated by *Nardus stricta*. In 1947 Thomas and Trinder measured peak nutrient concentrations in a *Nardus* sward in April followed by a gradual decline. The concentrations of Mg, Mn and Cu at Corney Fell South were similar to those observed by Thomas and Trinder. In 1974, Powell and Malcolm reported mean concentrations of K, Ca and Mg in *Nardus* of 0.477 %, 1340 and 550 mg kg^{-1} respectively; in this study although the values were greater the relative concentrations were comparable showing approximately 6 %, 100 and 100 mg kg^{-1} respectively.

Data presented within this study has supported temporal changes in nutrient composition that has been published from other comparable studies. This will allow data to be directly compared to similar studies and the understanding of the effects of K application to be more clearly understood

5.7.8 Chapter 5 summary

Soils

All four sites had received a similar total deposition of ^{137}Cs. Thornholme East and Corney Fell North were the two sites with greatest organic matter content in the soil and Thornholme West had a thin organic layer which was underlain by a sandy substrate as shown in Figure 5.5. All four sites showed a reduction in ^{137}Cs with increasing soil depth when expressed as Bq kg^{-1}, however, at Corney Fell North and Thornholme West this did not occur until depths exceeded 10 cm. The concentration of K in the interstitial soil water was highest at Thornholme West and lowest at Corney Fell North, whilst the highest Mg and Cu concentrations were found in the soil analysed from Corney Fell North. The total amount of K collected in the lysimeters at Thornholme East and West was comparable.

Biomass

Above-ground standing biomass was highest at the Thornholme East site and least at Corney Fell South throughout the study period. Thornholme East appeared to be the only site where the biomass was lower in the winter period. The transfer of ^{137}Cs from soil to plant followed a seasonal pattern with lower concentrations during the winter period and greater concentrations in the spring and summer months except for Thornholme West. At this site the concentration of ^{137}Cs in the vegetation significantly increased in the winter period, the cause of this increase will be considered in subsequent chapters.

Data presentation

Data presented in Chapter 5 is in a range of formats which included per unit volume, unit mass and unit area. These unit measurements show that when other factors are considered the differences between the sites can greatly changed. For example, the concentration of Cu in vegetation when expressed as g kg^{-1} appears to infer that vegetation sampled from Thornholme West had the highest Cu concentration whilst if the data is presented as g m^{-2} it is clear that the highest Cu content was present at Thornholme East. Chapter 5 has therefore demonstrated that any review of the effects of the countermeasure must consider how the data is presented and interpreted.

5.7.9. Conclusions

It has been demonstrated that the study sites selected to evaluate the effectiveness of potash as a countermeasure represent a diverse range of soil and vegetation types. It can therefore be concluded that as hypothesis one and two were dependent on a range of soil types being selected then these hypotheses can now be statistically tested in subsequent chapters within this thesis.

Chapter 5 has established the natural trends in nutrients at each of the four study sites for the study period. It is not a principle aim of this thesis to determine the controlling factors of each of these variables or how the variables are interrelated.

However, this discussion has considered how many factors at each site temporally vary and how the differences between the sites may have originated.

The natural variability in the transfer and availability of nutrients at all of the study sites has been shown in Chapter 5. The chapter has provided data that will allow seven of the hypotheses within the thesis to be statistically tested and conclusions to be drawn from such testing. The chapter has also shown that changes in the nutrient concentration in the soil may not be reflected in the biomass.

Chapter 6

The effect of the potash applications on ^{137}Cs.

6.1 Introduction

Chapter 6 is the first chapter that presents results of applying KCl to the field sites. As a countermeasure, an application of KCl would not occur if it could not significantly reduce the transfer of ^{137}Cs from soil to plant. Therefore, prior to any reporting of the potential side-effects of application, it must be determined if the countermeasure reduced the transfer of ^{137}Cs from soil to plant (hypothesis 1, section 1.1). Chapter 6 presents data to test this hypothesis.

It was considered that an application of 200 kg K ha^{-1} would induce a significantly greater reduction in the transfer of ^{137}Cs from soil to plant than an application of 100 kg K ha^{-1} (hypothesis 2, section 1.1). Chapter 6 presents and tests data to determine if this hypothesis was valid. Chapter 6 also tests hypotheses 2, 4 and 5 which consider the longevity of the countermeasure and any difference in the effectiveness of the countermeasure between two successive years.

Chapter 2 identified that the transfer of ^{137}Cs from soil to plant could be presented in a range of formats and considered the various merits of such formats. Chapter 6 statistically examines the effect that the treatments had on the activity concentrations in the biomass using the following formats; activity concentrations CR's, Tag's and total flux. A discussion of the differences between presenting the data in these varying formats occurs in section 6.3.

6.2 Cs-137 in above-ground biomass

Thornholme East

The effect of the potash treatments on the activity concentration of ^{137}Cs in the above-ground biomass is shown in Figure 6.1(a). From July 1997 until June 1998 there was a significant interaction of treatment and time which decreased the ^{137}Cs activity concentration within the above-ground biomass ($p< 0.01$). Comparisons between the potash treatments gave the following results:

1) There was no significant difference between the activity concentration in the control plots and the plots treated with 100 kg K ha^{-1}.
2) Significantly lower activity concentrations in the biomass were found in plots treated with 200 kg K ha^{-1} compared to the control plots ($p< 0.001$).
3) There was no significant difference between the 100 kg K ha^{-1} plots and the plots treated with 200 kg K ha^{-1}.

The treatment effect on the 200 kg K ha^{-1} plots was not statistically significant until April 1998, however Figure 6.1(a) suggests that in September 1997, the mean ^{137}Cs activity concentration had already decreased. This reduction was approximately 30 % of the mean activity concentration in the control plots and occurred from September until November 1997. Plots treated with 100 kg K ha^{-1} also appeared to show a mean reduction in activity concentration of approximately 50 %, which was apparent from October until January 1998. In February 1998, plots treated with 100 and 200 kg K ha^{-1} had a mean concentration of ^{137}Cs in the biomass that was greater than the controls, however, the high variability between the replicate plots meant that this was not statistically significant.

Following the repeat application of potash in June 1998, the effect of the treatment on the ^{137}Cs activity concentration in the biomass was variable. During the second year of sampling (June until October 1998) there was no significant effect of time on ^{137}Cs activity concentration. Comparisons between the treatments over the second year showed that:

1) There was no significant difference in ^{137}Cs activity concentration between the control plots and the plots treated with a repeat application of 100 or a single application of 200 kg K ha^{-1}.
2) The plots treated with a repeat application of 200 kg K ha^{-1} had significantly less ^{137}Cs activity concentration than the control plots, plots treated with a single application of 200 kg K ha^{-1} and plots treated with a repeat application of 100 kg K ha^{-1} ($p < 0.001$).

The repeat application of potash to plots on Thornholme East significantly reduced the ^{137}Cs activity concentrations compared to the single application of 200 kg K ha^{-1} in August, September and October 1998 ($p < 0.05$). Figure 6.1(a) shows that in October the mean activity concentration on the repeat 100 and 200 kg K ha^{-1} plots was approximately 50 and 67 %, respectively, that of the mean concentration in the control plots. The effectiveness of a single application of K differed between experimental years. A single application of 200 kg K ha^{-1} applied in June 1997 caused a reduction in activity concentration of 50 % ^{137}Cs by September 1997. A single application applied to different plots at Thornholme East in June 98 showed no treatment effect in September and October of the same year.

Thornholme West

The effect of the potash application on the ^{137}Cs activity concentration in the above-ground biomass is shown in Figure 6.1(b). Over the study period there was a significant interaction of treatment and time ($p < 0.001$). Comparisons between the potash treatments showed that:

1) There was no significant difference in ^{137}Cs activity concentration between the control plots and the plots treated with 100 kg K ha^{-1}.
2) Vegetation treated with 200 kg K ha^{-1} contained significantly lower ^{137}Cs activity concentrations relative to both the control plots and the plots treated with 100 kg K ha^{-1} ($p < 0.001$).

There were no statistically significant differences between any of the three treatments until January 1998, when ^{137}Cs activity concentrations in plots treated with 200 kg K ha^{-1} decreased significantly relative to the control plots. This trend also occurred in February and April of 1998 ($p < 0.05$).

Figure 6.1(b) shows that mean activity concentration of ^{137}Cs in plots treated with 100 or 200 kg K ha^{-1} were 33 and 50 % lower, respectively, than the control plots in October 1997. High activity concentrations of ^{137}Cs recorded in the control plots in January 1998 were not reflected in the plots treated with potassium. On this sampling date the mean activity concentration in the biomass fell to between 2 and 25 % of the ^{137}Cs activity within the control plots (200 and 100 kg K ha^{-1} plots respectively). In February and April 1998, the mean activity concentration within the treated plots remained lower than that of the control plots. However, in May 1998, the biomass sampled from 100 kg K ha^{-1} plots had mean activity concentrations greater than those of the control plots. This effect continued into June 1998 when plots treated with both 100 and 200 kg K ha^{-1} had increases in the mean activity concentration of ^{137}Cs of almost 100 %.

Corney Fell North

The effect of the potash application on the ^{137}Cs activity concentrations in the above-ground biomass at Corney Fell North is shown in Figure 6.1(c). Over the study period, there was a significant effect of both time ($p< 0.001$) and treatment ($p< 0.001$) on the ^{137}Cs activity concentration, but no significant interaction. Comparisons between treatments showed that:

1) There was no significant difference between the control plots and the plots treated with 100 kg K ha^{-1}.
2) Plots treated with 200 kg K ha^{-1} contained a significantly lower ^{137}Cs activity concentration than the other treatments ($p< 0.001$).

Four months after potash application, activity concentrations within the plots treated with 200 kg K ha^{-1} were significantly lower than those measured within the control plots or plots treated with 100 kg K ha^{-1}. However, Figure 6.1(c) suggests that the potassium may have been effective from the first sampling date in July 1997, when the mean activity concentration in the plots treated with 200 kg K ha^{-1} was approximately 50 % that of the control plots. In September 1997, all the plots treated with potash had a mean ^{137}Cs activity concentration of around 30 to 50 % less than the control plots. In October, the difference between the ^{137}Cs activity concentration within the plots treated with 100 kg K ha^{-1} and the control plots was negligible. However, plots treated with 200 kg K ha^{-1} still had 70 % less ^{137}Cs activity than the control plots. In January 1998 the activity concentration measured in the 100 kg K ha^{-1} plots was almost twice the mean activity concentration in the control and the 200 kg K ha^{-1} plots.

Corney Fell South

Temporal trends in ^{137}Cs activity concentrations within the above-ground biomass at Corney Fell South are shown in Figure 6.1(d). There was a significant effect of time ($p< 0.0001$) and treatment ($p< 0.0001$) on the ^{137}Cs activity concentration though there was no significant interaction of treatment and time. Comparisons between the treatments gave the following results:

1) Plots treated with 100 or 200 kg K ha^{-1} showed significantly lower ^{137}Cs activity concentrations than the control plots ($p< 0.0001$).
2) No significant differences in the ^{137}Cs activity concentrations occurred between the plots treated with 100 kg K ha^{-1} and those treated with 200 kg K ha^{-1}.

In September 1997, a significantly lower activity concentration of ^{137}Cs was recorded in plots treated with 100 and 200 kg K ha^{-1} than the control plots ($p< 0.05$). The treatments reduced activity concentration by 50 to 75 % relative to the control plots. Significantly reduced ^{137}Cs activity concentrations in the 100 kg K ha^{-1} plots continued until February 1998 ($p< 0.05$), whilst in the 200 kg K ha^{-1} treatment the effect only remained significant until January 1998 ($p< 0.05$). Figure 6.1(d) shows, although not statistically significant, that the mean ^{137}Cs activity concentration within the biomass remained lower in the plots treated with potassium than the control plots in May and June 1998.

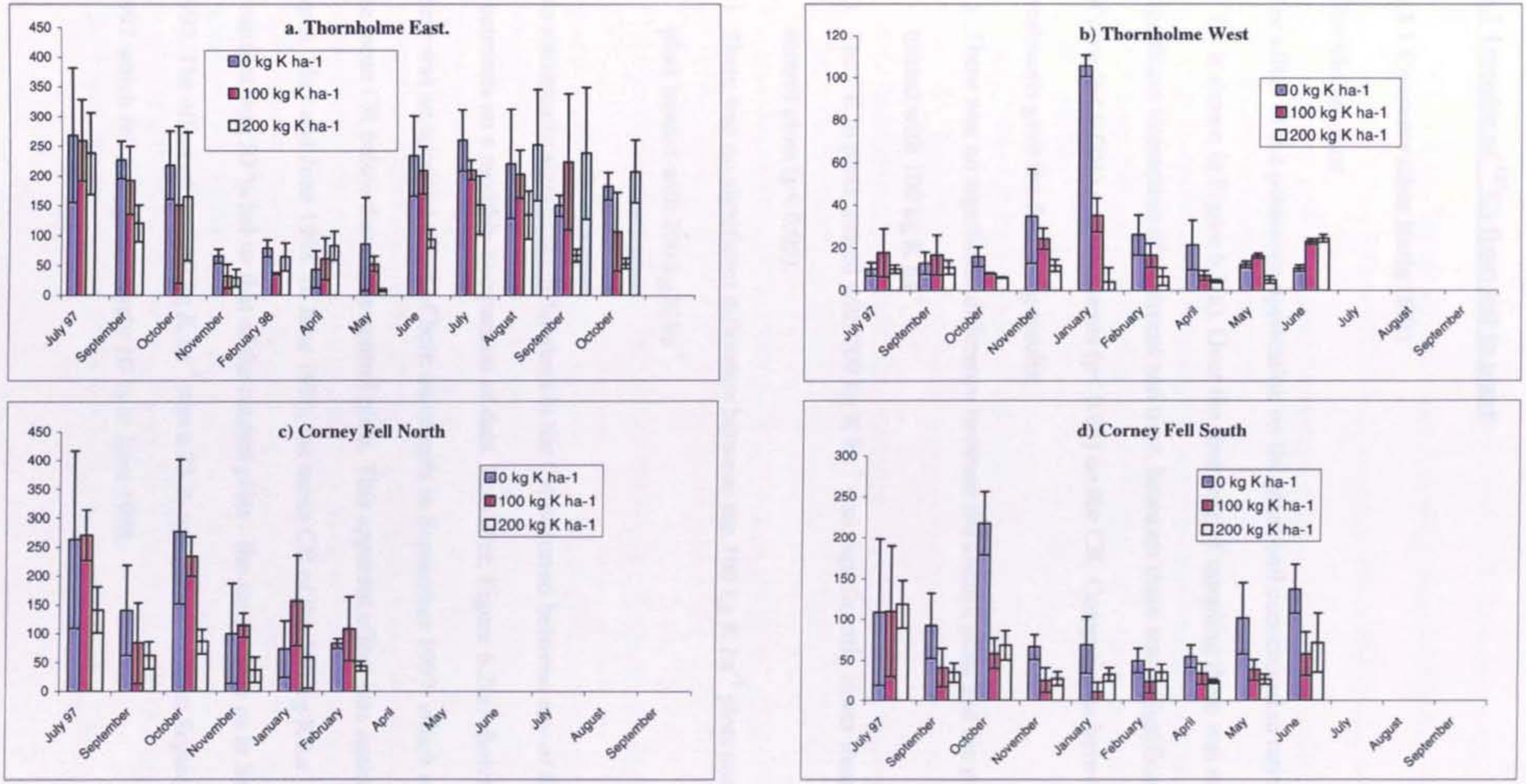


Figure 6.1 Activity concentration of ^{137}Cs in above-ground standing biomass (Bq kg^{-1})

6.3 Transfer of ^{137}Cs from soil to plant

6.3.1 Concentration Ratio (CR)

Thornholme East

The effect of the potassium application on the plant-soil concentration ratio (CR) of ^{137}Cs is shown in Figure 6.2(a). Over the first year of sampling there was no significant interaction of treatment and time, however there was a significant effect of time ($p< 0.001$) and treatments ($p< 0.05$) on the CR. Comparisons between the treatments gave the following results:

1) There was no significant difference between the control plots and the plots treated with 100 kg K ha^{-1}.
2) The CR in plots treated with 200 kg K ha^{-1} was significantly lower than the control plots ($p< 0.05$).
3) There was no significant difference between the 100 kg K ha^{-1} plots and the plots treated with 200 kg K ha^{-1}.

No statistically significant differences in the CR occurred between any of the three treatments on a monthly comparison of data. However, Figure 6.2(a) shows that there was an apparent effect of both treatments in September 1997, which reduced the mean CR below that of the control plots. This apparent effect was again seen in April, May and June 1998. In June 1998, the mean CR of the 200 kg K ha^{-1} treatment was 50 % below that of the control plots - the same value as in September 1997. The effect of the 100 kg K ha^{-1} was a 25 % reduction in CR in September 1997 which fell to approximately 10 % in June 1998.

Following the repeat application of potash in June 1998, the effect of the treatments on the ^{137}Cs CR was highly variable. From June until October 1998, there were significant ($p < 0.001$) effects of both time and treatment on the CR, but no significant interaction of treatment and time. Comparisons between treatments from June until October 1998 showed that:

1) There was no significant difference in the CR between the control plots and the plots treated with a repeat application of 100 kg K ha^{-1} or a single application of 200 kg K ha^{-1}.
2) The CR was significantly lower in plots treated with a repeat application of 200 kg K ha^{-1} than the control plots, plots treated with a repeat application of 100 kg K ha^{-1} and plots treated with a single application of 200 kg K ha^{-1} ($p < 0.001$).
3) There was no significant difference between the plots treated with a repeat application of 100 kg K ha^{-1} and the plots treated with 200 kg K ha^{-1}.

The CR was significantly lower in August 1998 in plots that had been treated with a repeat application of 200 kg K ha^{-1} than the control plots ($p < 0.05$). Figure 6.2(a) shows that the mean CR in the plots treated with a repeat application of K was less than the mean CR of the controls from July 1997 until the end of sampling in October 1998 (with the exception of 100 kg K ha^{-1} plots in August). Figure 6.2(a) also shows that effect of a single application of 200 kg K ha^{-1} varied between successive years, the CR was reduced by 30 % more in September 1997 than in September 1998. The repeat application of 200 kg K ha^{-1} appeared to enhance the reduction in the CR, in October 1997 the mean CR was 15 % lower than the mean of the control plots, whilst in 1998 this reduction had increased to 36 %.

Thornholme West

The effect of the potash application on the plant-soil concentration ratio is shown in Figure 6.2(b). There was a significant effect of time ($p < 0.001$) and treatment ($p < 0.001$) over the study period, but no significant interaction of treatment and time. Comparisons between the potash treatments showed that:

1) There was no significant difference in the ^{137}Cs CR between the control plots and the plots treated with 100 kg K ha^{-1}.
2) Vegetation treated with 200 kg K ha^{-1} had significantly lower CR values than the control plots or plots treated with 100 kg K ha^{-1} ($p < 0.001$).

There were no statistically significant differences in the CR of ^{137}Cs between any of the three treatments in any month over the study period. However, Figure 6.2(b) shows that in October 1997, plots treated with 100 and 200 kg K ha^{-1} had mean CR values which were 50 and 67 %, respectively, of that of the control plots. In November 1997, plots treated with 200 kg K ha^{-1} had CR values 60 % lower than the control plots, however, plots treated with 100 kg K ha^{-1} had a mean CR 28 % greater than the control plots. In February and April of 1998, plots treated with 100 and 200 kg K ha^{-1} had CR values which were 50 and 80 % lower than the mean of the controls. In June 1998, both K treatments appeared to have caused the CR to increase by 40 %.

Corney Fell North

The effect of the potash application on the plant-soil concentration ratio is shown in Figure 6.2(c). Over the sampling period there was a significant effect of time (p<

0.001) and treatment ($p < 0.001$) but, no significant interaction of treatment and time. Comparisons between the potash treatments showed that:

1) There was no significant difference between the control plots and the plots treated with 100 kg K ha^{-1}.
2) Plots treated with 200 kg K ha^{-1} had significantly lower CR values than the control plots ($p < 0.001$) and plots treated with 100 kg K ha^{-1} ($p = 0.0012$).

There were no significant differences in the CR's between any of the three treatments in any month over the whole study period. However, for July 1997 Figure 6.2(c) shows there was an almost immediate effect of the 200 kg K ha^{-1} treatment, reducing the mean CR of ^{137}Cs to 60 % of the control plots. In September 1997, plots that had been treated with either 100 or 200 kg K ha^{-1} had CR's which were half those of the control plots. From November 1997 until February 1998, the 200 kg K ha^{-1} treatment reduced the mean CR by 50 %, however, plots treated with 100 kg K ha^{-1} had a mean CR value similar to the control.

Corney Fell South

The effect of the potash treatments on the plant-soil concentration ratio is shown in Figure 6.2(d). Over the sampling period there was a significant effect of time ($p < 0.001$) and of treatment ($p < 0.001$) but no significant interaction. Comparisons between the potash treatments showed that:

1) The CR was significantly lower in plots treated with 100 or 200 kg K ha^{-1} than in the control plots ($p < 0.001$).
2) There was no significant difference in the CR between the 100 kg K ha^{-1} plots and the 200 kg K ha^{-1} plots.

In October 1997 treated plots had a significantly lower CR than the control plots. Figure 6.2(d) also shows that these lower CR values were apparent from September 1997 until June 1998. In September 1997, the mean CR within the treated plots was approximately 50 % of that of the controls. A 50 % reduction in the CR was maintained almost uniformly from September 1997 until May 1998. In May 1997, plots treated with 100 and 200 kg K ha^{-1} had mean CR values which were 70 and 33 %, respectively, of the control values.

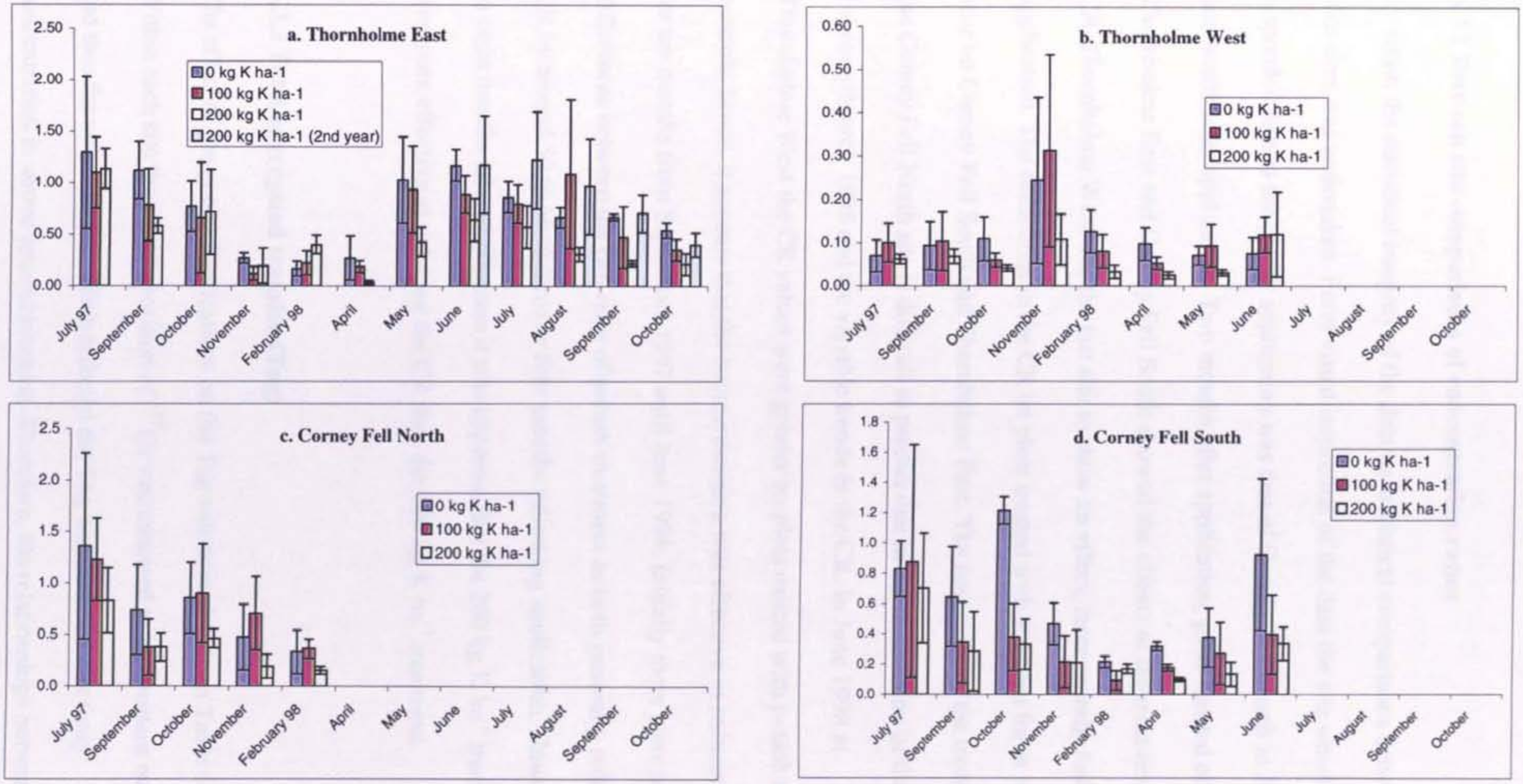


Figure 6.2 Concentration ratio soil: above-ground standing biomass

6.3.2 Between site comparisons of concentration ratios

To retain the statistical integrity of the data no statistical comparisons between the four sites was undertaken. Form visual inspection of the data the site which responded first to the potash application was that of Corney Fell North in July 1997, one month after application. Two months after application, plots located on Thornholme East and Corney Fell South showed the effects of the treatment on the CR. Thornholme West was the last site to show an effect, three months following application. The reductions in the CR on plots treated with K lasted for at least one year on Corney Fell South and Thornholme East. The longevity of the treatments on the Corney Fell North site is difficult to predict due to the destruction of the site in February/March 1998 and the variable trends in the CR. In June 1998 at Thornholme West the CR values were greater on plots treated with potash than the controls, hence, it appears that the countermeasure was effective in reducing the CR for ten months from September 1997 until June 1998. Initially there were no differences between the two rates of potash treatment as both generally reduced the CR by around 50 to 60 % three or four months following application. However, six to eight months after application it was apparent that the 200 kg K ha^{-1} treatment was more effective at reducing the CR than the 100 kg K ha^{-1} treatment.

6.3.3 Total aggregated transfer (Tag)

The effect of the potash applications on the Tag values is shown on Table 6.1. Within each site the total deposition of ^{137}Cs was assumed to be constant over time and thus the only variable which affected the Tag was that of the activity concentration in above-ground biomass. Therefore, the relationships between the

Tag values within each site are the same as for the activity concentration values reported in Figure 6.1.

Table 6.1 Derivied Tag values of treatments at all four experimental sites.

Thornholme East	**Treatment**			
Month	Control	100 kg K ha^{-1}	200 kg K ha^{-1}	200 kg K ha^{-1} (2nd year)
July 97	0.0284	0.0275	0.0252	
September 97	0.0240	0.0203	0.0128	
October 97	0.0231	0.0160	0.0175	
November 97	0.0069	0.0034	0.0030	
January 98	0.0083	0.0038	0.0068	
February 98	0.0045	0.0064	0.0087	
April 98	0.0091	0.0055	0.0009	
May 98	0.0247	0.0221	0.0100	
June 98	0.0275	0.0222	0.0160	
July 98	0.0233	0.0215	0.0143	0.0267
August 98	0.0159	0.0237	0.0071	0.0252
September 98	0.0194	0.0113	0.0056	0.0220
October 98	0.0133	0.0078	0.0050	0.0105

Thornholme West	**Treatment**		
Month	Control	100 kg K ha^{-1}	200 kg K ha^{-1}
July 97	0.0009	0.0017	0.0009
September 97	0.0012	0.0016	0.0010
October 97	0.0015	0.0007	0.0006
November 97	0.0033	0.0023	0.0011
January 98	0.0099	0.0033	0.0004
February 98	0.0024	0.0015	0.0006
April 98	0.0020	0.0006	0.0004
May 98	0.0011	0.0015	0.0005
June 98	0.0010	0.0022	0.0023

Corney Fell North	**Treatment**		
Month	Control	100 kg K ha^{-1}	200 kg K ha^{-1}
July 97	0.0295	0.0303	0.0158
September 97	0.0157	0.0094	0.0070
October 97	0.0310	0.0262	0.0097
November 97	0.0112	0.0128	0.0042
January 98	0.0082	0.0176	0.0067
February 98	0.0092	0.0122	0.0049

Corney Fell South	**Treatment**		
Month	Control	100 kg K ha^{-1}	200 kg K ha^{-1}
July 97	0.0122	0.0123	0.0133
September 97	0.0103	0.0046	0.0039
October 97	0.0244	0.0065	0.0076
November 97	0.0074	0.0028	0.0030
January 98	0.0076	0.0012	0.0036
February 98	0.0055	0.0027	0.0039
April 98	0.0061	0.0037	0.0027
May 98	0.0113	0.0043	0.0030
June 98	0.0153	0.0064	0.0080

The data presented in Table 6.1 shows that between the four study sites there was little difference in the overall relative reduction in Tag values for each treatment. In 1997, plots treated with potash typically had values 50 to 60 % lower than the controls. In 1998, treated plots generally had lower Tag values than the control plots and plots treated with 200 kg K ha^{-1} generally had lower Tag values than those treated with 100 kg K ha^{-1}.

6.3.4 Flux of ^{137}Cs from soil to above-ground biomass

Table 6.2 shows the percentage of ^{137}Cs transferred from the soil into the above-ground biomass at each site and on each sampling occasion. No statistical testing of this flux data was undertaken.

Thornholme East

The effect of the potash treatments on the flux of ^{137}Cs from soil to plant was apparent two months after application. In September 1997, the 100 and 200 kg K ha^{-1} treatments reduced the flux by 22 and 43 %, respectively. In November 1997, both treatments reduced the flux by 44 %, but in January and February 1998, there was no apparent effect of the potash treatments. In April 1998, the 100 and 200 kg K ha^{-1} treatments reduced the flux of ^{137}Cs by 50 and 90 % respectively. One year after KCl application in June 1998 the 200 kg K ha^{-1} treatment reduced the flux of ^{137}Cs from soil to plant by 60 %, however, there appeared to be little effect of the 100 kg K ha^{-1} treatment in May and June 1998.

The re-application of potash in June 1998 did not appear to affect the flux of ^{137}Cs from soil to plant until September 1998. This lag of time between application and the detection of an effect was the same in 1997. The reapplication of 200 kg K ha^{-1} caused a reduction in the flux of ^{137}Cs by 84 and 66 % in September and October 1998 respectively. In plots treated with 100 kg K ha^{-1} the flux was reduced by 40 and 45 % in the same months. In plots treated with a single application of 200 kg K ha^{-1} in 1998, the effect was similar to that of a repeat 100 kg K ha^{-1} treatment with reductions of 40 and 50 % in September and October 1998. These values also indicate that at Thornholme East there was no change in the effects of the 200 kg K ha^{-1} application in September and October 1997, compared with 1998.

Thornholme West

An effect of the potash application on the flux of ^{137}Cs was not detected until three months after application. In October 1997, the flux of ^{137}Cs in the plots treated with 100 and 200 kg K ha^{-1} was 43 and 56 % lower than that of the control plots. The effect of the treatments reached a maximum in January 1998 with a reduction in the flux by 66 and 95 % (100 and 200 kg K ha^{-1} plots respectively). In May 1998, the 100 kg K ha^{-1} treatment no longer had a negative effect on the flux and in June 1998 the effects of both treatments enhanced the flux of ^{137}Cs by 120 %.

Corney Fell North

The effect of the potash treatments on the flux of ^{137}Cs was apparent on the first sampling occasion in July 1997 when the 100 and 200 kg K ha^{-1} treatments caused a reduction in the flux of 23 and 55 %, respectively; in September 1997 these reductions increased to 55 and 66 %. In October and November 1997 the effects of the100 kg K ha^{-1} treatment appeared to diminish with reductions of 32 and 24 % compared to the control. In January and February 1998 the 100 kg K ha^{-1} treatment appeared to no longer have an effect as the treatment increased the flux value by 50 and 7 % respectively. In comparison the 200 kg K ha^{-1} treatment continued to reduce the flux of ^{137}Cs by 54 % in February 1998.

Corney Fell South

The effects of the potash treatments in reducing the flux of ^{137}Cs were apparent from September 1997 until the end of sampling in June 1998. The reductions in flux due to the two treatments were similar throughout the study with noticeable differences only occurring in January, April and May 1997. The reductions in transfer ranged from 40 to 55 % over the entire study with no observable trends in treatment effect over time.

Table 6.2 % Flux of ^{137}Cs from soil to above ground biomass.

Thornholme East	Treatment			
Month	Control	100 kg K ha^{-1}	200 kg K ha^{-1}	200 kg K ha^{-1} (2nd year)
July 97	1.5696	1.4980	1.5294	
September 97	1.4132	1.1191	0.8077	
October 97	1.3105	0.8637	1.0929	
November 97	0.2510	0.1168	0.1014	
January 98	0.2775	0.1272	0.2360	
February 98	0.1635	0.2127	0.3022	
April 98	0.3363	0.1633	0.0305	
May 98	1.1059	1.0190	0.4647	
June 98	1.6152	1.2181	0.9461	1.5968
July 98	1.3588	1.0932	0.8752	1.1433
August 98	0.8644	1.0694	0.4480	0.9194
September 98	1.2513	0.7519	0.3316	0.7403
October 98	0.9421	0.5190	0.3219	0.4506

Corney Fell North	Treatment		
Month	Control	100 kg K ha^{-1}	200 kg K ha^{-1}
July 97	0.8860	0.6899	0.4058
September 97	0.4686	0.2153	0.1687
October 97	0.8337	0.5793	0.2218
November 97	0.3420	0.2604	0.1032
January 98	0.2401	0.3747	0.1735
February 98	0.2639	0.2844	0.1233

Thornholme West	Treatment		
Month	Control	100 kg K ha^{-1}	200 kg K ha^{-1}
July 97	0.0307	0.0579	0.0358
September 97	0.0407	0.0513	0.0385
October 97	0.0459	0.0266	0.0201
November 97	0.1008	0.0740	0.0368
January 98	0.2968	0.1056	0.0116
February 98	0.0690	0.0415	0.0167
April 98	0.0744	0.0214	0.0120
May 98	0.0408	0.0537	0.0160
June 98	0.0314	0.0748	0.0780

Corney Fell South	Treatment		
Month	Control	100 kg K ha^{-1}	200 kg K ha^{-1}
July 97	0.2365	0.1971	0.2136
September 97	0.1760	0.0720	0.0630
October 97	0.3621	0.1033	0.1194
November 97	0.1201	0.0464	0.0456
January 98	0.1333	0.0190	0.0545
February 98	0.0895	0.0457	0.0580
April 98	0.1001	0.0632	0.0418
May 98	0.1998	0.0621	0.0418
June 98	0.2466	0.1124	0.1089

6.4 Chapter 6 discussion

Chapter 6 was the first chapter that considered the effect of KCl application to the study sites. It has been shown that the application of KCl was capable of causing significant reductions in the concentration of ^{137}Cs in the biomass. However, the effectiveness of the KCl application varied between rate of KCl application and between site. At Thornholme East, Thornholme West and Corney Fell North the application of 200 kg K ha^{-1} produced significantly greater reductions than an application of 100 kg K ha^{-1}, whilst at Corney Fell South there were no significant difference between the two potash applications.

The variability in the effectiveness of the KCl application between treatments and time is likely to have been influenced by site characteristics and the behaviour of K in the soil which is considered in Chapter 7. Chapter 2 identified that the concentration of K in the soil needed to be evaluated when determining the effectiveness of an application of KCl to reduce ^{137}Cs transfer. A general discussion of the effects of K application on the soil and its effect on ^{137}Cs in the biomass is presented in a general discussion of the effects of KCl in Chapter 10.

Data presented in Chapter 6 showed that the highest monthly reduction of ^{137}Cs transfer at Thornholme East and both Corney Fell sites occurred three to four months following application of potash (Table 6.3).

Table 6.3 Maximum relative reduction in ^{137}Cs activity (based on activity concentrations in plants and soils)

Site	Treatment (kg K ha^{-1})	Reduction in ^{137}Cs compared to control (%)
Thornholme East	100	53 (November)
	200	58 (November)
Corney Fell North	100	41 (September)
	200	69 (October)
Corney Fell South	100	74 (October)
	200	69 (October)

The maximum reductions in the flux values (Table 6.4) are similar to the CR values (Table 6.3) and any differences between these two values reflect differences in the vegetation mass sampled from each of the plots.

Table 6.4 Maximum relative reduction in ^{137}Cs activity (based on % flux)

Site	Treatment (kg K ha^{-1})	Reduction in ^{137}Cs compared to control (%)
Thornholme East	100	34 (October)
	200	60 (November)
Corney Fell North	100	55 (September)
	200	74 (October)
Corney Fell South	100	73 (October)
	200	67 (November)

Tables 6.3 and 6.4 both show that the treatments reduced ^{137}Cs transfer by up to 74 %. The tables also show that an application of 200 kg K ha^{-1} was more effective than the 100 kg K ha^{-1} treatment in highly organic soils such as Corney Fell North and Thornholme East, whilst there was little difference between treatments on soils which had a thinner organic horizon such as Corney Fell South.

The effectiveness of the countermeasure may vary between successive years due to climatic differences, to test this, at Thornholme East the application of KCl occurred in 1997 and 1998. Analysis of this data showed that the format of data presentation is critical in assessing the effect of the treatments. If the data was expressed as activity concentrations, CR or Tag values there was a significant effect of a 200 kg K ha^{-1} treatment in 1997 yet no effect in 1998 (Figures 6.1, 6.2 and Table 6.1). However, when the data was reported as flux values, summarised in Table 6.5, marked reductions in ^{137}Cs flux which exceed those in 1997 occur.

Table 6.5 Reduction in ^{137}Cs flux from soil to plant at Thornholme East 1997 and 1998 for an application of 200 kg K ha^{-1}.

	% reduction in ^{137}Cs flux		
Year	July	September	October
1997	3	43	17
1998	16	41	53

The format of the data presented is therefore critical when assessing any effect of the KCl application.

In 1998 KCl was reapplied to plots treated with 100 and 200 kg K ha^{-1} in 1997. Plots treated with a repeat application of 200 kg K ha^{-1} recorded a reduction of the ^{137}Cs concentration in the biomass by over 50 % in 1998 compared to a single application of KCl. However, plots treated with a repeat application of 100 kg K ha^{-1} showed no such enhanced reduction in ^{137}Cs concentration.

Chapter 5 identified that at Thornholme West the transfer of ^{137}Cs from soil to plant significantly increased in the winter period. Data generated in this chapter infers that this period the KCl application was effective at reducing the transfer of ^{137}Cs from soil to plant. However, such reductions may be attributable to the relative increase of ^{137}Cs concentration in the control plots rather than any effect of K application. Further data is required from chapters 7, 8 and 9 before a discussion of the effects of K application at Thornholme West can be made in Chapter 10.

The longevity of the application in producing a reduction in ^{137}Cs transfer is difficult to determine at Thornholme West since further data is required before it can be established whether KCl application had any effect on ^{137}Cs in the biomass. The literature review identified that the effectiveness of a KCl application would be dependent on the longevity of K in the soil, thus the longevity of the application in reducing ^{137}Cs transfer is discussed in Chapter 10.

6.5 Chapter 6 conclusions

A number of hypotheses were tested within chapter 6; 1) The countermeasure significantly reduces the transfer of ^{137}Cs from soil to plant in a range of upland soils; 2) The reduction in the ^{137}Cs concentration in the biomass as a result of potassium application is not affected by the depth of the organic horizon; 3) An application of 200 kg K ha^{-1} has a significantly greater effect on reducing the transfer of ^{137}Cs from soil to plant than an application of 100 kg K ha^{-1}; 4) The countermeasure is significantly capable of reducing the ^{137}Cs transfer from soil to plant for greater than one year, and 5) There is no difference between the effectiveness of the countermeasures between two successive years.

Chapter 6 has been able to show that hypotheses 1, 3 and 5 are valid, however acceptance is dependent on the units of measurement used to present the data. The effects of K application in reducing ^{137}Cs in the biomass persist for at least one year at Thornholme East and Corney Fell South. It is impossible to determine if the effects of K application persisted for a year at Corney Fell North due to its destruction in early 1998. Further information is required to determine the mechanism that produced significant reductions of ^{137}Cs in the biomass at Thornholme West in the winter period and to test the validity of hypotheses 2 and 4.

Chapter 7

The effect of the potash application on potassium within the soil and standing above-ground biomass

7.1 Introduction

This study aimed to determine the effects of an addition of K on the soil and plant biomass over a range of organic soils. It was therefore necessary to establish whether the supplementary application of potash significantly changed the concentration of K in the soil such that it may effect other nutrients in the soil and biomass. As the aim of the thesis was to determine the 'side effects' of KCl application, Chapter 7 does not attempt to test any specific hypothesis but aims to generate data that will permit a discussion of the effect of changing K concentration in the soil and biomass.

Chapter 7 presents data on K in the lysimeter water, in soil and in biomass in sections 7.2, 7.3 and 7.4 respectively. The amount of K was quantified using standard methodologies described in Chapter 4. At each site the concentration of K added through precipitation was assumed to be uniform over the experimental plots. Such inputs of K from precipitation were quantified and discussed in Chapter 5. Statistical analysis of data presented in this chapter was undertaken using the GLM model outlined in Chapter 4.

7.2 Loss of potassium from the soil

Thornholme East

The effect of the potash treatments on the K collected in the lysimeter water is shown in Figure 7.1. From July 1997 until June 1998, the total K in the lysimeters showed a significant interaction between treatment and time ($p < 0.05$).

Comparisons between the treatments gave the following results:

1) Significantly more K was lost from plots treated with 100 kg K ha^{-1} ($p < 0.01$) or 200 kg K ha^{-1} ($p < 0.001$) than the control plots.
2) Significantly less K was lost from the 100 kg K ha^{-1} plots compared to plots treated with 200 kg K ha^{-1} ($p < 0.001$).

In any single sampling month there were no statistically significant differences between plots treated with 100 kg K ha^{-1} and the control plots. However, there were significantly greater quantities of K present in the lysimeter water from plots treated with 200 kg K ha^{-1} than either the control or 100 kg K ha^{-1} plots in July 1997 ($p < 0.01$). In August 1997 plots treated with 200 kg K ha^{-1} had significantly greater quantities of K in the lysimeters than the control plots ($p < 0.01$). Figure 7.1 shows that although not statistically significant, a greater quantity of K was recorded in the lysimeter water of plots treated with potash than the control plots from July until December 1997. The figure also shows that the lysimeters installed beneath plots treated with 200 kg K ha^{-1} contained the most K. In July 1997, one month after potash application, 2000 mg more K was lost from plots treated with 200 kg K ha^{-1} than the control plots. This is equivalent to 10 % of the total amount of K added to the soil surface. The loss of K from the upper soil profiles fell rapidly and in November 1997 less than 1 % of the total K added to the soil surface was detected in the lysimeter water. However, over the first five months following potash application almost 17 % of the K applied to the 200 kg K ha^{-1} plots and 5 % of the K applied to the 100 kg K ha^{-1} plots had been collected in the lysimeter water.

Following the re-application of potash to the Thornholme East site in June 1998, the amount of K in the lysimeter water was only significantly affected by treatment ($p< 0.0001$). Comparisons between the four treatments showed that:

1) Significantly more K was lost from plots treated with potash than the control plots ($p< 0.001$).
2) There were no significant differences between potash treatments.

From June 1998 until October 1998, the amount of K present in the lysimeter water declined over time in all the plots treated with potash. In July 1998, significantly greater quantities of K were collected from all treated plots than the control plots ($p< 0.01$). However, in September 1998, three months after potash application there were no significant differences between the treatments. Figure 7.1 shows that greater amounts of K were collected from plots treated with a single application of 200 kg K ha^{-1} than from plots treated with a repeat application of potash. From July until October 1998, (assuming that all the potash added in 1997 had been either permanently retained within the soil system or lost from it), the K in the lysimeter water accounted for 16.7 and 4.9 % of the K added to plots via a repeat application of 100 and 200 kg K ha^{-1}, respectively. Sixteen percent of the K added to plots with a single application of 200 kg K ha^{-1} in June 1998 was collected in the lysimeter water from June until October. A rapid decline in the amount of K in the lysimeters occurred, from approximately 5 % in July to less than 1 % of the remaining K in October 1998.

Thornholme West

The effect of the potash treatments on the K in the lysimeter water is shown in Figure 7.2. The amount of K in the lysimeter water, was only significantly affected by treatment ($p< 0.05$), with significantly greater losses occurring in plots treated with 200 kg K ha^{-1} than the control plots ($p< 0.05$). There were no statistically significant differences between any of the three treatments on any single sampling occasion. Figure 7.2 shows that in August and November 1997, the mean concentration of K present in the lysimeter water from plots treated with 200 kg K ha^{-1} was greater than the controls and the plots treated with 100 kg K ha^{-1}. The K collected from plots treated with 200 kg K ha^{-1} represented 2 % of the K applied to the soil surface.

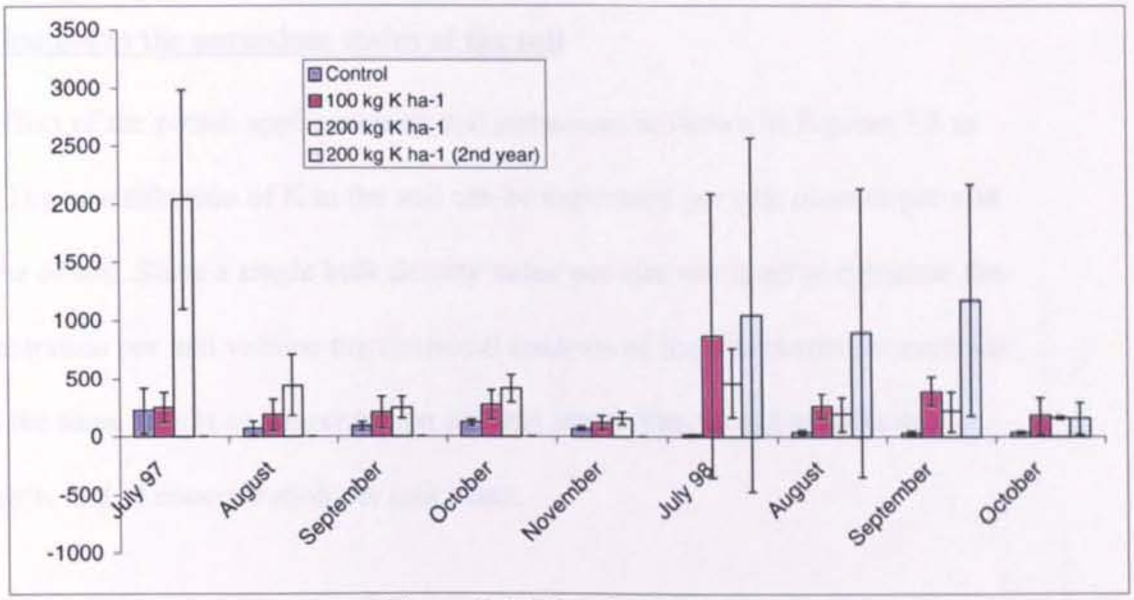


Figure 7.1. Thornholme East
Total K present in lysimeter water (mg m^{-2})
(mean and one standard deviation)

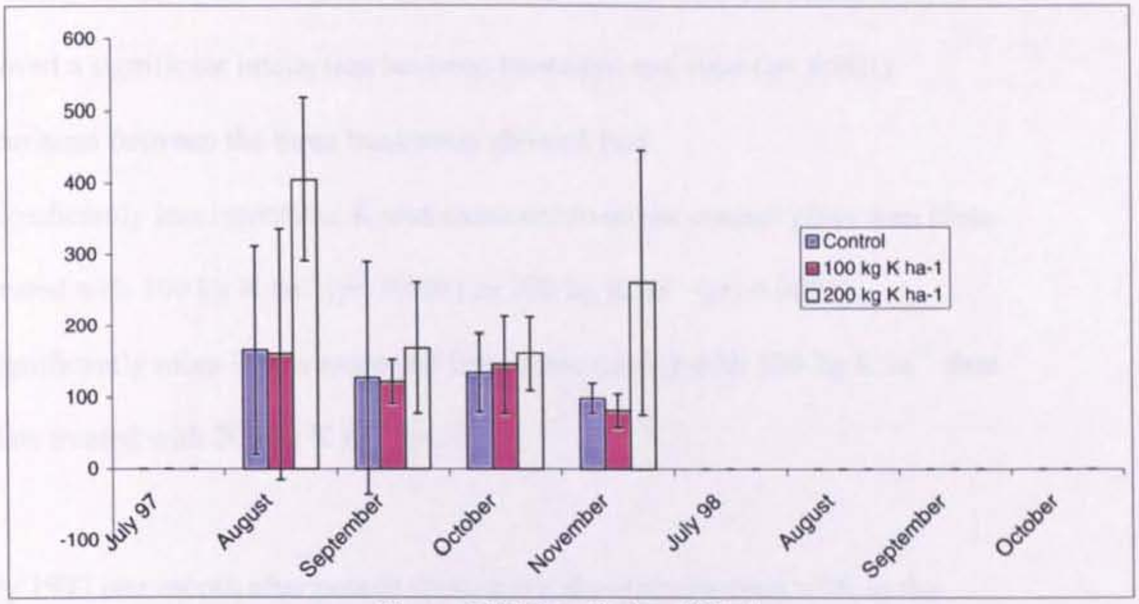


Figure 7.2 Thornholme West.
Total K present in lysimeter water (mg m^{-2})
(mean and one standard deviation)

7.3 Changes in the potassium status of the soil

The effect of the potash application on soil potassium is shown in Figures 7.3 to 7.10. The concentration of K in the soil can be expressed per unit mass or per unit volume of soil. Since a single bulk density value per site was used to calculate the concentration per unit volume the statistical analysis of the treatments for each site gives the same results as concentration per unit mass. The format used in this section is that of concentration per unit mass.

7.3.1 Potassium in the soil interstitial water

Thornholme East

The effect of the potash treatments on the concentration of K in the interstitial soil water is shown in Figure 7.3. From July 1997 until June 1998 the concentration of K showed a significant interaction between treatment and time ($p < 0.001$). Comparisons between the three treatments showed that:

1) Significantly less interstitial K was extracted from the control plots than plots treated with 100 kg K ha^{-1} ($p < 0.001$) or 200 kg K ha^{-1} ($p < 0.0001$).
2) Significantly more K was extracted from plots treated with 100 kg K ha^{-1} than plots treated with 200 kg K ha^{-1} ($p < 0.05$).

In July 1997 one month after potash application the concentration of K in the interstitial water was significantly greater in plots treated with 200 kg K ha^{-1} than the control plots ($p < 0.01$). There were no other significant differences between the treatments until June 1998 when the concentration of K in plots treated with either 100 or 200 kg K ha^{-1} was significantly greater than the control plots ($p < 0.05$).

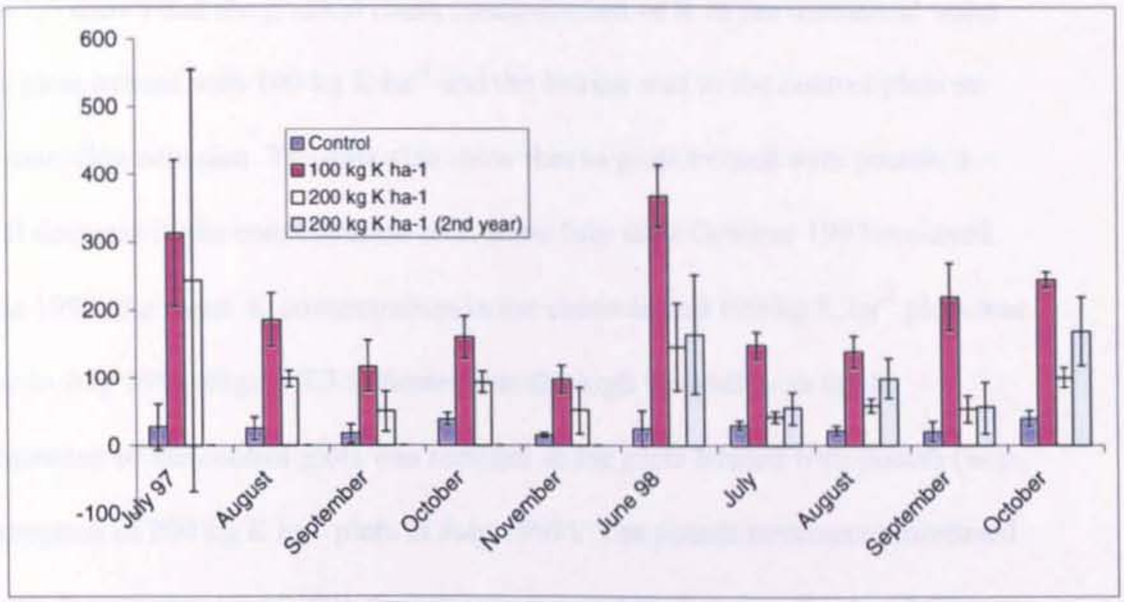


Figure 7.3 Thornholme East.
Concentration of K in interstitial water (mg kg^{-1} dry soil)
(mean and one standard deviation).

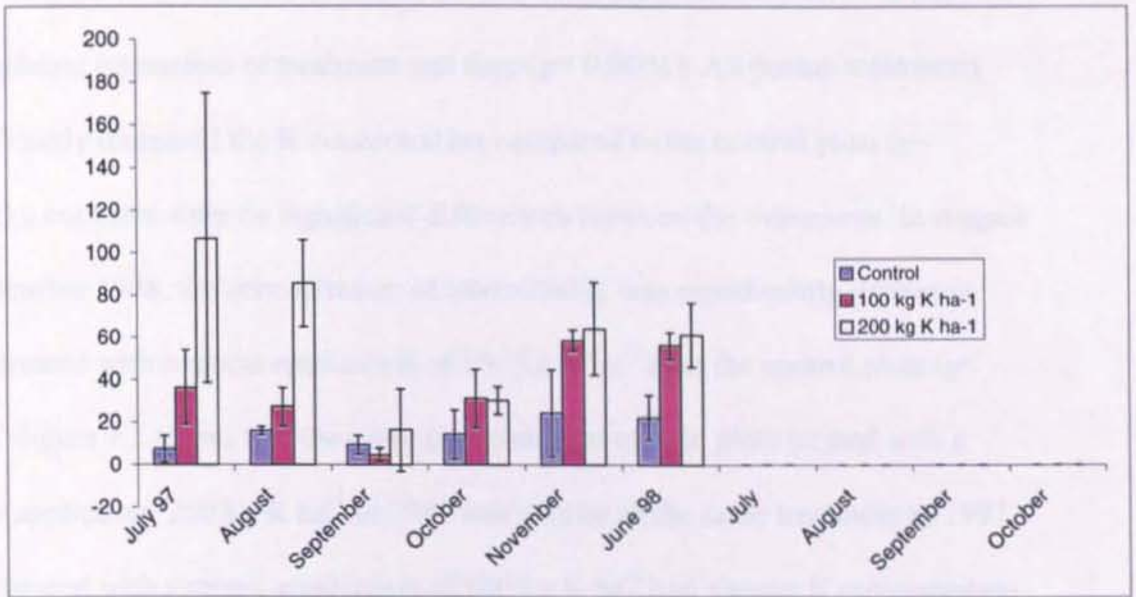


Figure 7.4 Thornholme West.
Concentration of K in interstitial water (mg kg^{-1} dry soil)
(mean and one standard deviation).

Figure 7.3 shows that the greatest mean concentration of K in the interstitial water was in plots treated with 100 kg K ha^{-1} and the lowest was in the control plots on every sampling occasion. The data also show that in plots treated with potash, a general decrease in the concentration of K from July until October 1997 occurred. In June 1998, the mean K concentration in the controls and 100 kg K ha^{-1} plots was similar to July 1997. Figure 7.3 indicates that the high variability in the K concentration of the control plots was reduced in the plots treated with potash (with the exception of 200 kg K ha^{-1} plots in July 1997). The potash treatments increased the mean K concentration within the interstitial water by between three and fifteen times the mean value in the control plots. The greatest relative increases occurred in July 1997 and June 1998.

Following the re-application of potash in June 1998 the concentration of K showed a significant interaction of treatment and time ($p< 0.0001$). All potash treatments significantly increased the K concentration compared to the control plots ($p< 0.0001$), but there were no significant differences between the treatments. In August and October 1998, the concentration of interstitial K was significantly greater in plots treated with a repeat application of 100 kg K ha^{-1} than the control plots ($p< 0.05$). Figure 7.3 shows that the mean concentration of K in plots treated with a single application 200 kg K ha^{-1} in 1998 was similar to the same treatment in 1997. Plots treated with a repeat application of 100 kg K ha^{-1} had a mean K concentration in the interstitial soil water greater than any of the other plots on every sampling occasion.

Thornholme West

The effect of the potash treatments on the concentration of K in the interstitial soil water is shown in Figure 7.4. From July 1997 until June 1998 the concentration of K in the interstitial water showed a significant interaction between treatment and time ($p < 0.01$). Comparisons between the three treatments showed that:

1) Plots treated with potash had significantly more K in the interstitial water than the control plots ($p < 0.001$).
2) Plots treated with 200 kg K ha^{-1} had significantly more K in the interstitial water than plots treated with 100 kg K ha^{-1} ($p < 0.01$).

In July and August 1997 the concentration of K in the interstitial soil water was significantly greater in plots treated with 200 kg K ha^{-1} than either the control plots or the plots treated with 100 kg K ha^{-1} ($p < 0.05$). Figure 7.4 also shows that on every sampling occasion plots treated with potash had a mean concentration of K at least double that of the control plots. One month after potash application in July 1997, plots treated with 200 kg K ha^{-1} had almost three times more K in the interstitial water than plots treated with 100 kg K ha^{-1}, however, in November 1997 differences between potash treatments were negligible.

Corney Fell North

The effect of the potash treatments on the concentration of K in the interstitial soil water is shown in Figure 7.5. Over the sampling period, there was a significant effect of time and treatment ($p < 0.0001$) on the concentration of K, but no significant interaction between these two factors. Comparisons between the three treatments showed that:

1) There was no significant difference in the concentration of K between plots treated with 100 kg K ha^{-1} and the control plots.
2) Significantly greater amounts of K were present in the interstitial soil water on plots treated with 200 kg K ha^{-1} plots than either the control plots ($p< 0.0001$) or 100 kg K ha^{-1} plots ($p< 0.001$).

In July and August 1997, plots treated with 200 kg K ha^{-1} had significantly greater concentrations of K in the interstitial water than the control plots ($p< 0.05$). Figure 7.5 shows that in the first four months following potash application there was no apparent difference between the mean concentration of K in the control plots and plots treated with 100 kg K ha^{-1}. In contrast, from July until September 1997 the concentration of K in plots treated with 200 kg K ha^{-1} was far greater than either the mean of control or 100 kg K ha^{-1} plots. In November 1997, both potash treatments had a similar mean K concentration (though highly variable) which was around four times greater than the mean control concentration. However, as the site was destroyed in February or March 1998 it is impossible to determine if this trend continued in 1998.

Corney Fell South

The effect of the potash treatments on the concentration of K in the interstitial soil water is shown in Figure 7.6. Over the sampling period, there was a significant effect of both time ($p< 0.0001$) and treatment ($p< 0.001$) on K in the interstitial water. Comparisons between the three treatments showed that:

1) There was no significant difference between the concentration of K in the control plots and plots treated with 100 kg K ha^{-1}.

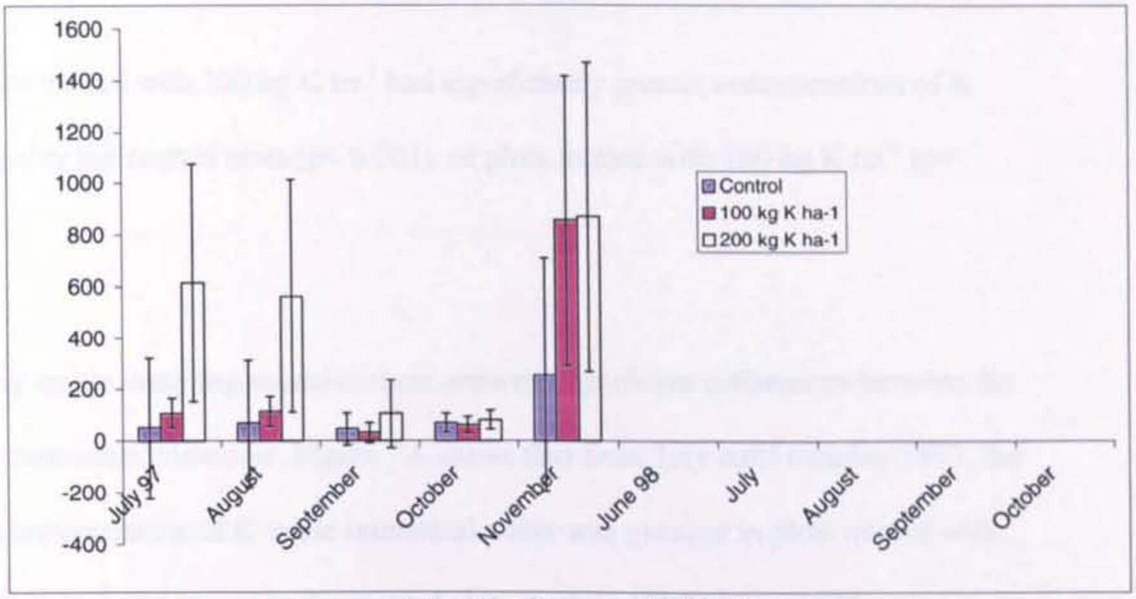


Figure 7.5 Corney Fell North
Concentration of K in interstitial water (mg kg^{-1} dry soil)
(mean and one standard deviation).

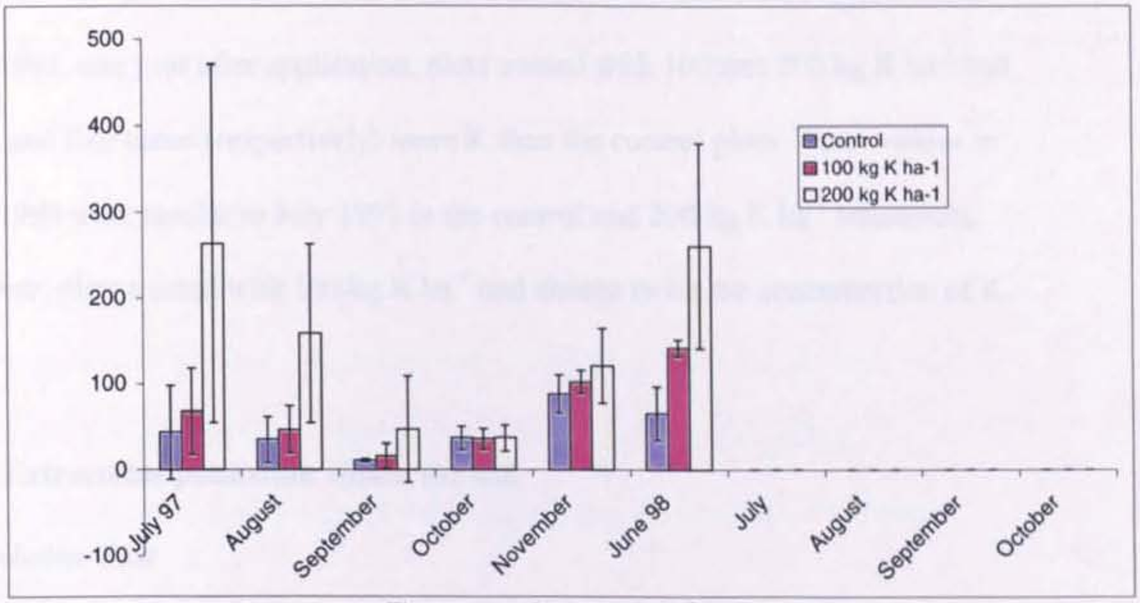


Figure 7.6 Corney Fell South
Concentration of K in interstitial water (mg kg^{-1} dry soil)
(mean and one standard deviation).

2) Plots treated with 200 kg K ha^{-1} had significantly greater concentrations of K than either the control plots ($p< 0.001$), or plots treated with 100 kg K ha^{-1} ($p< 0.05$).

On any single sampling occasion there were no significant differences between the three treatments. However, Figure 7.6 shows that from July until October 1997, the mean concentration of K in the interstitial water was greatest in plots treated with 200 kg K ha^{-1} and lowest in the control plots. In July 1997, the mean K concentration in plots treated with 100 and 200 kg K ha^{-1} was 50 and 600 % (respectively) greater than the control plots. This difference between the treatments declined over time such that in October there was no apparent difference. In November 1997 a small difference between the treatments occurred again, and in June 1998, one year after application, plots treated with 100 and 200 kg K ha^{-1} had twice and four times (respectively) more K than the control plots. These values in June 1998 were similar to July 1997 in the control and 200 kg K ha^{-1} treatments, however, plots treated with 100 kg K ha^{-1} had almost twice the concentration of K.

7.3.2 Extractable potassium within the soil

Thornholme East

The concentration of K extracted from the soil using ammonium acetate is shown in Figure 7.7. The concentration of K extracted showed a significant effect of both time and treatment ($p< 0.0001$) but no significant interaction. Comparisons between the three treatments showed that:

1) Both potash treatments had significantly greater K concentrations than the control treatment ($p<0.001$).
2) Plots treated with 200 kg K ha^{-1} had a significantly greater concentration of K than plots treated with 100 kg K ha^{-1} ($p< 0.001$).

There were no significant differences between any of the treatments on any single sampling date. However, Figure 7.7 shows that on every sampling date plots treated with 200 kg K ha^{-1} had the greatest concentration of extractable K and that the concentration was generally greater in plots treated with 100 kg K ha^{-1} than the control plots (the only exception being in November 1997). Figure 7.7 also shows that the concentration of K in plots treated with 200 kg K ha^{-1} was typically 200 % that of the control plots and only in November 1997 did this relative difference fall to 33 %. Plots treated with 100 kg K ha^{-1} showed smaller increases in K than the 200 kg K ha^{-1} treatment, generally between 5 and 50 % greater than the control plots.

Following the reapplication of potash in June 1998 and the establishment of the new treatment plots, there was a significant effect of time ($p< 0.001$) and treatment ($p= 0.001$) on the concentration of extractable K in the soil, but no significant interaction between treatment and time. Comparisons between the treatments showed that:

1) All three of the potash treatments had significantly greater concentrations of K than the control plots ($p< 0.01$).
2) There were no significant differences between any of the three potash treatments.

There were no significant differences in the concentration of extractable K between the four treatments on any single sampling occasion from July 1997 until June 1998. Figure 7.7 shows that following reapplication of potash the difference between the mean of the control plots and plots treated with a reapplication of 200 kg K ha^{-1} reduced from approximately 100 % in the first year to 25 % in the second year. Plots treated with a single application of 200 kg K ha^{-1} in June 1998 failed to demonstrate the relative increases in K concentration apparent in 1997. In the second sampling season there was little consistency as to which of the potash treatment contained the greatest concentration of K extractable in the soil.

Thornholme West

The concentrations of K in the soil which could be extracted with ammonium acetate are shown in Figure 7.8. Over the sampling period the extracted K in the soil showed significant effects of both treatment ($p< 0.0001$) and time ($p< 0.05$) but no significant interaction. Comparisons between the treatments showed that:

1) There was no significant difference between the plots treated with 100 kg K ha^{-1} and the control plots.
2) Plots treated with 200 kg K ha^{-1} had a significantly greater concentration of K than plots treated with 100 kg K ha^{-1} ($p< 0.001$) and the control plots ($p< 0.0001$).

On any single sampling occasion there were no significant differences between the control plots and 100 kg K ha^{-1} plots. Plots treated with 200 kg K ha^{-1} had significantly more K than the control plots in February 1998 ($p< 0.05$) and plots treated with 100 kg K ha^{-1} in September 1997 ($p< 0.05$). Figure 7.8 shows that over

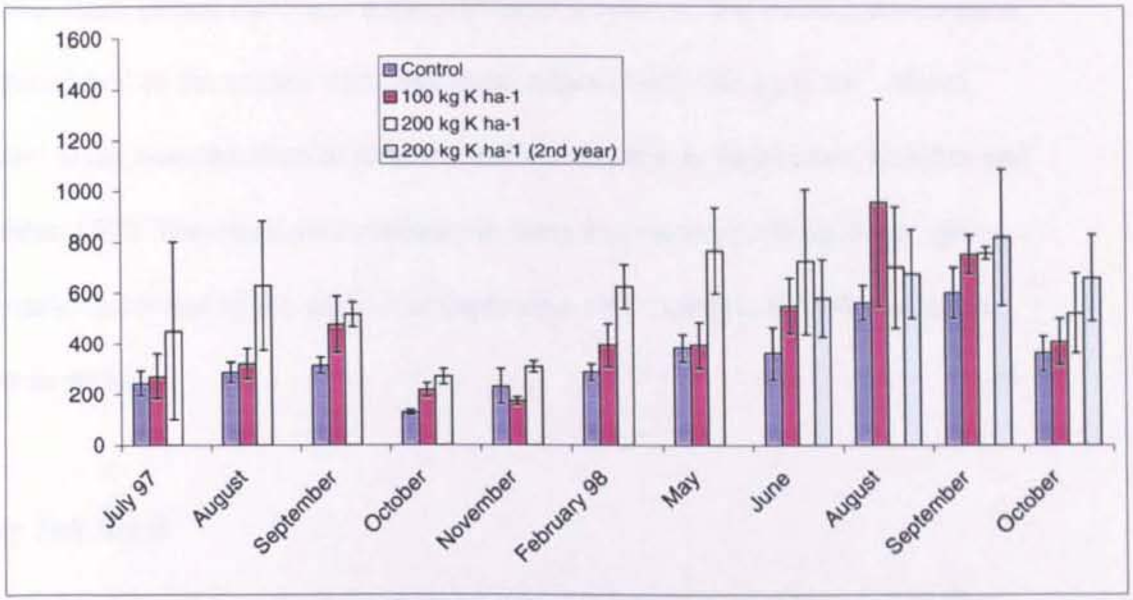


Figure 7.7 Thornholme East
Extracted K in the soil (mg kg^{-1} dry soil)
(mean and one standard deviation)

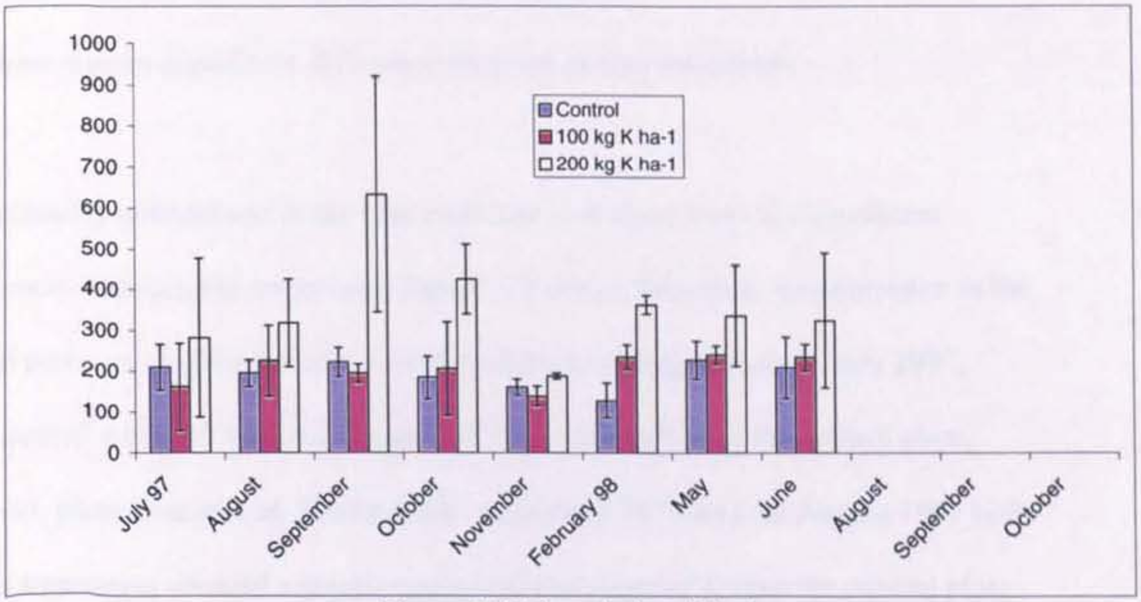


Figure 7.8 Thornholme West.
Extracted K in the soil (mg kg^{-1} dry soil)
(mean and one standard deviation)

the whole study period there was a little difference between the mean concentration of extractable K in the control plots and those treated with 100 kg K ha^{-1}. Initial increases in the concentration of K in the soil fell rapidly in September, October and November 1997. The mean concentration in plots treated with 200 kg K ha^{-1} plot was around twice that of the control in September and October, in 1998 the figure was 30 to 50 %.

Corney Fell North

The concentration of K extracted by ammonium acetate is shown Figure 7.9. The concentration of K showed a significant interaction of treatment and time ($p < 0.05$). Comparisons between the treatments showed that:

1) Significantly greater concentrations of K were detected in the soil from plots treated with potash than the control plots ($p < 0.05$).
2) There was no significant difference between potash treatments.

On a monthly comparison of the concentration of K there were no significant differences between the treatments. Figure 7.9 shows that the K concentration in the treated plots was highly variable over the whole sampling period. In July 1997, plots treated with 100 kg K ha^{-1} contained twice as much K as the control plots, however, plots treated with 200 kg K ha^{-1} contained 25 % less. In August 1997 both potash treatments showed a greater mean concentration of K than the control plots which persisted until November 1997.

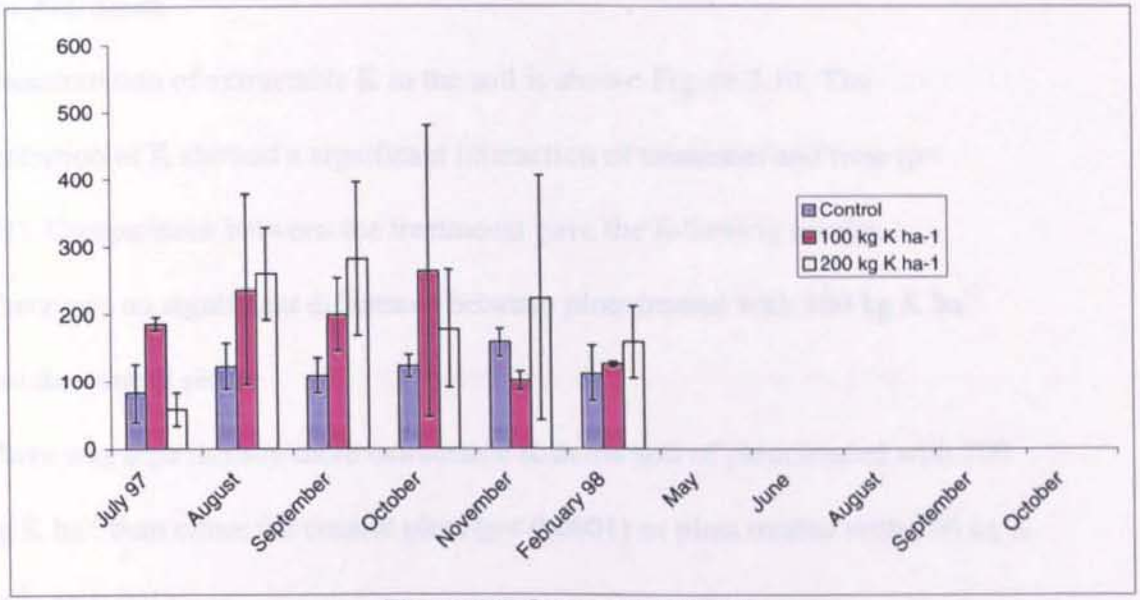


Figure 7.9 Corney Fell North.
Extracted K in the soil (mg kg^{-1} dry soil)
(mean and one standard deviation)

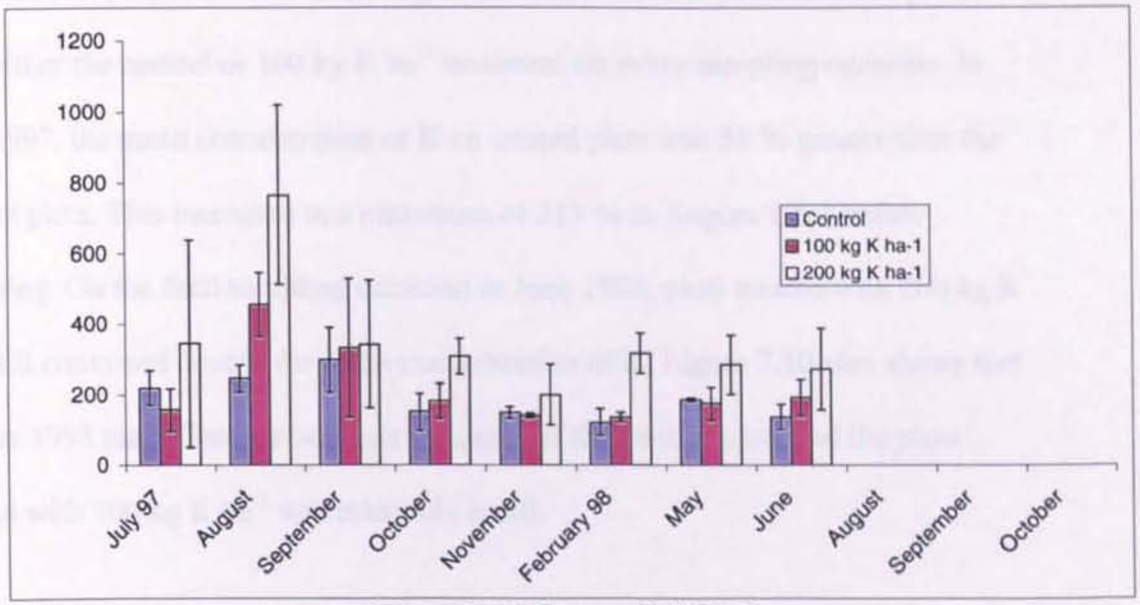


Figure 7.10 Corney Fell South
Extracted K in the soil (mg kg^{-1} dry soil)
(mean and one standard deviation)

Corney Fell South

The concentration of extractable K in the soil is shown Figure 7.10. The concentration of K showed a significant interaction of treatment and time ($p < 0.0001$). Comparisons between the treatments gave the following results:

1) There was no significant difference between plots treated with 100 kg K ha^{-1} and the control plots.
2) There was significantly more extractable K in the soil of plots treated with 200 kg K ha^{-1} than either the control plots ($p < 0.0001$) or plots treated with 100 kg K ha^{-1} ($p < 0.001$).

The treatment with 200 kg K ha^{-1} did not raise extractable K levels significantly relative to the control plots until August 1997 ($p < 0.05$). However, Figure 7.10 indicates that plots treated with 200 kg K ha^{-1} had a mean K concentration greater than either the control or 100 kg K ha^{-1} treatment on every sampling occasion. In July 1997, the mean concentration of K on treated plots was 58 % greater than the control plots. This increased to a maximum of 213 % in August 1997 before declining. On the final sampling occasion in June 1998, plots treated with 200 kg K ha^{-1} still contained double the mean concentration of K. Figure 7.10 also shows that in June 1998 the difference between the mean of the control plots and the plots treated with 100 kg K ha^{-1} was relatively small.

7.4 The effect of potash on the K concentration in the vegetation

The concentration of potassium in the vegetation can be expressed either in terms of mass (kg^{-1}) or area (m^{-2}). Both formats were statistically examined.

Thornholme East

The effect of the potash application on the concentration of K in the standing above-ground biomass is shown in Figure 7.11. There was no statistical differences between treatments from July 1997 until June 1998. However, there was a significant effect of both time ($p< 0.0001$) and treatment ($p< 0.05$) on the concentration of K, but no significant interaction between the two factors. Comparisons between the three treatments revealed that:

1) The concentration of K in plots treated with 100 kg K ha^{-1} was significantly greater than the control plots.
2) There was no significant difference in the concentration of K between plots treated with 200 kg K ha^{-1} and the control or 100 kg K ha^{-1}.

There were no significant differences in the concentration of K between the treatments within any given month. Figure 7.11 shows a greater mean concentration of K in plots treated with potash than the control plots from July 1997 until February 1998 (with the exception of November 1997). When the concentration of K in the vegetation was expressed per unit area the effect of the treatments remained similar, with two notable differences:

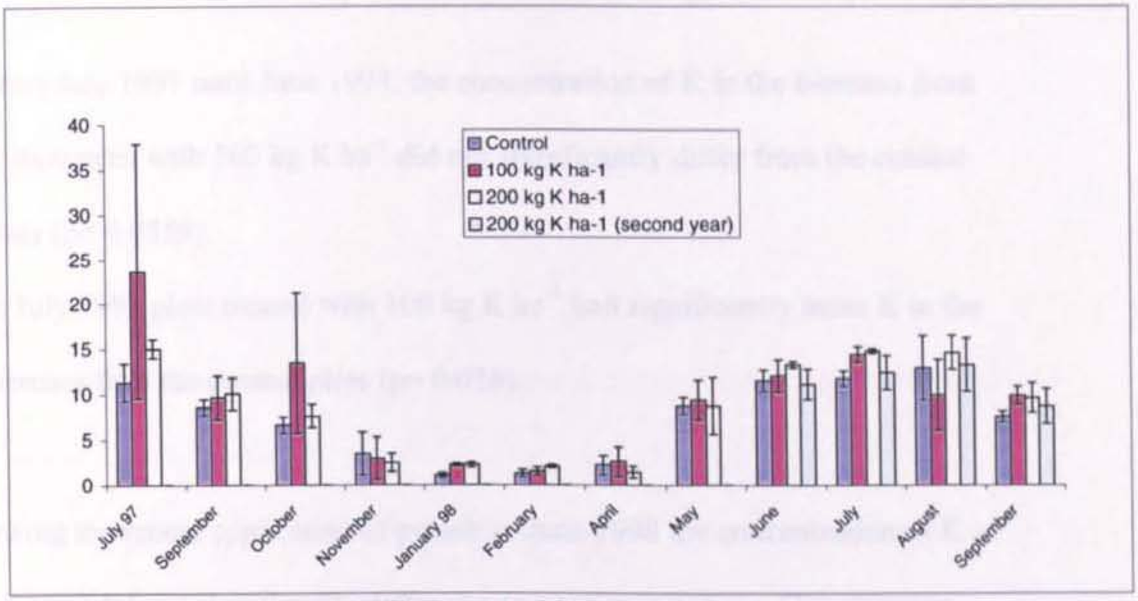


Figure 7.11 Thornholme East
Concentration of K in vegetation (g kg^{-1})
(mean and one standard deviation)

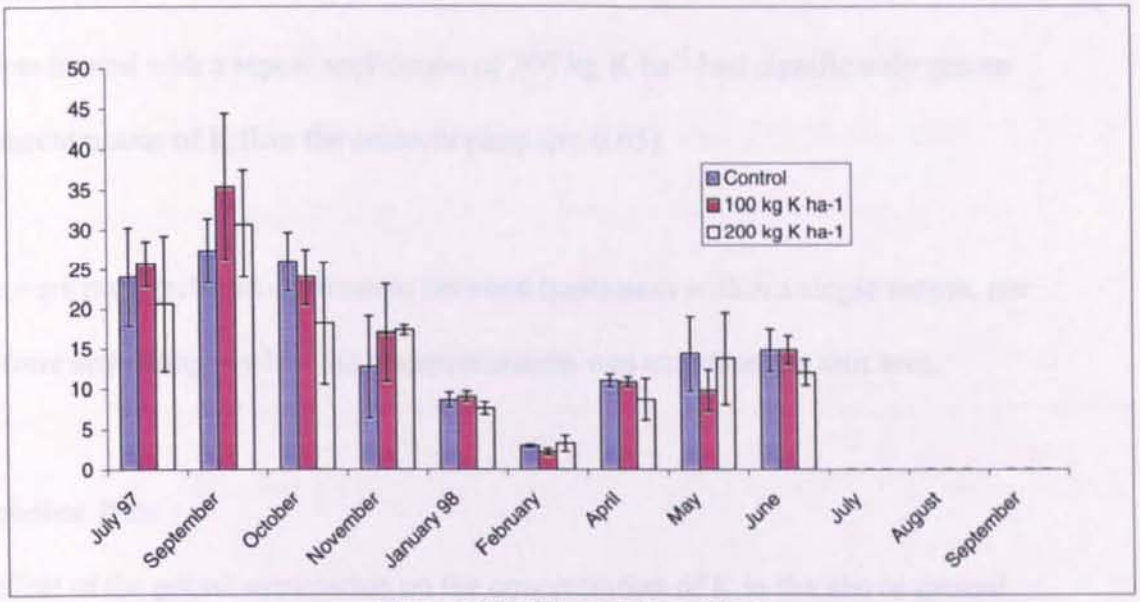


Figure 7.12 Thornholme West
Concentration of K in vegetation (g kg^{-1})
(mean and one standard deviation)

1) From July 1997 until June 1998, the concentration of K in the biomass from plots treated with 100 kg K ha^{-1} did not significantly differ from the control plots ($p = 0.0559$).
2) In July 1997 plots treated with 100 kg K ha^{-1} had significantly more K in the biomass than the control plots ($p = 0.016$).

Following the repeat application of potash in June 1998 the concentration of K in the biomass did not significantly differ due to treatment or time. Comparisons between all four treatments showed that:

1) There was no significant difference between plots treated with a repeat application of 100 kg K ha^{-1} or a single application of 200 kg K ha^{-1} and the control plots.
2) Plots treated with a repeat application of 200 kg K ha^{-1} had significantly greater concentrations of K than the controls plots ($p < 0.05$).

There were no significant differences between treatments within a single month, nor were there any changes when the K concentration was expressed as unit area.

Thornholme West

The effect of the potash application on the concentration of K in the above-ground standing biomass is shown in Figures 7.12. There was only a significant effect of time ($p < 0.0001$) on the concentration of K (per unit mass). There were no significant differences in the concentration of K between the treatments either over the entire sampling period or within any given month. Although, Figure 7.12 shows that the mean concentration of K within 100 kg K ha^{-1} plots was greater than the control plots from July 1997 until February 1998. Expressing the K concentration per unit area did not alter the statistical results.

Corney Fell North

The effect of the potash application on the concentration of K in the above-ground standing biomass is shown in Figures 7.13. Over the sampling there was only a significant of time ($p< 0.001$) on the concentration of K per unit mass. Comparisons between the three treatments showed that:

1) Plots treated with either 100 or 200 kg K ha^{-1} had significantly more K in the biomass than the control plots ($p= 0.0281$ and $p= 0.0482$ respectively).
2) There was no significant difference between the potash treatments.

There were no significant differences between the treatments within any given month, though Figure 7.13 shows that the mean concentration of K within plots treated with potash was greater than the control plots from July 1997 until the end of sampling in February 1998. When expressing the data per unit area statistical analysis showed no significant effects of the potash treatments.

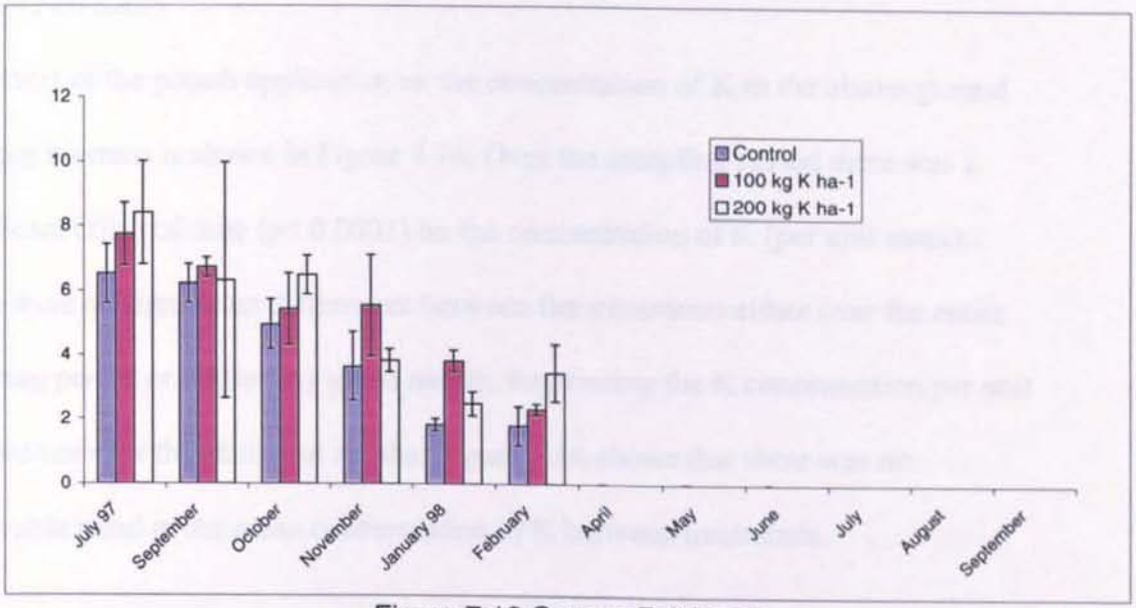


Figure 7.13 Corney Fell North
Concentration of K in vegetation (g kg^{-1})
(mean and one standard deviation)

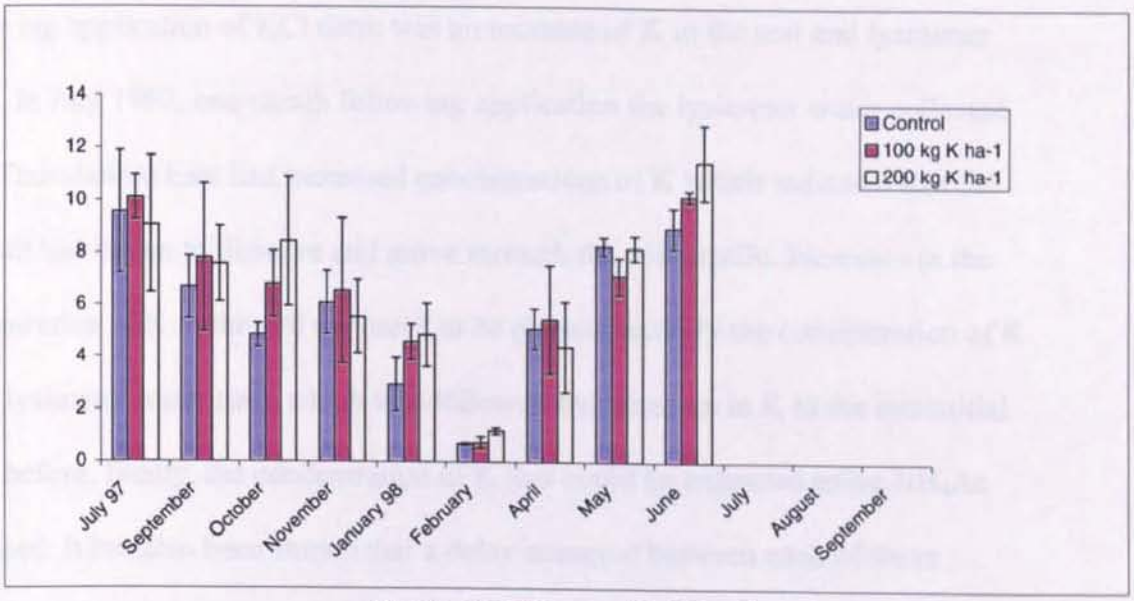


Figure 7.14 Corney Fell South
Concentration of K in vegetation (g kg^{-1})
(mean and one standard deviation)

Corney Fell South

The effect of the potash application on the concentration of K in the above-ground standing biomass is shown in Figure 7.14. Over the sampling period there was a significant effect of time ($p< 0.0001$) on the concentration of K (per unit mass). There were no significant differences between the treatments either over the entire sampling period or within any given month. Expressing the K concentration per unit area did not alter the statistical results. Figure 7.14 shows that there was no observable trend in the mean concentration of K between treatments.

7.5 Chapter 7 discussion

Chapter 7 did not test any of the hypotheses presented in section 1.1.

Following application of KCl there was an increase of K in the soil and lysimeter water. In July 1997, one month following application the lysimeter water collected from Thornholme East had increased concentrations of K which indicated that the KCl salt had begun to dissolve and move through the soil profile. Increases in the concentration of K in the soil appeared to be phased, initially the concentration of K in the lysimeter water rose, which was followed by increases in K in the interstitial water before, finally, the concentration of K that could be extracted using NH_4Ac increased. It has also been shown that a delay occurred between each of these phases, which is likely to be attributable to the time required for the K ion to move from the mass flow water onto the soil particles.

The application of KCl to the Thornholme East plots in June 1998 resulted in a greater loss of K from the plots which were treated with a single application of 200 kg K ha^{-1} in 1998 than any of the plots where reapplication occurred. The effect of reapplying 100 kg K ha^{-1} to the soil was that the plots had a similar mean concentration of K in the interstitial water as plots that had been treated with a single application of 200 kg K ha^{-1}. The cause of this effect may either be due to an enhancement of the concentration in plots treated with 100 kg K ha^{-1} following reapplication, or, a reduction in the concentration in plots treated with a single application of 200 kg K ha^{-1} due to greater losses from the soil. However, as the effect of adding a single application of 200 kg K ha^{-1} on the interstitial soil water was similar in 1998 as 1997 (Table 7.1) it is likely that reapplication of 100 kg K ha^{-1} enhanced the effect.

Table 7.1 Relative increase in concentration of K in the interstitial water at Thornholme East for an application of 200 kg K ha^{-1}.

	% increase of K in interstitial water		
Year	July	September	October
1997	1133	289	245
1998	1021	256	257

At Thornholme West and Corney Fell South the application of KCl had no significant effect on the concentration of K in the biomass. At Corney Fell North both KCl treatments induced a significant increase in K concentration in the biomass, whilst at Thornholme East significant increases of K in the biomass occurred on plots treated with 100 kg K ha^{-1} KCl in 1997 and plots treated with a repeat application of 200 kg K ha^{-1} in 1998. The underlying cause of this difference between Corney Fell North and the other three sites may be the differing physical properties of the site which were characterised in Chapter 5. Chapter 10 considers how these properties interrelate and why this effect was recorded at Corney Fell North.

7.6 Chapter 7 conclusions

Chapter 7 has shown that the application of K significantly increased the concentration of K in the soil and at some sites in the biomass. Chapter 10 will allow consideration of such increases and the potential side-effects of KCl application.

Chapter 8

Secondary effects of the potash application on the soil

8.1 Introduction

Through GLM statistical analysis, this chapter aims to determine the validity of the eighth hypothesis given in section 1.1, that the application of K significantly raises soil pH. Subsequently, it examines the effect of potash application on the chemistry of the lysimeter water and interstitial soil water. In section 8.5 the effects of application on extractable Mg, Cu and Ca are shown. This chapter will also provide data to permit hypothesis 6 to be tested, which states that the effect (of the K application) on other nutrients depends on the underlying geology.

8.2 The effect of potash application on soil pH

Thornholme East

There was a significant interactive effect between treatment and time on the soil pH over the first year of study ($p < 0.05$). There were also significant differences in the soil pH between treatments:

1) The soil pH was significantly ($p < 0.01$) greater in all plots treated with potash than the control plots.
2) The soil pH was significantly ($p < 0.01$) greater in plots treated with 200 kg K ha^{-1} than plots treated with 100 kg K ha^{-1}.

Figure 8.1(a) shows that the mean pH of plots treated with potash was generally greater than the control plots. However, the pH in the plots treated with potash was only significantly greater than the control plots in July and August 1997 ($p < 0.05$). Following the reapplication of potash there was a significant effect on the pH in all four treatments:

1) The soil pH was significantly greater in all plots treated with potash than the control plots ($p < 0.0001$).
2) The soil pH was significantly greater in plots treated with either a single or repeated application of 200 kg K ha^{-1} than plots treated with a repeated application of 100 kg K ha^{-1} ($p < 0.0001$).
3) The soil pH was significantly greater in plots treated with a repeated application of 200 kg K ha^{-1} than plots treated with a single application of 200 kg K ha^{-1} ($p < 0.0001$).

Within each month the soil pH of all the plots treated with potash was significantly greater than the control plots from one month after application until the end of sampling in October 1998 ($p < 0.001$).

Thornholme West

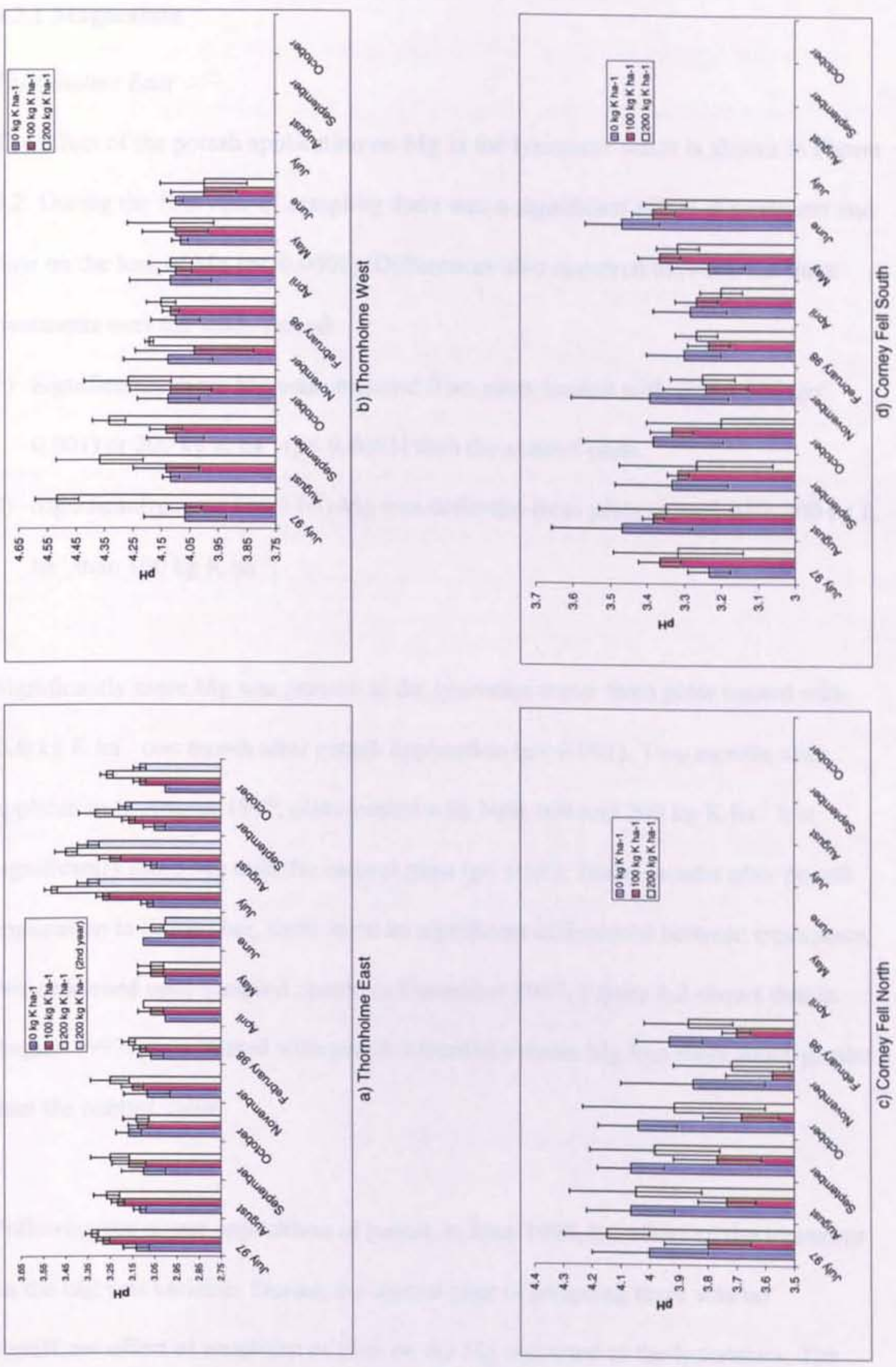
The effect of the potash application on soil pH can be examined in Figure 8.1(b). Data analysis showed that the 200 kg K ha^{-1} treatment significantly increased the pH of the soil and that there was a significant interaction between treatment and time ($p < 0.0001$). There was no significant difference between the pH of the soil treated with 100 kg K ha^{-1} and the control. Over the duration of the study the pH of the soil from plots treated with 200 kg K ha^{-1} was significantly greater than the pH of the control plots and plots treated with 100 kg K ha^{-1} only in July and August 1997 ($p < 0.05$). Figure 8.1(b) also shows that from October 1997 all three treatment plots had a similar mean soil pH.

Corney Fell North

The effect of the potash application on the soil pH can be examined in Figure 8.1(c). The addition of 100 kg K ha^{-1} significantly increased the acidity of the soil over the study period ($p < 0.01$). After an initial small increase in soil pH one month after application the mean soil pH of plots treated with 200 kg K ha^{-1} fell below the mean pH of control plots.

Corney Fell South

Figure 8.1(d) illustrates that the effect of potash application on the pH of the soil on Corney Fell South was highly variable over the study period. There was no significant difference in the soil pH over time or between treatments. The mean value of the plots treated with potash was only greater than that of the control plots one month after potash application in July 1997 and in May 1998.



a) Thornholme East

b) Thornholme West

c) Corney Fell North

d) Corney Fell South

Figure 8.1 Soil pH (mean and one standard deviation)

8.3 Loss of nutrients from the soil

8.3.1 Magnesium

Thornholme East

The effect of the potash application on Mg in the lysimeter water is shown in Figure 8.2. During the first year of sampling there was a significant effect of treatment and time on the loss of Mg ($p < 0.0001$). Differences also occurred between the three treatments over the study period:

1) Significantly more Mg was collected from plots treated with either 100 ($p < 0.001$) or 200 kg K ha^{-1} ($p < 0.0001$) than the control plots.
2) Significantly more ($p < 0.05$) Mg was collected from plots treated with 200 kg K ha^{-1} than 100 kg K ha^{-1}.

Significantly more Mg was present in the lysimeter water from plots treated with 200 kg K ha^{-1} one month after potash application ($p < 0.001$). Two months after application in August 1997, plots treated with both 100 and 200 kg K ha^{-1} lost significantly more Mg than the control plots ($p < 0.05$). Three months after potash application in September, there were no significant differences between treatments, this continued until sampled ceased in December 1997. Figure 8.2 shows that in August 1997, plots treated with potash recorded a mean Mg loss three times greater than the control value.

Following the repeat application of potash in June 1998, the effect of the treatment on the Mg was variable. During the second year of sampling there was no significant effect of treatment or time on the Mg collected in the lysimeters. The differences between treatments over the first year of study were:

1) No significant differences occurred between the control plots and the plots treated with a repeat application of either 100 or 200 kg K ha^{-1}.
2) Plots treated with a single application of 200 kg K ha^{-1} lost significantly more Mg than either the control plots or plots treated with a repeat application of 100 or 200 kg K ha^{-1} ($p < 0.05$).

In September 1998, the lysimeter water taken from plots treated with a single application of 200 kg K ha^{-1} contained significantly more Mg than any of the other treatments ($p < 0.05$). The high variability in Mg loss (see Figure 8.2) meant that for other months there were no other statistically significant differences between the four treatments, though in July 1998 the mean values for all plots treated with potash was greater than the control plots.

Thornholme West

Changes in the amount of Mg in the lysimeter water at Thornholme West are illustrated in Figure 8.3. There was a significant effect of time on the concentration of Mg ($p < 0.0001$) over the sampling period. Comparisons between the three treatments showed that:

1) Significantly more Mg was collected from plots treated with either 100 ($p < 0.001$) or 200 kg K ha^{-1} ($p < 0.0001$) than the control plots.
2) No significant difference occurred between plots treated with 100 or 200 kg K ha^{-1}.

One month following potash application significantly greater amounts of Mg were lost from plots treated with 200 kg K ha^{-1} than the control plots ($p < 0.05$). There were no other significant differences between the treatments on any single sampling occasion. Figure 8.3 shows that throughout the period of sampling plots treated with either 100 or 200 kg K ha^{-1} lost more Mg than the control plots.

8.3.2 Manganese

There were no significant effects of the potash treatment on the amount of Mn in the lysimeter water at either of the Thornholme sites. The mean concentrations and standard deviations are presented in table 8.1.

Table 8.1 Details of the concentration of Mn detected in the lysimeter water collected from Thornholme East and West

		Mn concentration mg Mn kg^{-1} dry soil	
Site	**Treatment**	**Mean**	**Standard deviation**
Thornholme East	Control	0.11	0.09
	100 kg K ha^{-1}	0.14	0.06
	200 kg K ha^{-1}	0.18	0.09
Thornholme West	Control	0.12	0.10
	100 kg K ha^{-1}	0.12	0.09
	200 kg K ha^{-1}	0.13	0.11

8.3.3 Calcium

Following the repeat application of potash in June 1998, the Ca in the lysimeter water was monitored at Thornholme East (see Figure 8.4). There was no significant effect of the treatment on the amount of Ca collected, but there was a significant effect of time ($p< 0.001$). The comparisons between the four treatments gave the following results:

1) There were no significant differences between the control plots and plots treated with either a repeat application of 100 or 200 kg K ha^{-1}.

2) Plots treated with a single application of 200 kg K ha^{-1} lost significantly more Ca than either the control plots ($p < 0.0001$) or plots treated with a repeat application of 100 or 200 kg K ha^{-1} ($p < 0.05$).

In September 1998, the lysimeter water from plots treated with a single application of 200 kg K ha^{-1} contained significantly more Ca than the control plots ($p < 0.05$). However, due to the high variability between replicate plots no other statistically significant differences were found. Figure 8.4 shows that in July 1998, all plots treated with potash had lost on average more Ca than the control plots. However, in August, such effects were no longer observable in plots treated with a repeat application, but only in plots treated with a single application.

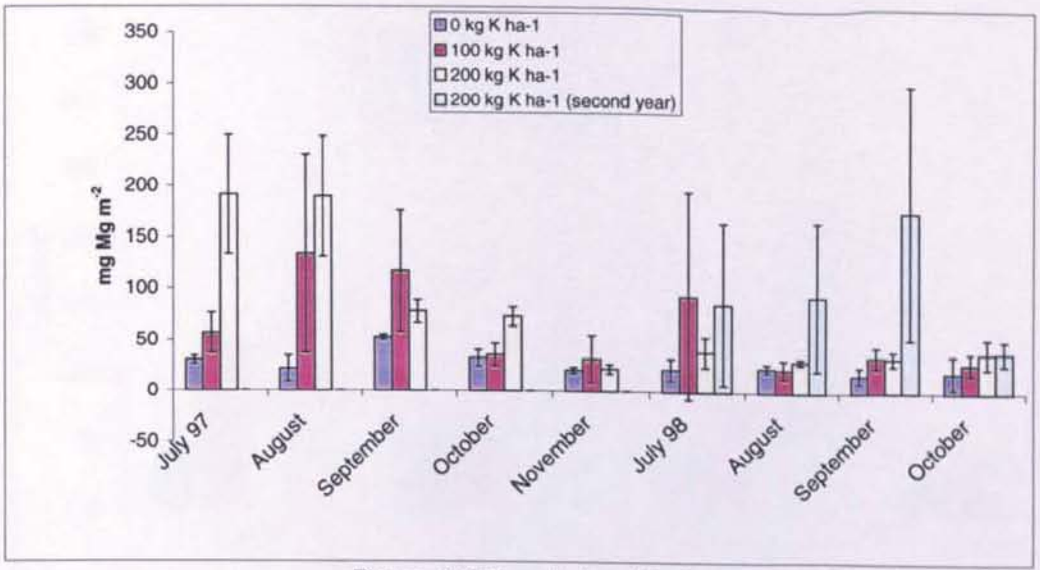


Figure 8.2 Thornholme East
Total Mg in lysimeter water (mg m^{-2})
(mean and one standard deviation)

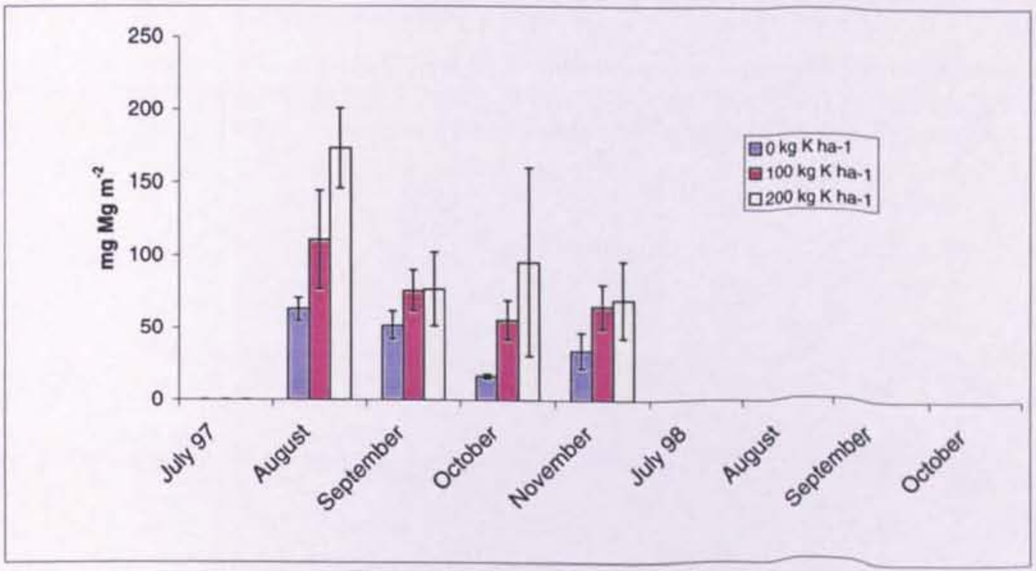


Figure 8.3 Thornholme West
Total Mg in lysimeter water (mg m^{-2})
(mean and one standard deviation)

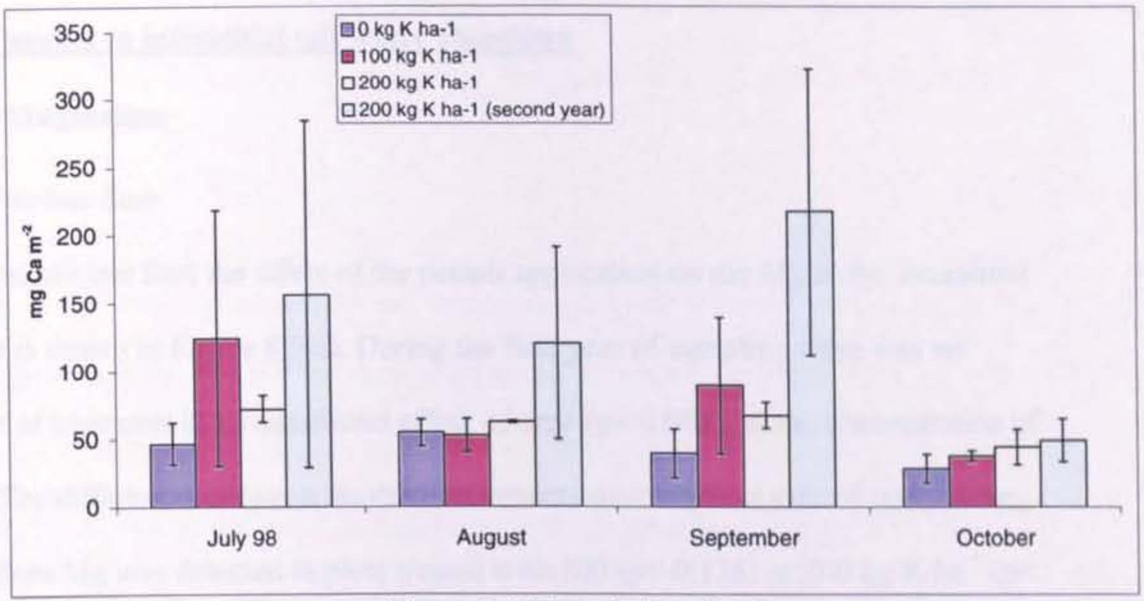


Figure 8.4 Thornholme East
Total Ca in lysimeter water (m^{-2})
(mean and one standard deviation)

8.4 Changes in interstitial soil water chemistry

8.4.1 Magnesium

Thornholme East

At Thornholme East the effect of the potash application on the Mg in the interstitial water is shown in Figure 8.5(a). During the first year of sampling there was no effect of treatment but a significant effect of time ($p < 0.001$) on the concentration of Mg. The differences between the three treatments over the first year of study were:

1) More Mg was detected in plots treated with 100 ($p = 0.128$) or 200 kg K ha^{-1} ($p < 0.001$) than the control plots.
2) There was no significant difference between plots treated with 200 or 100 kg K ha^{-1}.

Figure 8.5(a) shows that following potash application the mean concentration of Mg in the interstitial water of treated soil was greater than in the control plots. Although plots treated with 100 kg K ha^{-1} had the highest mean values, these were not significantly different from the control plots or from plots treated with 200 kg K ha^{-1}. In September 1997 the concentration of Mg was significantly greater in plots treated with 200 kg K ha^{-1} than the concentration in the control plots ($p < 0.05$).

The effect of the reapplication of potash in June 1998 was variable. During the second year of sampling there was a significant effect of treatment and time on the Mg concentration in the interstitial water ($p < 0.001$). The effects between the treatments were:

1) No significant difference between control plots and plots treated with either a repeat application of 100 or 200 kg K ha^{-1}.

2) Plots treated with a repeat application of 200 kg K ha^{-1} contained significantly more Mg than any other treatments ($p< 0.001$) between July 1998 and October 1998.

Figure 8.5(a) shows that plots treated with a repeat application of 100 or a single application of 200 kg K ha^{-1} had a higher mean concentration of Mg in the interstitial water than the control plots, or plots treated with a repeat application of 200 kg K ha^{-1}. However, when in comparing the concentrations between treatments in given months the concentration of Mg was only significantly greater in plots treated with a single application of 200 kg K ha^{-1} in July, August and September 1998.

Thornholme West

Figure 8.5(b) illustrates differences in Mg concentration in the interstitial water between treatments and sampling dates. Over the sampling period there was no significant effect of treatment or time on the concentration of Mg. The differences between treatments were:

1) Significantly more Mg was present in plots treated with 100 or 200 kg K ha^{-1} than the control plots ($p< 0.0001$).
2) There was no significant difference between plots treated with 200 kg K ha^{-1} and plots treated with 100 kg K ha^{-1}.

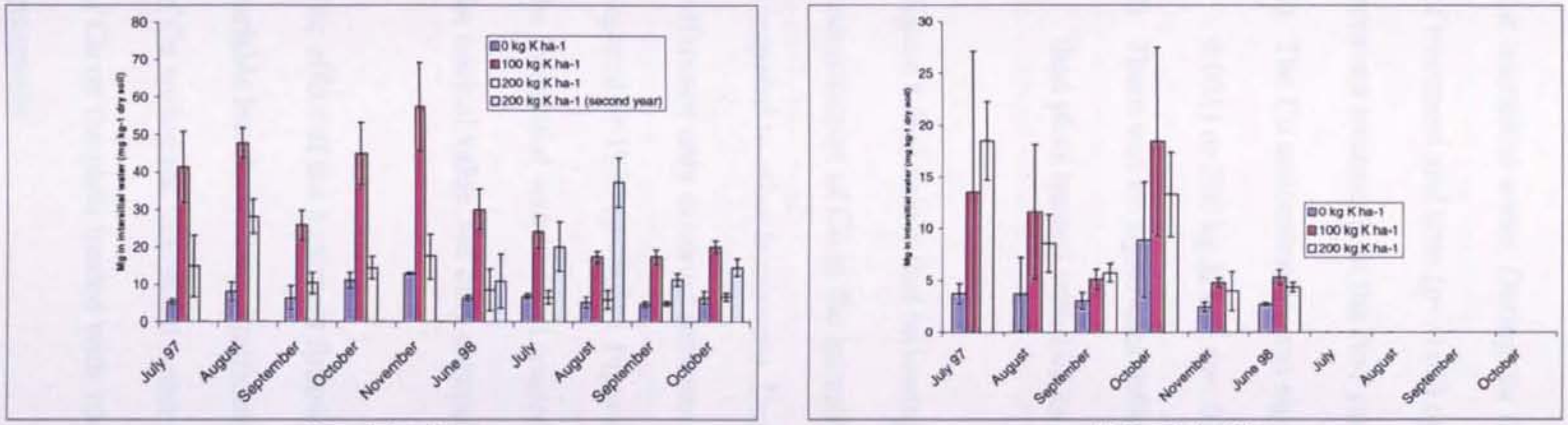
Figure 8.5(b) shows that following the potash application mean concentration of Mg in the interstitial water of plots treated with potash was greater than the control plots on every sampling occasion, though there were no significant differences on any sampling date.

Corney Fell North

Trends in the concentration of Mg in the interstitial water are shown in Figure 8.5(c). There were no significant effects of treatment or time on the concentration of Mg. Initially following the potash application there was a greater mean concentration of Mg in the interstitial water of soil treated with potash than the control plots which lasted until September 1997, but there was high variability within replicate plots.

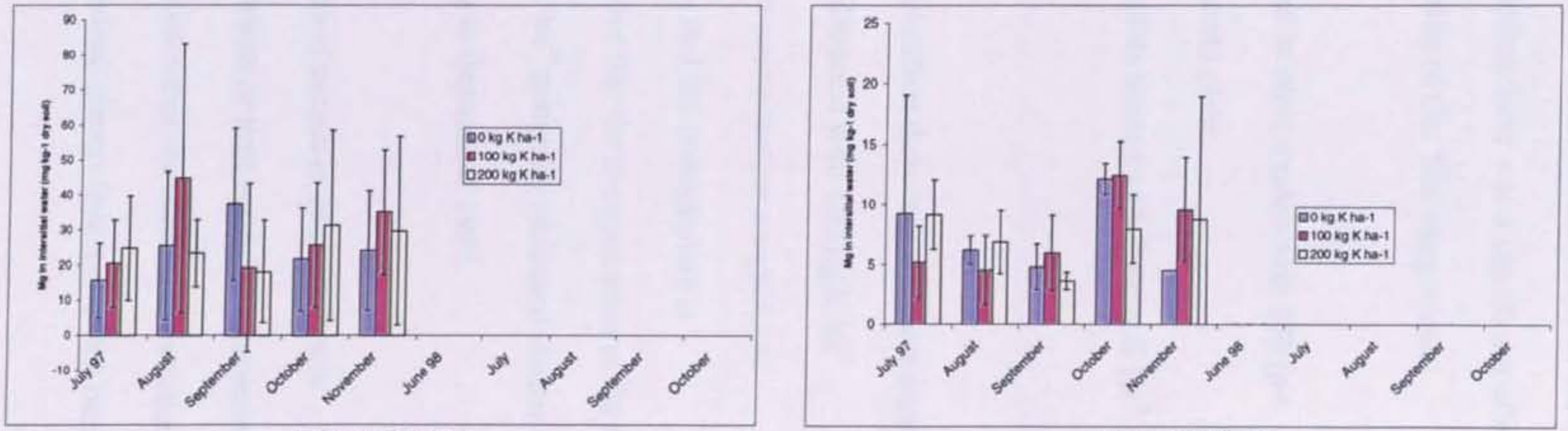
Corney Fell South

Changes in the concentration of Mg in the interstitial water over the sampling period are shown in Figure 8.5(d). There were no significant effects of treatment or time. Figure 7.5(d) shows that following the potash application there were no distinct trends in the mean concentration of Mg and between-plot variability was high.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 8.5 Concentration of Mg in interstital water
(mean and one standard deviation).

8.4.2 Copper

Thornholme East

Figure 8.6(a) shows the effect of the potash application on concentrations of Cu in the interstitial water. During the first year of sampling there was a significant effect of treatment and time ($p < 0.05$) on the concentration of Cu. The comparisons between treatments in the first year showed that:

1) The Cu concentration was significantly greater in plots treated with 100 ($p < 0.001$) or 200 kg K ha^{-1} ($p < 0.01$) than the control plots.
2) There was no significant difference between plots treated with 200 kg K ha^{-1} than plots treated with 100 kg K ha^{-1}.

Figure 8.6(a) shows that following the potash application there was a greater mean concentration of Cu in the interstitial water of soil treated with 100 kg K ha^{-1} compared to other treatments. Despite this greater concentration a significant difference only occurred between both treatments and the control plots in September 1997 ($p < 0.05$). Figure 8.6(a) also shows that the concentration of Cu in the interstitial water of soil treated with 200 kg K ha^{-1} generally remained similar to the control value, the only exception to this being in September 1997.

The effect of the treatment following reapplication of potash in June 1998 was variable but showed no significant effects of treatment or time on the concentration of Cu within the interstitial water. Figure 8.6(a) shows that the mean concentration of Cu on the plots treated with 100 kg K ha^{-1} remained greater than any of the other treatments.

Thornholme West

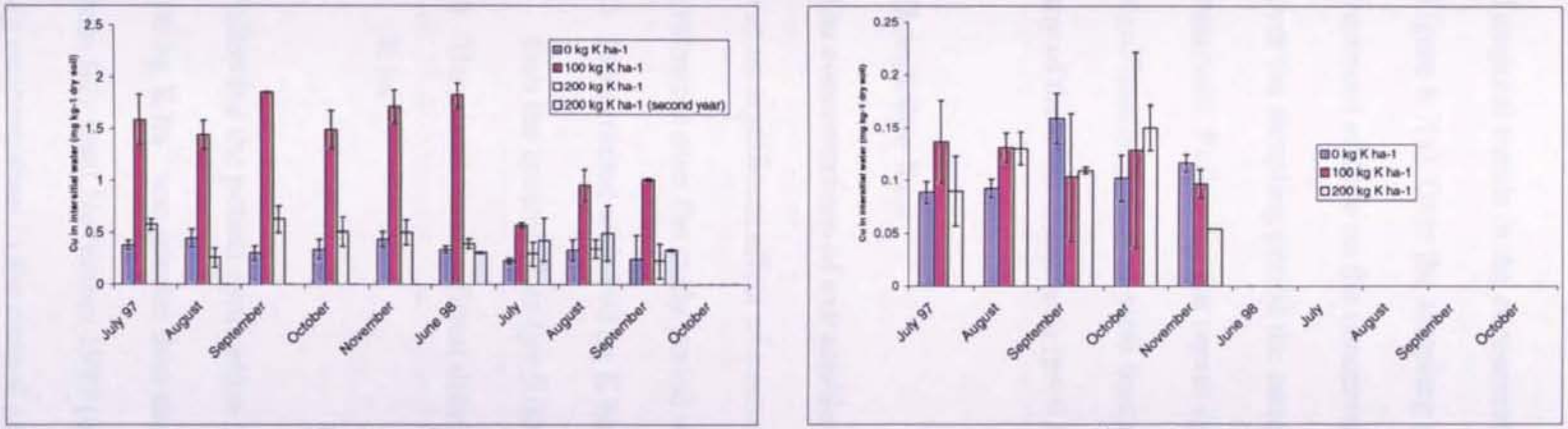
Temporal trends in the concentration of Cu in the interstitial water are shown in Figure 8.6(b). There were no significant differences between treatments or over time. All three treatments had a similar mean Cu concentration over the whole study period and there was high variability between the replicate plots within each treatment.

Corney Fell North

The high variability in the concentration of Cu between replicate plots at Corney Fell North is indicated in Figure 8.6(c). There were no significant differences between any of the treatments over the study period and mean concentrations of Cu were similar between treatments.

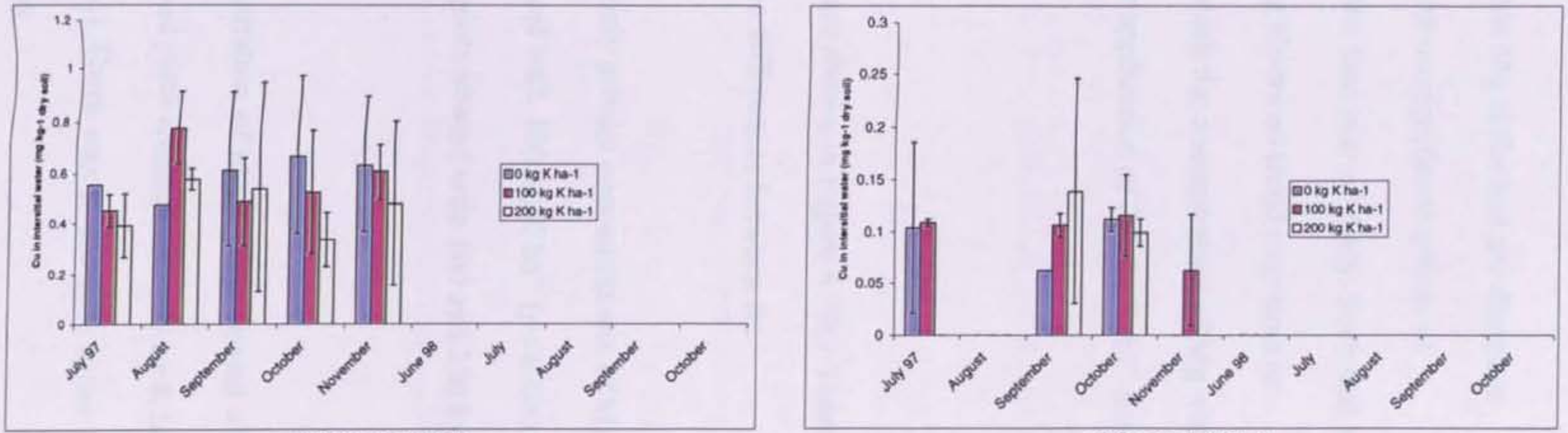
Corney Fell South

The incompleteness of Cu data for this site limited statistical analysis of the data. There was no significant difference in the concentration of Cu between treatments or over time. Figure 8.6(d) no general trends in the data over time and high variability between replicate plots.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 8.6 Concentration of Cu in interstital water (mg kg^{-1} dry soil) (mean and one standard deviation).

8.5 Changes in the extractable nutrients

8.5.1 Magnesium

Thornholme East

Temporal trends in the concentration of extractable Mg in the soil are shown in Figure 8.7(a). Over the sampling period there were no significant effects of treatment or time on the concentration of Mg in the first year of study. Such that the over the sampling period the concentration of Mg shows no trend over time or treatment. Following the repeat application of potash the concentration of Mg was significantly greater in plots treated with a single application of 200 kg K ha^{-1} than any of the other treatments ($p < 0.05$).

Thornholme West

The concentrations of extractable Mg in the soil are shown in Figure 8.7(b). There was no significant effect of treatment or time. The differences between the treatments over the study period were:

1) Plots treated with 200 kg K ha^{-1} had significantly greater concentrations of Mg than the control plots ($p < 0.001$) or plots treated with 100 kg K ha^{-1} ($p < 0.0001$).
2) There was no significant difference between plots treated with 100 and 200 kg K ha^{-1}.

Following the potash application the mean concentration of Mg in plots treated with 200 kg K ha^{-1} was greater than the control plots and plots treated with 100 kg K ha^{-1} from July until November 1997 (see Figure 8.7(b)). There was an increase in the Mg concentration in the control plots in June 1998.

Corney Fell North

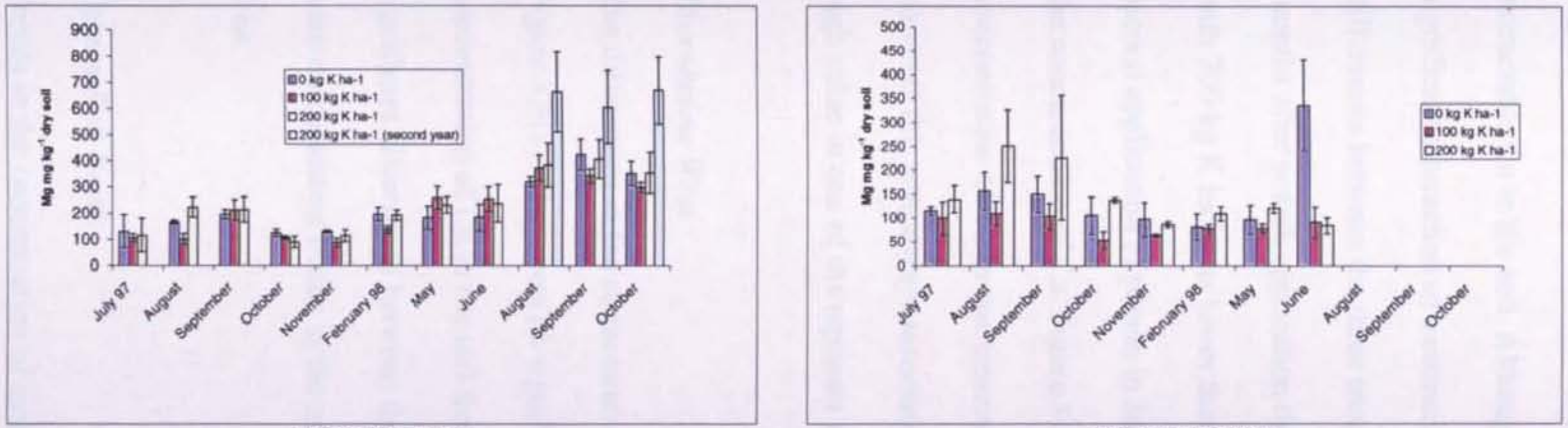
Changes in the concentration of extractable Mg are shown in Figure 8.7(c). There was a significant effect of treatment and time over the sampling period ($p< 0.01$). The comparisons between the treatments showed the following:

1) No significant difference in the concentration of Mg was found between the control plots and any of the plots treated with potash.
2) Plots treated with 200 kg K ha^{-1} had significantly greater concentration of Mg than plots treated with 100 kg K ha^{-1} ($p< 0.05$).

Figure 8.7(c) shows that the mean Mg concentration was highly variable within each treatment, between treatments and between sampling dates, with no apparent general trend over time.

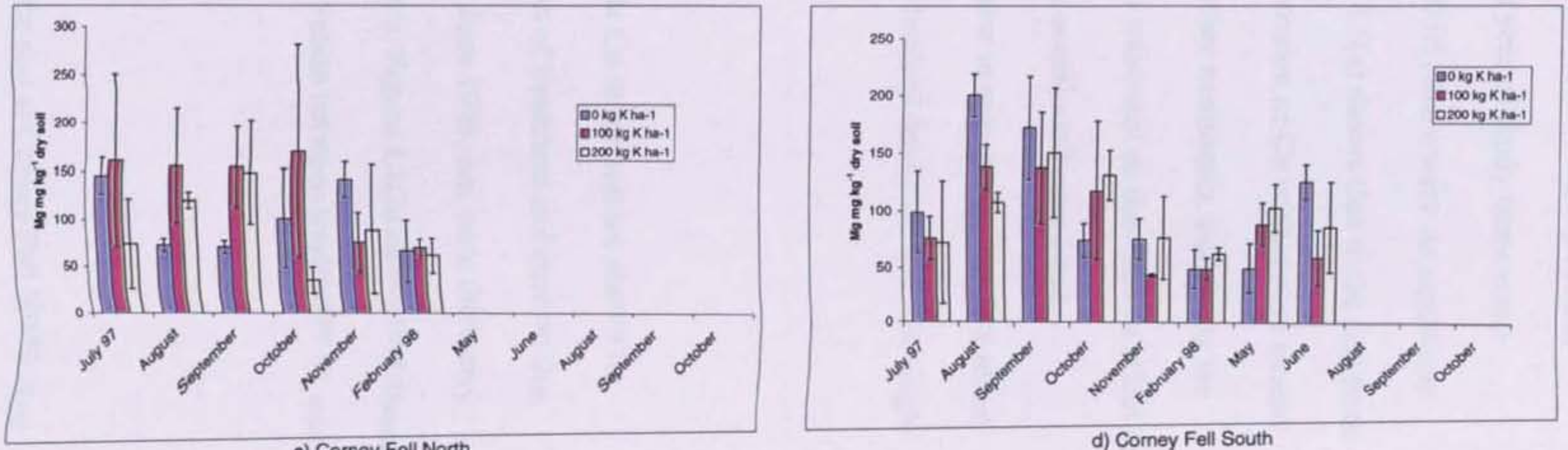
Corney Fell South

Figure 8.7(d) illustrates the differences in extractable Mg between treatments and sampling dates. There was a significant interactive effect of treatment and time on the concentration of Mg ($p< 0.01$) from July 1997 until June 1998, but no significant differences between the three treatments over the study period. The mean Mg concentration was lower in plots treated with potash than the control plots for the first four months following application.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 8.7 Extracted Mg in the soil (mg kg^{-1})
(mean and one standard deviation)

8.5.2 Copper

Thornholme East

Figure 8.8(a) shows the effect of potash application on the concentration of extractable Cu in the soil. Although over the first year of study there was a significant interaction of treatment and time ($p< 0.01$) there were no significant differences between the three treatments. Figure 8.8(a) shows that in the first three months after potash application the mean concentration of Cu within plots treated with 200 kg K ha^{-1} was lower than either of the other treatments. Following the second application of potash in June 1998 neither treatment or time had an effect on the concentration of Cu. Figure 8.8(a) shows that occasionally the mean concentration of Cu in one treatment was far greater in one month than any other, however this was always associated with a high standard deviation due to a single high value in one of the replicate plots.

Thornholme West

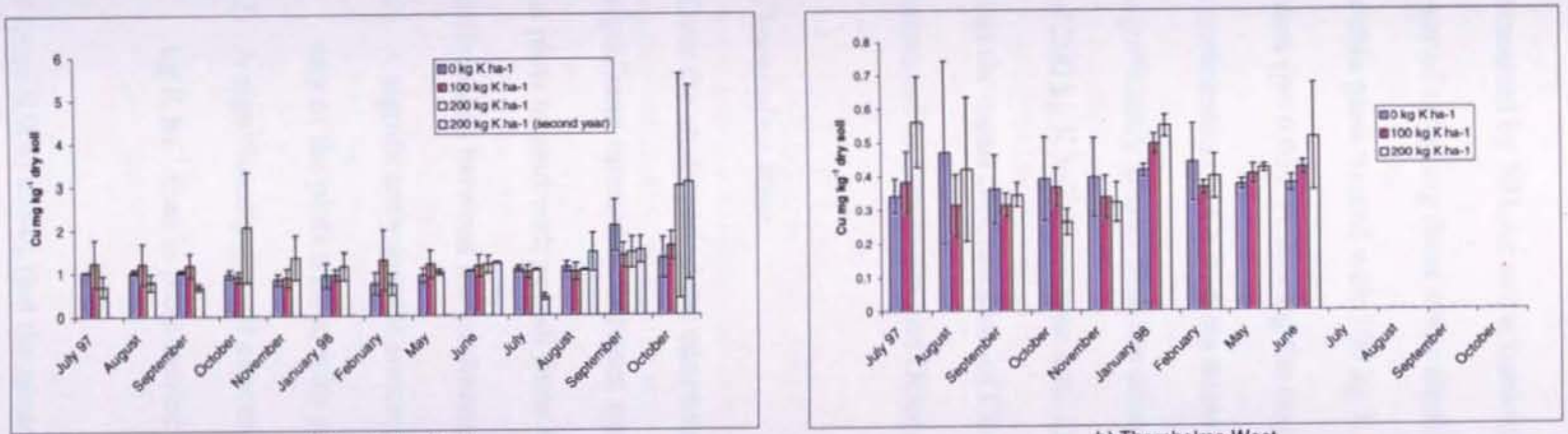
The differences in the concentration of extractable Cu in the soil are shown in Figure 8.8(b). There was no significant interaction of treatment and time on the concentration of Cu in the soil from July 1997 to June 1998, nor were there any significant differences between the three treatments. Figure 8.8(b) shows that there were no consistent trends in the mean Cu concentration between treatments or over time.

Corney Fell North

Trends in the concentration of extractable Cu in the soil at Corney Fell North are illustrated in Figure 8.8(c). Over the study period there were no significant effects of treatment or time, however, Figure 8.8(c) does show that in the first three months after potash application the mean concentration of Cu within the control plots was greater than in the plots which with potash.

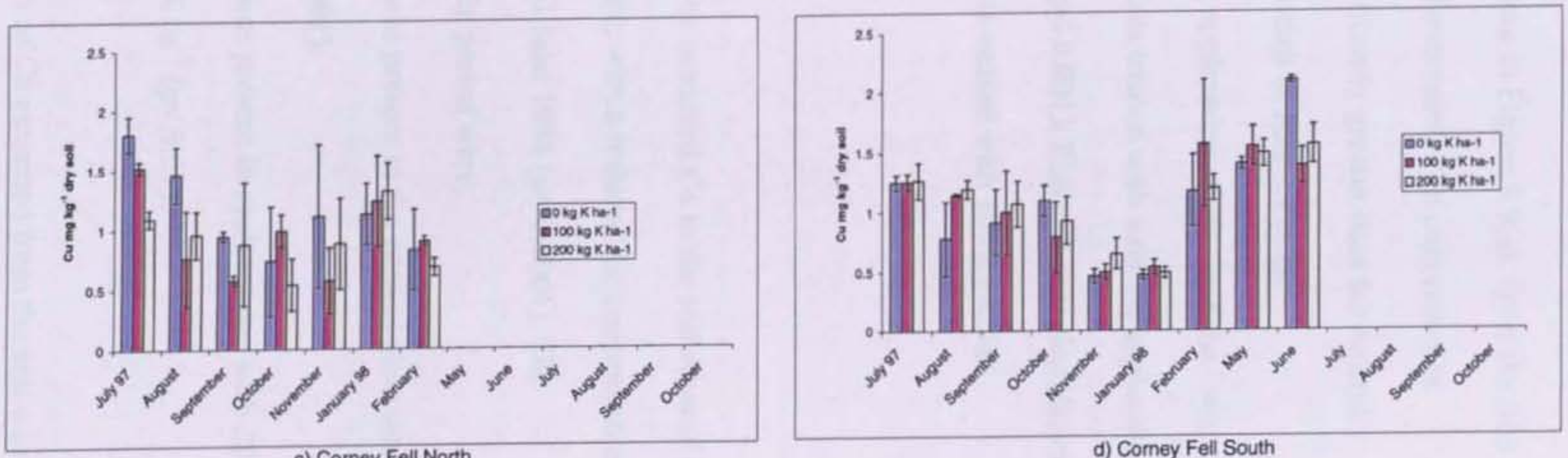
Corney Fell South

Figure 8.8(d) shows the trends in the concentration of extractable Cu in the soil at Corney Fell South. There was a significant ($p > 0.01$) effect of treatment and time on the Cu concentration, over the study period, however, there were no significant differences between the three treatments.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 8.8 Extracted Cu in the soil (mg kg^{-1})
(mean and one standard deviation)

8.5.3 Calcium

Thornholme East

The effect of the potash application on the concentration of Ca (which could be measured by NH_4Ac extraction) in the soil is shown in Figure 8.9(a). Over the first year of sampling there was a significant effect of treatment. The concentration within plots treated with 100 kg K ha^{-1} was significantly greater than the control plots ($p< 0.05$). Following the reapplication of potash in June 1998 the concentration of Ca in plots treated with a single application of 200 kg K ha^{-1} was significantly greater than the control plots and plots treated with a repeat application of 200 kg K ha^{-1} from June until October 1998 ($p< 0.001$). Figure 8.9(a) also shows that the mean concentration of Ca within the plots treated with 100 kg K ha^{-1} increased in September and October 1998.

Thornholme West

Over the study period the concentration of NH_4Ac extracted Ca in the soil showed a significant interaction between treatment and time, which reduced the concentration in plots treated with potash from November until June 1998 ($p< 0.0001$). The differences between the treatments over the study period were:

1) A significantly greater concentration of Ca was present in the control plots than any of the plots treated with potash ($p< 0.0001$).
2) A significantly greater concentration of Ca was present in plots treated with 200 kg K ha^{-1} than in plots treated with 100 kg K ha^{-1} ($p< 0.01$).

Figure 8.9(b) shows that the mean concentration of Ca extracted from the soil was greater in the control plots than plots treated with potash on every sampling occasion, however differences were only significant from October 1997 until May 1998 ($p < 0.001$). In June 1998 the mean concentration of all the treatments were similar to each other and to the concentrations in July 1997.

Corney Fell North

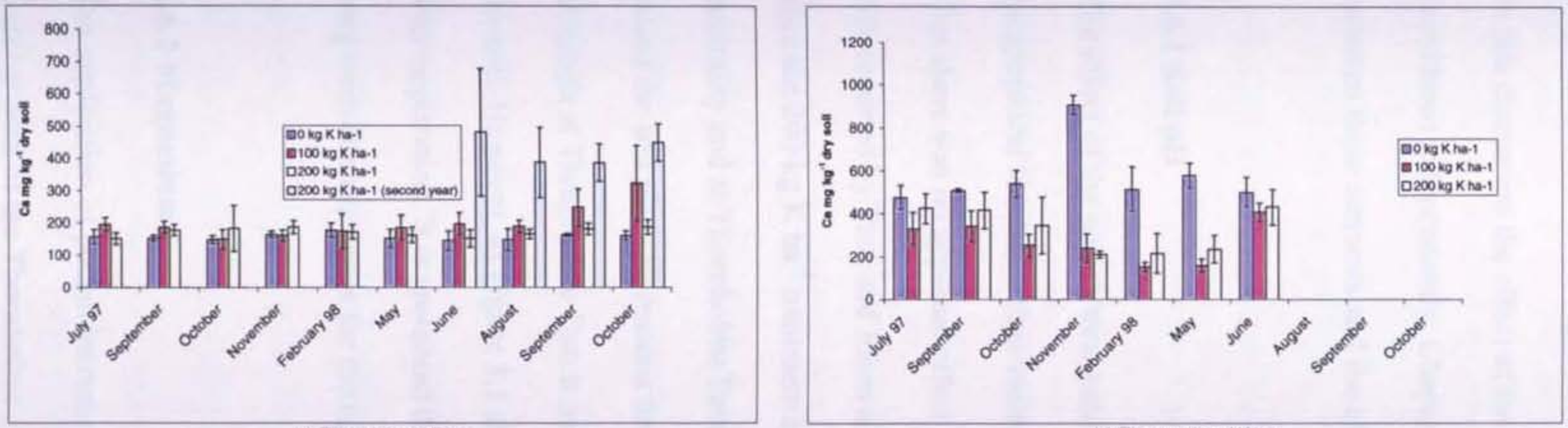
The concentration of extractable Ca in the soil at Corney Fell North was not significantly different between treatments or over time. Figure 8.9(c) indicates that in July 1997 the mean concentration of Ca was greater within plots treated with potash. However, in October 1997 such an effect was no longer observable. On the final sampling date on February 1998 the mean concentration of Ca was lower in plots treated with potash than the control plots.

Corney Fell South

Figure 8.9(d) shows that there was high variability in the concentration of extractable Ca between replicate plots over the study period. There were no significant effects of time or treatment over the whole study period. Comparison between the treatments showed that:

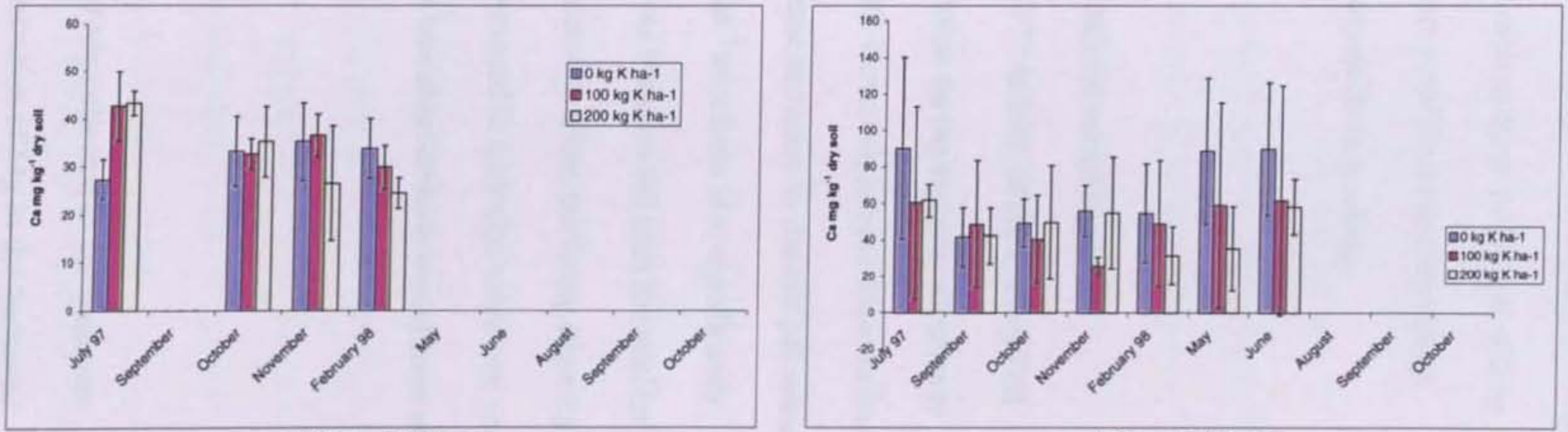
1) Significantly less Ca was present in plots treated with potash than the control plots ($p < 0.05$).
2) There was no significant difference between the plots treated with 100 and 200 kg K ha^{-1}.

Although there were no significant differences between the three treatments on a monthly comparison, the mean concentration in the control plots was greater than in those treated with potash on every sampling occasion except September 1997.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 8.9 Extracted Ca in the soil
(mean and one standard deviation)

8.6 Chapter 8 discussion

The effect of the K applications on the soil chemistry has been shown to be difficult to determine due to the high natural variability in nutrients in the soil and soil water. In this discussion the effect of the application on each nutrient in the soil will be considered independently. Chapter 10 will consider possible interrelationships between these nutrients and the effects on the ecosystems as a whole.

8.6.1 Soil pH

The effect of the potash treatments on the pH of the soil varied between geographical localities, thus validating hypothesis 7. At both of the Corney Fell sites there was no apparent effect of the K application on the soil pH, which was also reported by Paul and Jones at this site in 1995. However, at both Thornholme sites the 200 kg K ha^{-1} treatment induced significant increases in the soil pH toward neutrality and at Thornholme East the 100 kg K ha^{-1} treatment also significantly raised the soil pH. The reasons for these differences between the sites are unclear although at Thornholme East it may have been related to a low buffering capacity of the soil. However, as Figure 8.1 shows, soil pH returned to a similar value one year after application. It is presumed that as this effect was short-lived it would have no long-term consequences for the ecosystem.

8.6.2 Magnesium

The application of potash increased the amount of Mg collected in the lysimeter water at both of the Thornholme sites. The concentration of Mg in the lysimeter water was greatest shortly after application, which rapidly reduced to concentrations which were comparable to those of the controls. This effect was also recorded by Rafferty et al., (1998) and attributed to Mg present within the KCl salt. The potash applied had low concentrations of trace element contamination in the salt of which Mg composed 2 % by mass. However, in this study all Mg data has been corrected for the Mg in the salt by assuming that the relative concentrations of K : Mg in the salt were also reflected in the lysimeter water (assuming that K and Mg were leached at the same rate through the soil). For example, if 100 mg of K was measured in the lysimeter water and 3 mg of Mg was also measured, the reported figure would be 1 mg Mg. As the Mg ion is a more strongly charged ion and therefore more likely to be retained in the soil there is the potential that in reporting the data in this format, under-reporting of Mg loss from the soil may occur. However, the author considered that it was necessary to account for Mg added from the supplementary additions to the soil from the potash. In 1960, Hovland and Caldwell also reported that the application of KCl to an organic soil caused the loss of Mg from the soil system. Thus, it can be assumed that the detection of Mg in the lysimeter water did represent the KCl application inducing a net loss of Mg from the soil.

The concentration of Mg in the interstitial soil water also increased following potash application. This was still apparent following correction of the data for Mg in the salt, as outlined above. The potash appears to have induced a movement of Mg from the soil particle surface into the interstitial water from where it could be leached and detected in the lysimeter water. John and Vimpany (1999) also reported that the addition of KCl to an organic soil increased Mg displacement into the soil solution (interstitial water).

Soil extractions using NH_4Ac indicated that the concentration of Mg was highly variable between replicate treatment plots and that there was no general effect of the treatment on extractable Mg in the first year of study. In 1998, plots treated with a single application at Thornholme East showed an increase in the concentration of extractable Mg, though this was not matched by any increase in the interstitial soil water. However, the lysimeter water samples indicated increased losses of Mg from the soil on plots treated with a single application of 200 kg ha^{-1} K in 1998. The results from 1998 indicate that the effect of the treatment on Mg in the soil varied temporally. This effect may have been recorded as the loss of Mg was small in comparison to the total Mg extractable from the soil and biomass and the variability of Mg in the soil was relatively large. The effect of the K treatment on Mg was unlikely to have been of sufficient magnitude to induce hypomagnesemic effects in the vegetation or grazing animals at any of the sites. If a site which had been identified as deficient in Mg had been selected the application of K may have initially increased the concentration of plant available Mg before returning to levels of deficiency, however such a site was not available for examination. It is difficult to determine the decrease in the concentration of Mg which would be required to induce a hypomagnesemic effect in vegetation or grazing animals as the absorption of Mg by animals is highly variable between breed and plant species. Further research is required to identify the reduction in Mg that could induce hypomagnesemic effects in upland ecosystems.

8.6.3 Copper

Thornholme East was the only site which recorded a significant reduction in the concentration of Cu in the interstitial water, however, this was not mirrored in the extractable Cu in the soil. The effects of the potash treatment on Cu were limited to short-term effects on the soil water at this site. Hence, negative impacts on the Cu concentration on the biomass are not expected from these direct measurements of Cu in the soil.

8.6.4 Calcium

In the second year of the study, the concentration of Ca in the lysimeter water indicated that on plots that had been treated with a single application of KCl in 1998 there was a net loss of Ca from the soil. However, this effect was not apparent on plots treated with a second application of KCl. This may infer that the effect of the potash treatment was to displace the most loosely 'held' Ca in the soil and that any further loss of ions is prevented as the soil retains the remaining Ca more strongly than the KCl application could displace. Brady and Weil (1999) stated that following the addition of K to an acid soil, the K^+ ions could more easily replace the Ca^{2+} ions than the Al^{3+} ions, thereby inferring a loss of Ca from the soil particle surfaces which was shown in the lysimeter water.

The potash application appeared to have had no effect on the Ca which could be extracted from the soil using NH_4Ac at Thornholme East and Corney Fell North whilst at the Thornholme West and Corney Fell South the application of potash reduced the concentration of Ca in the soil. The reason for such an effect at Thornholme West is likely to have been the underlying calcic parental rock. Weathering of this calcic sandstone would have allowed the soil to accumulate a greater concentration of Ca in the soil which was easily exchanged. Therefore as the K application released allowed easily exchangeable Ca in the soil to be leached at

Thornholme West larger concentrations were lost. At Corney Fell South, the reason for such an effect is unclear as the site consistently had high variability between treatments. An inspection of Figure 7.9(d) does not indicate that there were any large differences between treatments. As the concentration of Ca in the soil was relatively high in comparison to that in the lysimeter water the high sample variation prevented an effect from being detected.

8.7 Chapter 8 conclusions

Chapter 8 has shown that the potash application significantly raised the soil pH at two of the experimental sites over the study period. It has also shown that the effect of potash application on other nutrients is dependent on the underlying geology, thus validating hypotheses 6 and 7.

Chapter 9

Secondary effects of the potash application on the vegetation

9.1 Introduction

Data presented in Chapter 9 shows the effect of the KCl application on the biomass at each of the four study sites. This chapter will show if the disruption of nutrients in the soil shown in Chapter 8 was shown by measurements of plant biomass. Section 9.2 shows the effect on the biomass whilst sections 9.3 to 9.8 show the effect on the Mg, Cu, Mn, Ca, Fe and Co in the biomass. Two hypotheses are tested in this chapter; that 'the effect on other nutrients depends on the underlying geology' and that 'the potassium application does not cause a significant increase in biomass production'.

9.2 Biomass

Thornholme East

There was no significant effect of treatment or time on the standing above-ground biomass from July 1997 until June 1998 (see Figure 9.1(a)). Comparisons between the three treatments showed that:

1) Plots treated with 100 kg K ha^{-1} had significantly less biomass than the control plots or plots treated with 200 kg K ha^{-1} ($p< 0.001$).
2) There was no statistically significant differences between the control plots and plots treated with 200 kg K ha^{-1}.

There were no significant differences between treatments on any single sampling occasion until April 1998, when plots treated with 100 kg K ha^{-1} had less biomass than the control plots ($p< 0.01$). Figure 9.1(a) shows that in the first three months following application plots treated with 200 kg K ha^{-1} had a higher mean biomass than the control plots, whilst the 100 kg K ha^{-1} treatment had lower biomass.

Following the reapplication of potash in June 1998, there was a significant interactive effect of treatment and time on the above-ground standing biomass ($p= 0.067$), though Figure 8.1(a) shows that there were no general trends between the treatments.

Thornholme West

There was a significant interactive effect of treatment and time on the standing above-ground biomass over the study period ($p< 0.05$). However, there were no significant differences between the three treatments on any single sampling occasion. Figure 9.1(b) shows that following potash application in June 1997 the mean biomass sampled from plots treated with 200 kg K ha^{-1} was greater than the control plots on every sampling occasion until February 1998.

Corney Fell North

Between the application of potash in June 1997 and February 1998, there was no effect of time or treatment on the standing above-ground biomass (see Figure 9.1(c)). However, comparisons between the three treatments showed that:

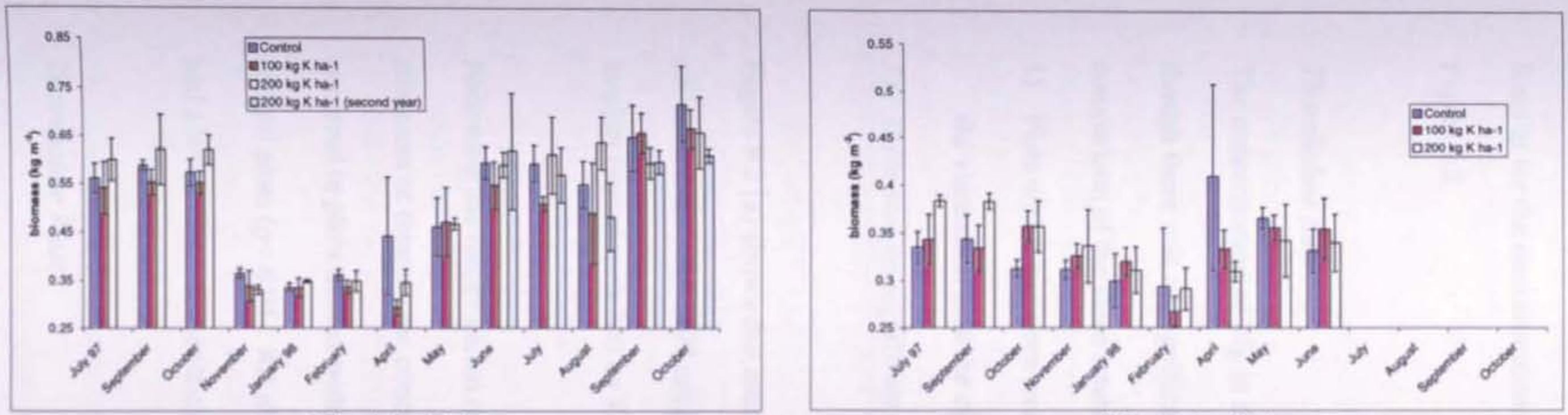
1) Plots which had been treated with potash contained significantly lower biomass than the control plots ($p< 0.001$).

2) Plots treated with 200 kg K ha^{-1} contained significantly more biomass than plots treated with 100 kg K ha^{-1} ($p < 0.05$).

In November 1997 and January 1998, the amount of biomass collected from the control plots was significantly greater than that collected from plots treated with 100 kg K ha^{-1} ($p < 0.05$). Figure 9.1(c) shows that from July 1997 to February 1998 treated plots recorded lower mean biomass per unit area than the control plots.

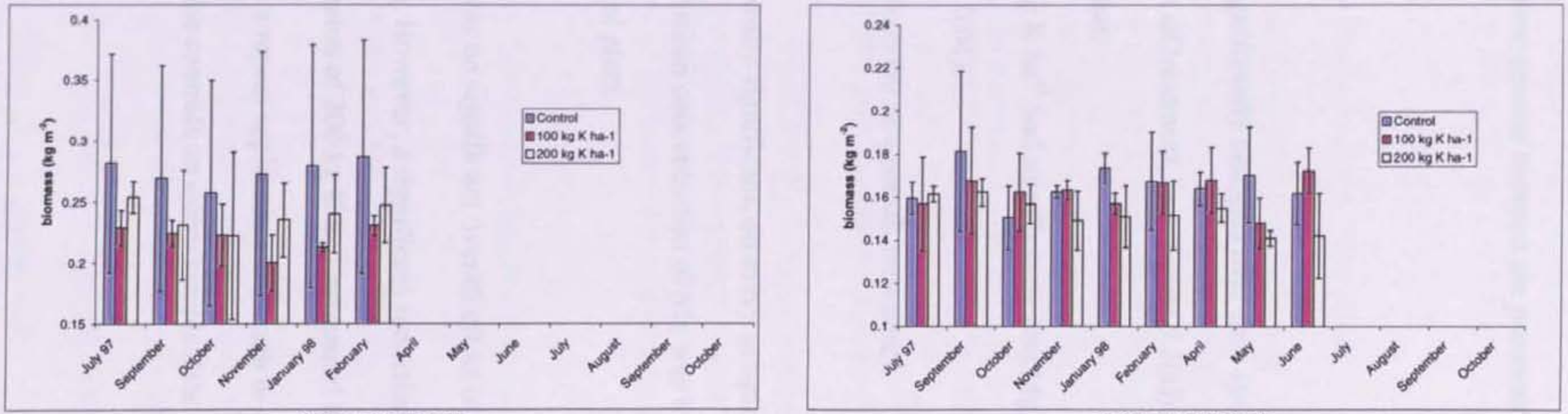
Corney Fell South

There were no significant differences in the biomass between the three treatments on any single sampling date (see Figure 9.1(d)). However, over the sampling period plots treated with 200 kg K ha^{-1} had significantly less biomass than the control plots ($p < 0.01$).



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 9.1 Above-ground standing biomass (kg m^{-2})
(mean and one standard deviation)

9.3 Magnesium

Results for the concentration of Mg in the above-ground biomass are presented in Figure 9.2.

Thornholme East

The concentration of Mg in the vegetation significantly changed over time ($p< 0.05$) though there was no significant overall effect of treatment, (see Figure 9.2(a)). A comparison of the three treatments showed that:

1) Plots which had been treated with 200 kg K ha^{-1} had significantly less Mg in the vegetation than the control plots ($p< 0.01$).
2) There was no significant difference between the two potash treatments.

Figure 9.2 (a) shows that although not statistically significant, on every sampling occasion from July 1997 until June 1998, the mean concentration of Mg was lower in plots treated with 200 kg K ha^{-1} than control plots.

Following the reapplication of potash there was no significant overall effect of treatment or time on the concentration of Mg. However, a significant reduction occurred in plots treated with a repeat application of 200 kg K ha^{-1} compared to the control plots ($p< 0.05$). All plots treated with a repeat application of potash in 1998 had a lower mean concentration of Mg than the controls on every sample date.

Thornholme West

Temporal changes in the concentration of Mg in the vegetation are shown in Figure 9.2(b). Over the sampling period there were no significant effects of treatment or time on the concentration of Mg. Comparisons between the three treatments showed that plots treated with 200 kg K ha^{-1} had a significantly lower concentration of Mg than either the control plots or plots treated with 100 kg K ha^{-1} ($p< 0.05$).

There were no significant differences between the treatments on any single sampling date until April 1998, when plots treated with 200 kg K ha^{-1} had a significantly lower Mg concentration than plots treated with 100 kg K ha^{-1} ($p< 0.05$). Plots treated with 100 kg K ha^{-1} generally showed a lower concentration values. On the two occasions where the mean concentration was greater the variability in the data was large due to a single high value.

Corney Fell North

The effect of the potash treatments on the concentration of Mg in the vegetation is shown in Figure 9.2(c). There was no significant effect of treatment or time on the Mg concentration. Comparisons between the three treatments from July 1997 until February 1998 showed that:

1) Plots treated with potash had a significantly lower concentration of Mg than the control plots ($p< 0.001$).
2) There was no significant difference between the two potash treatments.

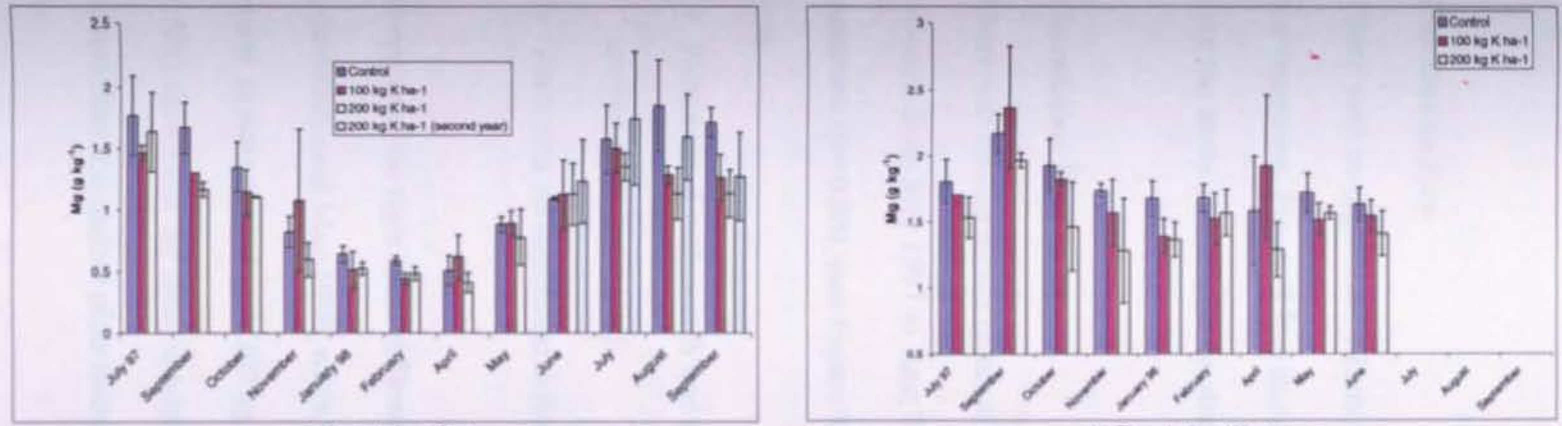
The only date on which a significant difference between the three treatments occurred was in October 1997 when the concentration of Mg in the control plots was less than the concentration in the plots treated with 200 kg K ha^{-1} ($p< 0.05$). However, Figure 9.2(c) shows that on every sampling date the mean Mg concentration was lower in plots treated with either 200 or 100 kg K ha^{-1} than the control plots, and that the mean concentration in the 200 kg K ha^{-1} plots was generally lower than the 100 kg K ha^{-1} plots.

Corney Fell South

There was a no significant effect of treatment or time on the concentration of Mg in the above-ground biomass (see Figure 9.2(d)). A comparison between the three treatments showed that:

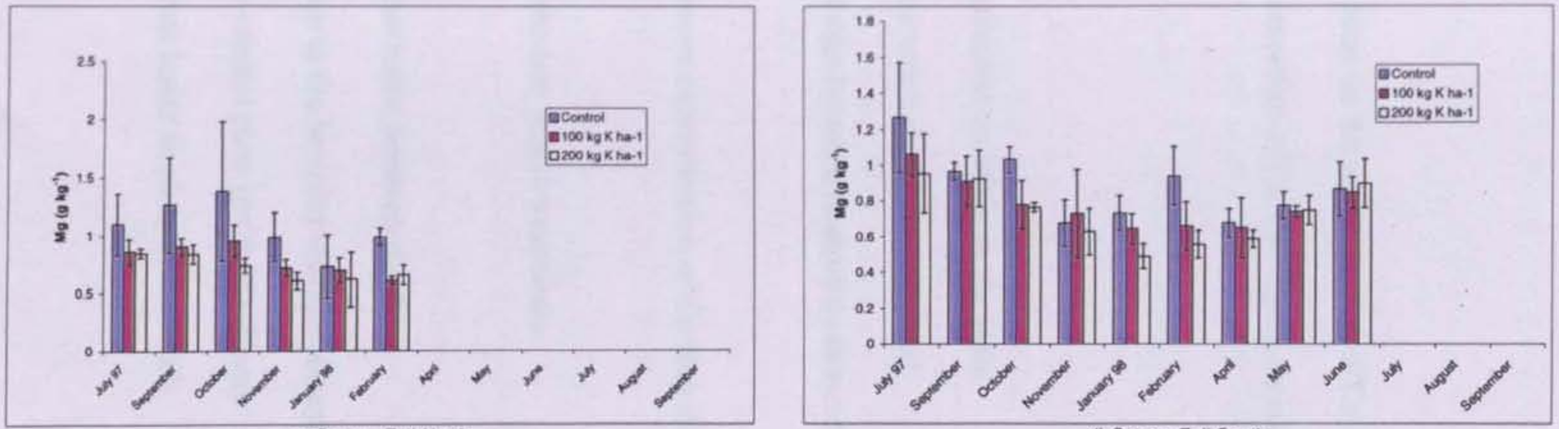
1) Plots which had been treated with potash had a significantly lower concentration of Mg in the vegetation than the control plots ($p< 0.01$).
2) There was no significant difference between plots treated with 100 or 200 kg K ha^{-1}.

No significant differences occurred between the three treatments on any single sampling occasion. However, Figure 9.2 (d) shows that on most sampling dates the mean concentration of Mg was lower in plots treated with 200 or 100 kg K ha^{-1} than the control.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 9.2 Concentration of Mg in standing above-ground biomass (g kg^{-1})
(mean and one standard deviation)

9.4 Copper

Results for the concentration of Cu in above-ground biomass are presented in Figure 9.3.

Thornholme East

There were no significant effects of treatment or time on the concentration of Cu in the vegetation. Figure 9.3(a) shows that the concentration of Cu was highly variable over the study period with no obvious trends.

Thornholme West

There was no significant effect of time on the concentration of Cu in the plant biomass from July 1997 to June 1998 though there was a significant effect of treatment ($p < 0.05$), (see Figure 9.3(b)). Comparisons between treatments showed that:

1) Plots treated with potash had a significantly lower concentration of Cu than the control plots ($p < 0.001$).
2) There was no significant difference between the two potash treatments.

There were no significant differences in Cu concentration between the three treatments until May 1998, when the concentration in the biomass was significantly lower in plots treated with 200 kg K ha^{-1} than the control plots ($p < 0.05$). Figure 9.3(b) shows that the mean concentration of Cu was lower in plots treated with potash than the control plots throughout 1998.

Corney Fell North

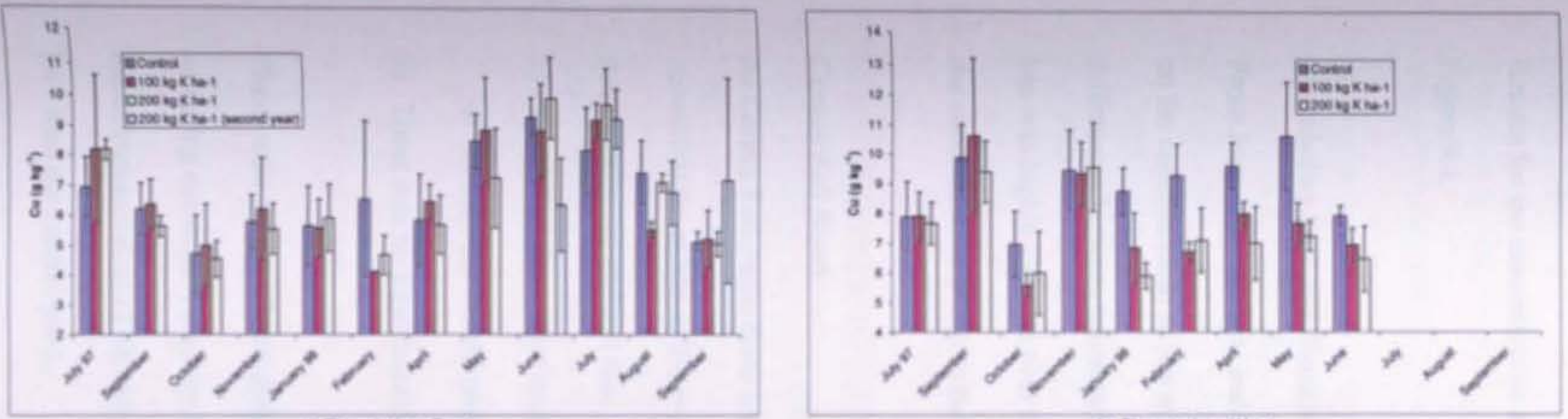
From July 1997 until February 1998, there was no significant effect of treatment or time on the concentration of Cu in the vegetation, nor were there any significant differences between the treatments. Figure 9.3(c) shows that the concentration of Cu was often highly variable with no overall trends between treatments.

Corney Fell South

From July 1997 to June 1998 there was a significant interaction of treatment and time on the Cu concentration within the plant biomass ($p< 0.05$). Comparisons between the three treatments showed that:

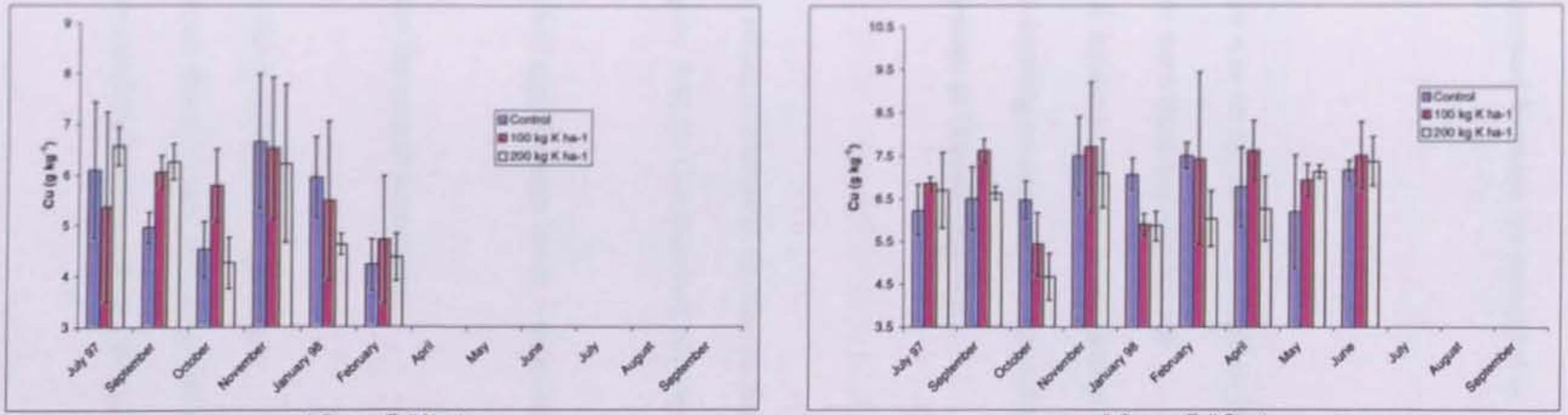
1) There was no significant difference between the control plots and any of the plots treated with potash.
2) Significantly more Cu was present in vegetation treated with 100 kg K ha^{-1} than within plots treated with 200 kg K ha^{-1} ($p< 0.05$).

There were no significant differences between treatments on any single sampling date. However, Figure 9.3(d) shows that from October 1997 until May 1998 the mean concentration of Cu in the biomass was lower in plots treated with 200 kg K ha^{-1} than the control plots.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 9.3 Concentration of Cu in standing above-ground biomass (g kg^{-1})
(mean and one standard deviation)

9.5 Manganese

Results for the concentration of Mn in above-ground biomass are presented in Figure 9.4.

Thornholme East and Thornholme West

From June 1997 until the end of sampling there was no effect of treatment or time on the concentration of Mn in the biomass, nor were there any significant differences between treatments. Figure 9.4(a & b) shows that the concentration of Mn was highly variable over the study period showing no apparent trends and that the concentration of Mn in the biomass was greater at Thornholme West

Corney Fell North

At Corney Fell North there was no significant effect of treatment or time on the concentration of Mn in the vegetation (see Figure 9.4(c)). Comparisons between the three treatments showed that:

1) Vegetation from plots treated with potash had significantly lower concentrations of Mn than the control plots ($p< 0.01$).
2) There was no significant difference between the potash treatments.

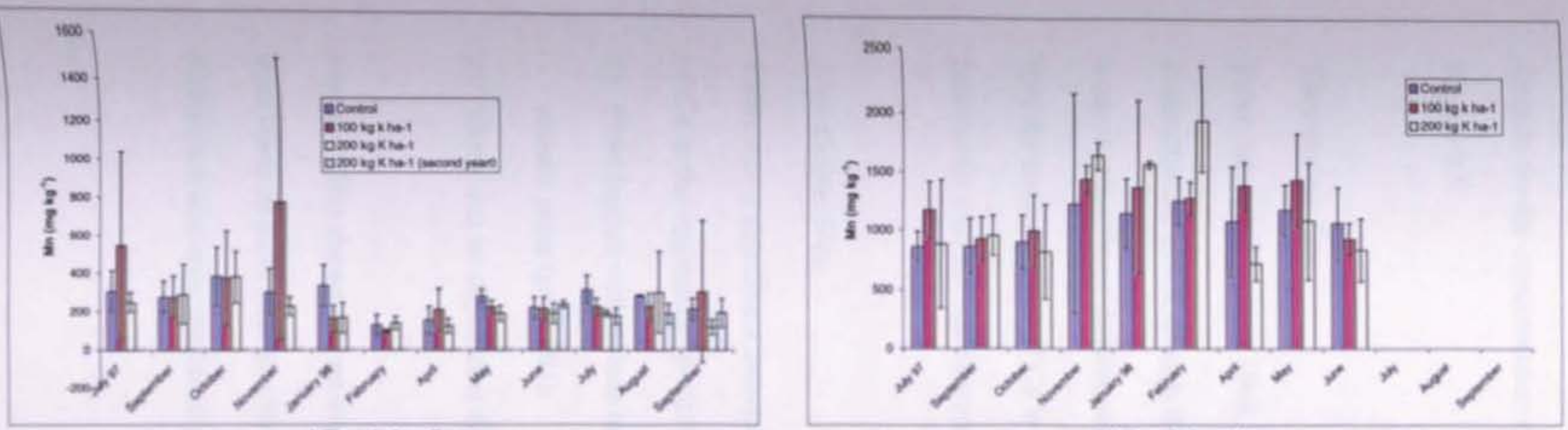
There were no significant differences between the treatments on any single sampling occasion. However, Figure 9.4(c) shows that on every sampling date the mean concentration of Mn was lower in plots treated with either 100 or 200 kg K ha^{-1} than the control plots.

Corney Fell South

There was no significant effect of treatment or time on the concentration of Mn in plants from July 1997 to June 1998 (see Figure 9.4(d)). A comparison between the three treatments showed that:

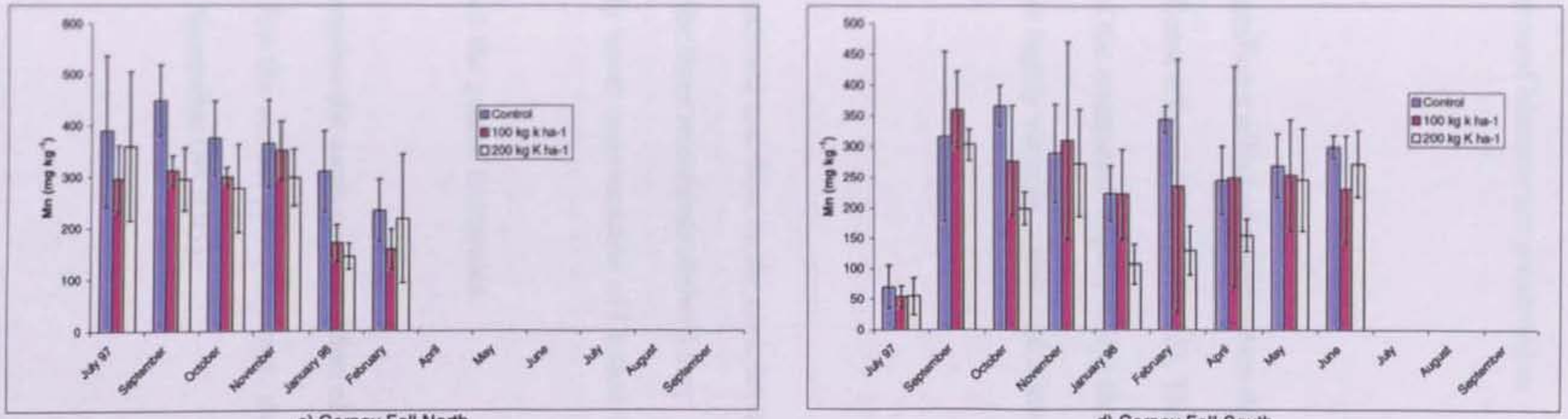
1) Plots treated with 200 kg K ha^{-1} had a significantly lower concentration of Mn than either the control plots ($p< 0.001$), or plots treated with 100 kg K ha^{-1} ($p< 0.05$).
2) There was no significant difference between the plots treated with 100 kg K ha^{-1} and the control plots.

In February 1998, the concentration of Mn within the vegetation was significantly lower in plots treated with 200 kg K ha^{-1} than the control plots ($p< 0.05$). Figure 9.4(d) shows that although the concentration of Mn was highly variable both within and between treatments, on every sampling occasion the mean concentration in plots treated with 200 kg K ha^{-1} was less than that of the control plots.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 9.4 Concentration of Mn in above-ground standing biomass (mg kg^{-1})
(mean and one standard deviation)

9.6 Calcium

Results for the concentration of Ca in above-ground biomass are presented in Figure 9.5.

Thornholme East

From July 1997 to June 1998, there was no significant effect of treatment on the concentration of Ca, though there was a significant effect of time ($p< 0.05$). There were no significant differences between any of the treatments. Figure 9.5(b) shows that the concentration of Ca in the biomass was highly variable within and between treatments with no visible trends.

Thornholme West

There was a significant interactive effect of treatment and time on the concentration of Ca in the vegetation ($p< 0.05$). Comparing the three treatments showed that:

1) Plots treated with potash had a significantly lower concentration of Ca than the control plots ($p< 0.001$).
2) There was no significant difference between the potash treatments.

Figure 9.5(c) shows that on every sampling occasion the mean concentration of Ca was lower in plots treated with 200 kg K ha^{-1} than the control plots, however, the difference was only statistically significant in November ($p< 0.05$).

Corney Fell North

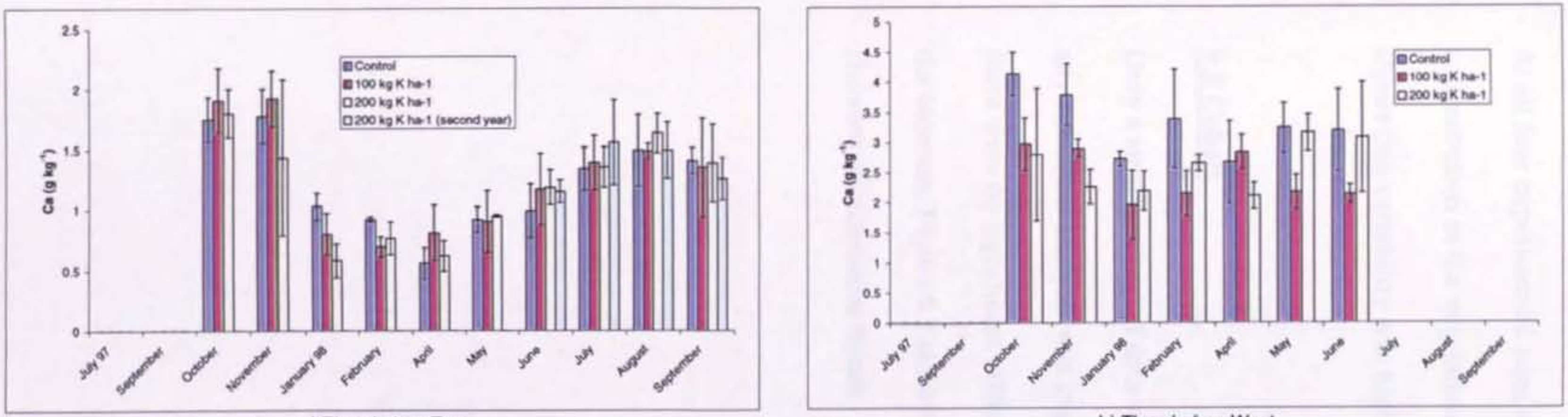
At this site the concentration of Ca in plants was significantly affected by an interaction between treatment and time ($p = 0.05$). A comparison between the three treatments showed that:

1) Plots treated with potash had significantly lower concentrations of Ca than control plots ($p < 0.001$).
2) There was no significant difference between plots treated with potash.

On every sampling occasion the mean concentration of Ca was significantly lower in plots treated with 100 or 200 kg K ha^{-1} than the control plots (except 100 kg K ha^{-1} in January 1998).

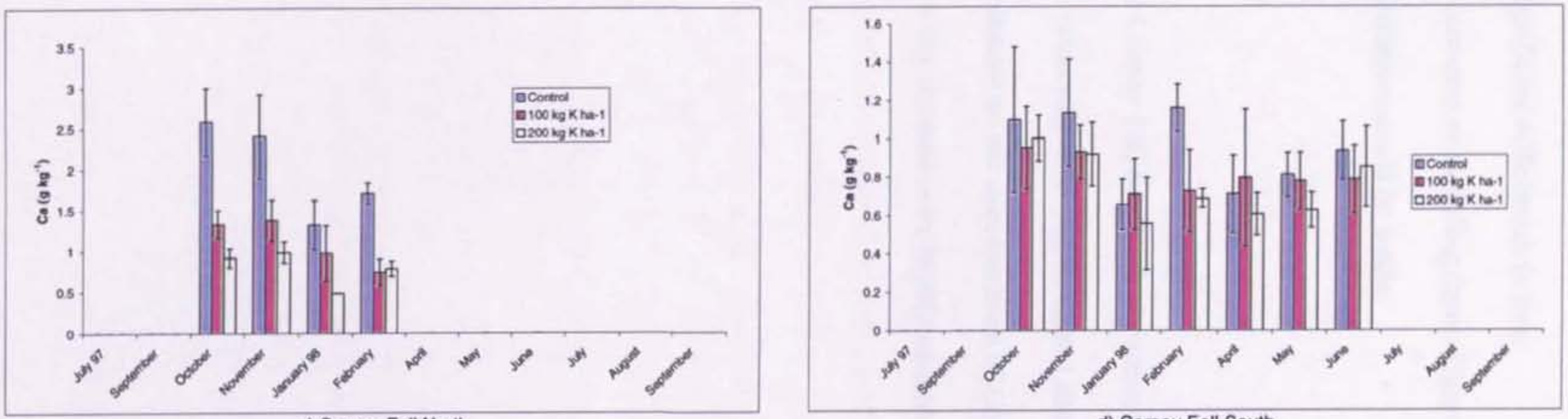
Corney Fell South

There was no significant effect of treatment or time on the concentration of Ca in the vegetation from October 1997 to June 1998 (see Figure 9.5(d)). Plots treated with 200 kg K ha^{-1} had a lower mean Ca concentration than the control plots on every sampling occasion though there were no significant differences on any one sampling occasion.



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

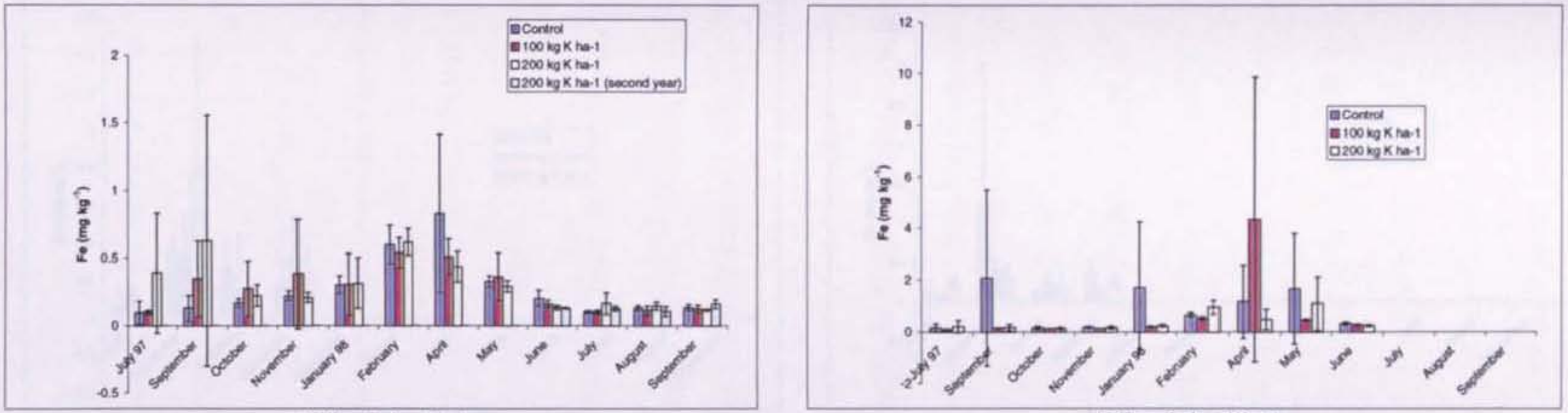
Figure 9.5 Concentration of Ca in above-ground standing biomass (g kg^{-1})
(mean and one standard deviation)

9.7 Iron

At all four experimental sites there were no significant differences in iron concentration in the vegetation between the treatments or sampling dates. Figure 9.6 shows that variability was high and no generalisations could be made.

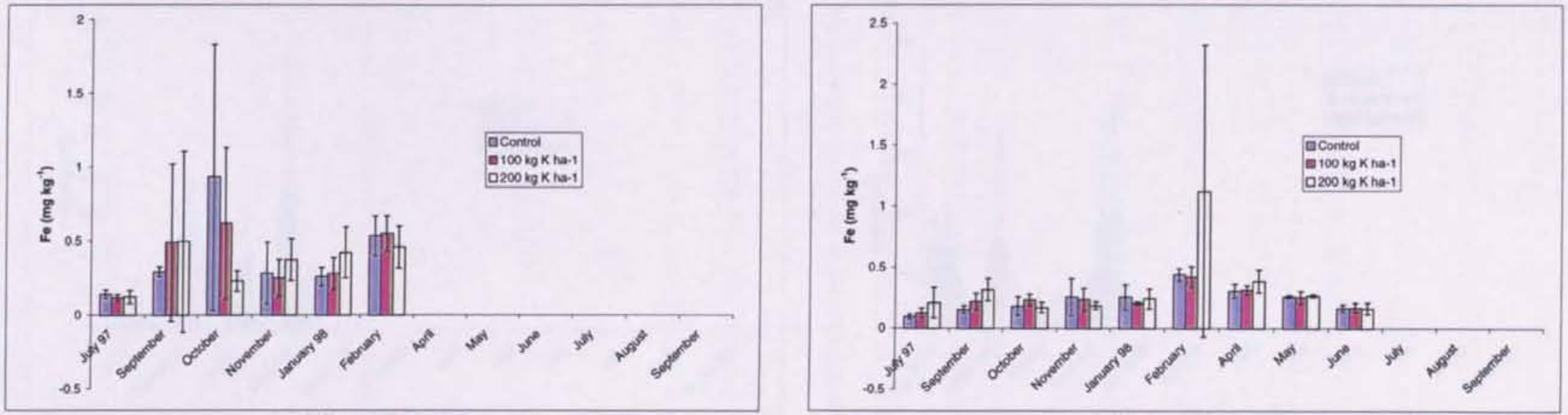
9.8 Cobalt

Only a small amount of data was available for Corney Fell South which meant that any statistical analysis was impossible. At the remaining three experimental sites there were no significant effects of time or treatment on the concentration of Co in the biomass. Figure 9.7 shows that within each site the data were highly variable showing no consistent trends.



a) Thornholme East

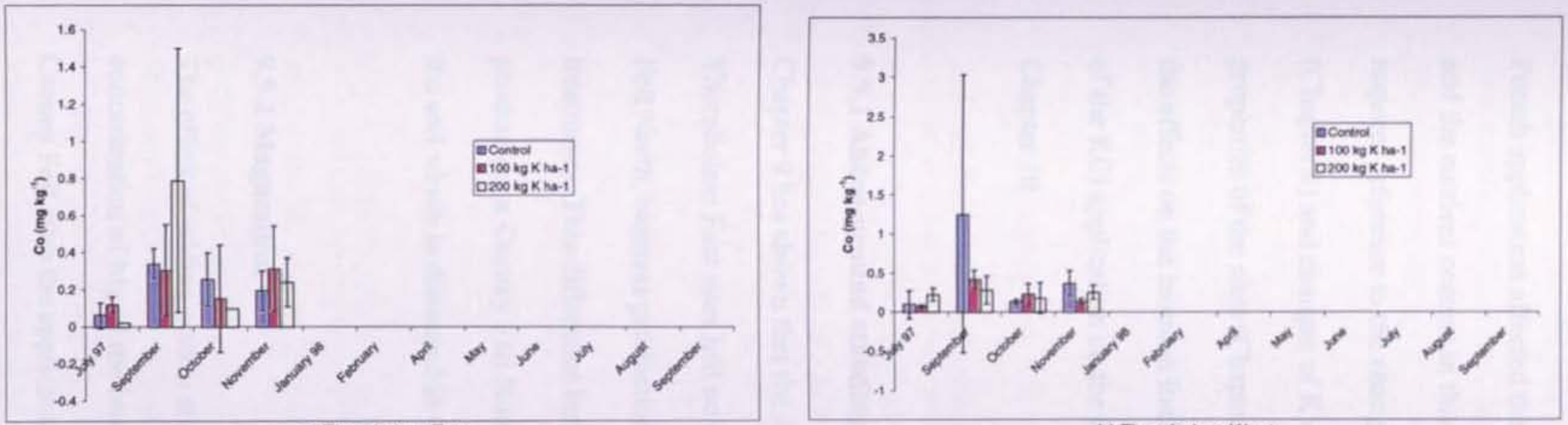
b) Thornholme West



c) Corney Fell North

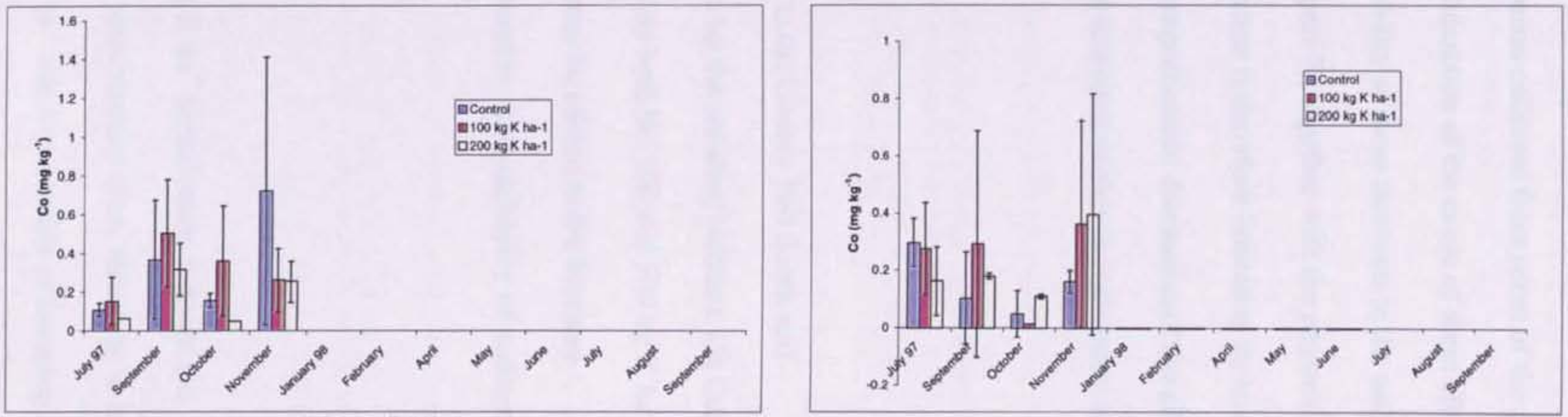
d) Corney Fell South

Figure 9.6 Concentration of Fe in standing above-ground biomass (mg kg^{-1})
(mean and one standard deviation)



a) Thornholme East

b) Thornholme West



c) Corney Fell North

d) Corney Fell South

Figure 9.7 Concentration of Co in above-ground standing biomass (mg kg^{-1})
(mean and one standard deviation)

9.9 Chapter 9 discussion

Potash application affected the amount of biomass collected from some of the sites and the nutrient content in this biomass. Consideration of the cause of these effects requires reference to the changes in the availability of these nutrients in the soil (Chapter 8) and changes of K in the soil (Chapter 7), together with the physical properties of the sites (Chapter 5). This discussion is therefore limited in its scope to the effects on the biomass itself and a more comprehensive discussion of the effects of the KCl application on the biomass and nutrient composition is undertaken in Chapter 10.

9.9.1 Above-ground standing biomass

Chapter 9 has shown that the addition of KCl to the Corney Fell South and Thornholme East sites had no consistent effect on the standing biomass. On Corney Fell North, biomass production was enhanced on both the 100 and 200 kg K ha^{-1} treatments. This difference between the sites may be related to the biomass production at Corney Fell North site being limited by the availability of nutrients in the soil which is discussed in Chapter 10.

9.9.2 Magnesium

The effect of adding potash at a rate of 200 kg K ha^{-1} significantly reduced the concentration of Mg in the biomass at all four experimental sites. However, at both Corney Fell sites the application of 100 kg K ha^{-1} was also capable of inducing a significant reduction in the concentration of Mg in the biomass. The cause for this reduction in Mg in the biomass is difficult to identify without considering the concentration of Mg in the soil and as such these changes are considered in Chapter 10. Stewart and Holmes (1953) also reported that the addition of K to grassland increased the production of biomass and that the concentration of Mg in this biomass decreased.

9.9.3 Copper

Stewart and Holmes (1953) stated that the application of K had little effect on the concentrations of most trace elements within the plant biomass. They continued, 'the only exception was Cu, for which the concentration within the biomass was generally reduced'. However, in this study the potash application had no overall effect on the concentration of Cu in the standing biomass, which was also reported by Rafferty, Dawson and Synott (1998).

9.9.4 Manganese

The effect of the potash treatment on Mn appeared to differ between geographical locations. At both Thornholme sites the concentration of Mn in the vegetation showed no change following KCl application. At the Corney Fell sites there was a negative effect on the concentration of Mn in the vegetation. The underlying mechanism for such differences is unclear. Rafferty, Dawson and Synott, (1998) demonstrated that KCl caused a reduction in Mn in the biomass on similar vegetation as Corney Fell North. This site showed the greatest and most consistent reductions in Mn concentrations in this study. In the soil, Mn exists in two principle forms: Mn^{2+} which is soluble, mobile and easily available, and Mn^{4+} which is practically insoluble, non-mobile and unavailable (Aubert and Pinta, 1977). In soils developed on calcareous or acidic parental geology, Mn ions are easily immobilised. In organic soils developed on basic parental rocks the availability of Mn for plant uptake is increased. Aubert and Pinta (1977), reported that as the acidity of a soil increased so did the loss of Mn from the soil through leaching. At both of the Corney Fell sites the application of KCl generally decreased the pH of the soil whereas at the Thornholme sites the pH of the soil was raised. Such decreases in soil pH at Corney Fell would have increased the loss of Mn from the soil whereas the rise of pH at the Thornholme sites prevented any loss occurring. Subsequently, the plant uptake of Mn at Corney Fell was reduced in treated plots whilst at Thornholme there was no effect.

9.9.5 Calcium

The potash application caused a reduction in the concentration of Ca in the biomass at both Corney Fell sites and Thornholme West. Stewart and Holmes (1953) and Berryman and Caldwell (1967) had reported that although the variability in the Ca concentration in the biomass was generally large, the application of K reduced the Ca concentration in biomass over successive years of cropping. The cause of this reduction requires consideration of Ca in the soil which is discussed in Chapter 10.

9.9.6 Iron and cobalt

The potash application appeared to have no effect on the concentration of Co or Fe in the standing above-ground biomass, showing highly variable results between sites and treatments. The problem of Cu deficiency in grazing animals is often directly related to the relative concentrations of Fe and Cu in the soil rather than exclusively the concentration of Cu. As the concentration of Fe did not significantly increased in the biomass at any of the sites examined it is unlikely that a copper deficiency would be induced as a direct result of KCl application.

The concentration of Co in the vegetation was so variable that no general conclusions could be drawn on the effects of the KCl application on Co availability to vegetation.

9.10 Chapter 9 conclusions

There was a significant reduction in the concentration of Mg in plots treated with potash compared to the control plots at all four sites. There was a significant reduction of Cu in the biomass for both treatments though this effect was limited to Thornholme West. Both Corney Fell sites showed a significant reduction in Mn concentration in plots treated with K in comparison to the controls. At the Thornholme sites no such effect was recorded. At Thornholme West and Corney Fell North plots treated with potash significantly lower concentrations of Ca in the biomass were observed.

Chapter 9 has demonstrated that an application of 200 kg K ha^{-1} to each of the experimental sites had no consistent effect on the amount of biomass collected from the treated plots, as such hypothesis 8 is accepted. Chapter 9 has also shown that the nutrients that are affected by the application of K differ between all four sites, as such this chapter does validate hypothesis 6 - that the effect on other nutrients depends on the underlying geology.

Chapter 10

Discussion

10.1 Introduction

Chapters 6 to 9 have shown the specific effects of the KCl applications on; the transfer of ^{137}Cs from soil to the biomass; K in the soil and biomass; and changes in other nutrients in the soil and biomass. Chapter 10 discusses the general effects of the KCl applications and how a change induced in one factor in the soil may have affected other nutrients in the soil and biomass.

Chapter 5 identified that at Thornholme West there was an increase in ^{137}Cs concentration in the winter months that could not be explained by the data presented, or comparable studies which have also shown a seasonal increase in the transfer of ^{137}Cs from soil to plant in the winter. Section 10.2 specifically discusses the underlying cause of this seasonal increase at Thornholme West and determines the cause of the reduction of ^{137}Cs transfer in the KCl treated plots at this site.

The study has shown that potash application increased the concentration of K in the soil (Chapter 7) and that the treatment reduced the transfer of ^{137}Cs from soil to plant (Chapter 6). However, to determine the direct effects of increasing the concentration of K in the soil on the concentration of ^{137}Cs in the biomass requires consideration of both data sets together. Section 10.3 discusses the effect raising the concentration of K in the soil on ^{137}Cs in the biomass.

The cause of the changes in the concentration of nutrients in the biomass (Chapter 9) must be a reflection of changes in nutrient availability in the soil. Section 10.4 of Chapter 10 discusses the possible cause of changes in nutrient concentration in the biomass by relating these changes to the effects of the application on the soil (Chapter 8). Chapter 10 does not consider parameters measured which have shown no change as it is assumed that the potash application had no effects on these parameters.

The longevity of a KCl application in the soil is of importance as this may determine the longevity of the effects on the soil and plant biomass, section 10.5 considers the longevity at the four sites.

Throughout this study the author has presented data in a number of units of measurement. In section 10.6 there is a discussion of the value of these formats and apparent differences between them and describes the contrasting effects that can be shown by displaying the data in these differing formats.

This study has been designed to produce practical recommendations for the effectiveness and side effects of a field application of KCl to reduce ^{137}Cs transfer in organic soils. Section 10.7 considers if the countermeasure is a viable option to reduce ^{137}Cs transfer into the food change when compared to other countermeasures such as AFCF, benonitite and clinoptilolite together with practical recommendations for the use of the countermeasure. A summary of the effects of the countermeasure and recommendations for further investigations are made in section 10.8. Final conclusions of the thesis and the eight hypotheses presented in section 1.1 are presented in section 10.9.

10.2 Thornholme West

The effectiveness of the potash application at Thornholme West is difficult to determine since the control plots showed a significant increase in the concentration of ^{137}Cs transferred into the above-ground biomass during the winter period 1997/1998. Chapter 5 considered that the observation may have been attributable to soil adhesion, though the possibility of this is low as the site was covered by a dense sward of vegetation over the sampling period. Campbell and Davies (1997) reported that the addition of calcium carbonate enhanced ^{137}Cs uptake in organic soils. At Thornholme West the underlying calcic sandstone at Thornholme West enhanced the concentration of Ca in the soil in November 1997 of the control plots (Figure 7.9(b)). As such elevated concentrations of Ca in soil were not recorded in the soil sampled from the plots treated with potash. Such increases in Ca in the soil may be the cause of high concentrations of ^{137}Cs in the vegetation. However, if this were the factor that caused such high concentration of ^{137}Cs in the biomass of the control plots, it may mean that the application of KCl had no effect on the ^{137}Cs in the biomass and that these plots were not true controls. Alternatively, it may mean that as Thornholme East showed that the application of KCl caused a significant loss of Ca from the soil that the treatments prevented any significant increase of Ca in the soil by increasing the loss of Ca through leaching. Thus, the ^{137}Cs concentration in the treated plots did not rise to such levels observed in the control plots.

The exact cause of the reduction in ^{137}Cs concentration in the biomass at Thornholme West has been shown to be difficult to identify, however as the treatment plots did produce a significant reduction in ^{137}Cs transfer it is concluded that the treatment was effective at Thornholme West. It is also concluded that further investigation is required to determine the exact effect of the countermeasure at sites underlain by Ca rich parent material.

10.3 Effect of potash on K availability and ^{137}Cs uptake

The review of published literature in Chapter 2 indicated that an application of KCl to a soil of low K status could reduce the transfer of ^{137}Cs from soil to plant. Chapter 6 showed that at all four sites this effect of the application did occur. The cause of such reductions is attributed to increases in K concentration in the soil and the behaviour of exchangeable K in the soil (Shaw, 1993). Exchangeable K in the soil is in dynamic equilibrium with K in the soil solution (Brady and Weil, 1999) therefore, there is a constant transfer of K from the exchangeable surfaces into the interstitial water where it may be transported into plant roots. Nisbet, Mocanu and Shaw (1994) showed that when the soil had low levels of interstitial K, i.e. < 0.5 meq 100 g^{-1} in loam and 0.3 meq 100 g^{-1} in sand, an application of K was an effective countermeasure. Montero et al., (1998) in the TEMAS project assumed a reduction factor of 5 for peat soil with exchangeable K ≤ 0.3 meq 100 g^{-1}. In this study exchangeable K was typically 0.5 meq 100 g^{-1} at both Thornholme sites and at Corney Fell South whilst at Corney Fell North it was around 0.3 meq 100 g^{-1}. According to Montero's calculation the countermeasure would not have been effective in three of the four sites. However, at all four sites, it has been shown that following an increase in the concentration of K in the interstitial water there was a subsequent reduction in the concentration of ^{137}Cs in the plant biomass. Thus, the values quoted by Montero for effective reductions in ^{137}Cs transfer appear to be inconsistent with the data from this study.

Potassium applied as a countermeasure reduces the transfer of ^{137}Cs from soil to plant at the root-soil interface, which generally move from the soil to the root surface via the soil solution. The relative concentration of K in the soil solution is therefore critical for the competition between Cs and K for plant uptake. Above a concentration of 20 μM K in the soil solution, the roots of *Triticum aestivum* are able to distinguish between Cs and K and competitively exclude Cs (Shaw, 1993). At Thornholme West, the concentration of K in the interstitial water of the control plots was approximately 0.15 mM. In July 1997 the application of 100 kg K ha^{-1} increased this value to 0.45 mM and the 1200 kg K treatment to 1.5 mM K. According to the data from Sandalls, (1989) reworked in Shaw (1993) such increases should have produced a decrease in the transfer coefficient by approximately 70 and 85 %. At Thornholme West, such an effect was not observed (see Figure 6.2(b)). However, over the sample period plots treated with 200 kg K ha^{-1} showed significant increases in biomass production (see Figure 9.1) which may indicate that growth was limited by K availability. As the concentration of ^{137}Cs within the biomass at Thornholme West was not effected by the K application it suggests that the input of K was insufficient to induce an effect on the transfer of Cs. This was also identified in the REDUP project (1999) where plant growth was stimulated, greater depletion of K in the soil occur such that the dose of fertiliser did not increase the concentration of K in the soil sufficiently to induce a reduction in ^{137}Cs transfer.

Although the relative difference in interstitial water K concentration between the treatments gradually declined over time, the mean concentration per unit volume of soil water was consistently greater in plots from August 1997 until November 1997. At Thornholme West in September and October 1997, the mean concentration of K in the interstitial water in the 100 kg K ha^{-1} plots was 1.05 mM and in the 200 kg K plots 1.1 mM. According to Shaw (1993), such concentrations could reduce the transfer coefficient by approximately 50 %. In November 1997, both 100 and 200 kg K ha^{-1} treatments had a negative effect on the transfer of ^{137}Cs from soil reducing the mean concentration by approximately 33 and 60 % respectively. However, such reductions in ^{137}Cs transfer may have been due the relative increase in ^{137}Cs in the controls rather than any effect of treatment. In November 1997 it is likely that the available K sources were depleted within the soil and although new biomass production was lower, the uptake of ^{137}Cs increased due to nutritional requirements in the control plots for K or ions analogous to K. However, in the plots treated with K, the high concentrations of K in the interstitial soil water and the lower total demand for K allowed the plant to exclude ^{137}Cs in favour of K. Thus, the concentration of ^{137}Cs in the above-ground biomass declined. From January until April of 1998, the high enhanced K levels in the interstitial water kept the concentration of ^{137}Cs in the vegetation low. In May and June of 1998, K in the soil again became limiting and the treatments had little effect except in enhancing biomass production.

It is therefore difficult to determine if the effect of the potash application on the treated plots was a true effect as the controls appeared to behave differently than the treated plots in the winter period of 1997/1998.

At Thornholme East and both Corney Fell sites, the concentration of K in the interstitial soil solution was typically between 0.23 and 0.27 mM. The application of KCl increased this value to between 0.54 and 0.66 mM in the 100 kg K ha^{-1} treatment and over 2 mM in the 200 kg K ha^{-1} treatments in July 1997. This had no effect on the activity concentration of ^{137}Cs at either Thornholme East or Corney Fell South in July 1997. At Corney Fell North there was no apparent effect on the activity concentration of the 100 kg K ha^{-1} treatment though there was a mean reduction of almost 50 % in the plots treated with 200 kg K ha^{-1}. Shaw (1993) suggested such values should reduce transfer by 50 % in the 100 kg K ha^{-1} treatment and by 70 % in the 200 kg K ha^{-1} treatment.

The reason for such different responses between sites to the KCl treatment may be due the soil moisture regime. At Corney Fell North the salt was able to move quickly into solution due to the high moisture content of the soil and therefore had a longer time to induce an effect in the vegetation. Further, vegetation sampled in July 1997 was likely to be dominated by biomass produced prior to K application, thus any reduction in ^{137}Cs would be diluted. The effect of the KCl application may have been far greater in July 1997 than consideration of activity concentrations, CR's or Tag values suggest. The flux of ^{137}Cs from soil to plant at Corney Fell North (see Table 5.2) was reduced by 24 % in plots treated with 100 kg K ha^{-1} and by 55 % in plots treated with 200 kg K ha^{-1}. Therefore, in July 1997 the flux values suggest that an application of 200 kg K ha^{-1} was twice as effective at reducing the transfer of ^{137}Cs from soil to plant than a treatment of 100 kg K ha^{-1}.

Table 6.5 showed that the effect of an application of potash of 200 kg K ha^{-1} at Thornholme East in 1998 in reducing the flux of ^{137}Cs from soil to plant was comparable to that in 1997 whereas activity concentrations, CR's and Tag values indicated no effect of the application in 1998. Table 7.1 showed that the relative increase of K in the interstitial water at Thornholme East for a treatment of 200 kg K ha^{-1} was similar in 1998 as in 1997. As such it must be concluded that the flux value represents a true reflection of the effect of an increase in the interstitial water on the ^{137}Cs concentration in the biomass. This result may have consequences for other studies which have attempted to determine the effectiveness of K as a countermeasure in environments where the soil and biomass production is heterogeneous. In using Tag values or CR's the study takes no account for the production of biomass over the area and as such the actual effect of the application may be reported to be greater or less than the actual measure. The author suggests that when a study is designed to determine the effects of a K application to vegetation the flux methodology should be used whereas if the study is concerned with grazing animals where biomass intake is uniform Tag values are appropriate.

The effect of a reapplication of KCl to the Thornholme East site did not have any significantly greater effect on the activity concentration on plots treated with 200 kg K ha^{-1} in 1997. However, it almost doubled the concentration of K in the interstitial soil water of plots treated with 100 kg K ha^{-1} in 1997 and 1998 and thereby induced a reduction in the activity concentration larger than that observed in 1997. The concentration of K extractable with NH_4Ac was also increased in all treated plots allowing the replenishment of K in the interstitial water. The reapplication of K to the 200 kg K ha^{-1} plots increased the reduction of ^{137}Cs (% flux values) by over 50 % compared to a single application. The concentration of K in the interstitial water (per unit volume) did not change from 1997 to 1998. However the increase in the concentration of easily exchangeable K in the soil allowed K concentrations in the interstitial water to be maintained for a greater period of time, thus potentially permitting greater reductions in ^{137}Cs transfer.

The concentration of available K within the soil can be determined using many methodologies, however, the resulting values only approximate the concentration available to the plant via the interstitial soil water. This study has demonstrated that the partitioning of K between the available fraction (NH_4Ac extraction) and the concentration in the soil water can vary by up to an order of magnitude between Corney Fell North and Thornholme East. However, when the concentrations of K in the interstitial water are compared between sites they show similar concentrations. The application of KCl to all four of the sites resulted in a similar increase in the concentration of K in the interstitial water, and, as the reduction in ^{137}Cs transfer was also comparable between the sites, the author concludes that the concentration of K in the interstitial water was the best measure of approximating the potential for a reduction in ^{137}Cs transfer.

10.4 Side effects of KCl applications

The principle side-effects of the KCl application detected in this study were on the biomass and nutrient concentration in the soil and vegetation which are considered in sections 10.4.1 and 10.4.2.

10.4.1 Standing above-ground biomass

The addition of KCl to the Corney Fell South and Thornholme East sites had no consistent effect on the standing biomass whilst at the Corney Fell North site, biomass production was enhanced by both the 100 and 200 kg K ha^{-1} treatments. Corney Fell North had a very low concentration of (NH_4Ac extractable) K in the soil in comparison to the other three sites (Figure 6.8) and a low volume of the soil was composed of clay particles (Figure 4.5), thus a large proportion of the extractable K was present in the interstitial soil water. As a result K in the interstitial water is likely to have been reduced by plant uptake and leached from the soil. As the concentration of K in the soil was low, vegetation at Corney Fell North would have been more likely to be limited by K than plants at the other three sites. The observed effect of an increase in interstitial K via potash application was, therefore, the probable cause of an increase in biomass production at this site. At Thornholme West, an increase in biomass production following K application only occurred at a rate of 200 kg K ha^{-1}. The high total proportion of clay particles in the soil (see section 5.7.1) may have delayed replenishment of the K in the interstitial water thus limiting plant growth. The addition of KCl could have increased the easily available forms of K, increasing the rate of K movement to the roots, thus, if biomass production were limited by K, biomass production would have been increased which was observed.

10.4.2 Nutrients

The application of KCl to the four experimental sites was only recorded as causing significant changes in the concentration of the nutrients Ca, Cu, K, Mg and Mn in the soil and biomass. However, as changes in K concentration in the soil and biomass have been discussed in Chapter 7 no further consideration is made in this chapter. There was no effect of the KCl application on the concentration of Mn in the lysimeter water and the effect of the change in concentration in the biomass was discussed in section 9.9.4. Thus the effect of the potash applications in this discussion is limited to Ca, Cu and Mg.

The application of KCl caused a reduction in the concentration of Ca in the biomass at Thornholme West and both Corney Fell sites. This effect may be attributable to a loss of easily exchangeable Ca from the soil by the K application. However, there was little apparent effect of the K application on Ca in the soil identified in Chapter 8. The loss of Ca from the soil surfaces may not have been detected by soil extraction using NH_4Ac due to the high variability in reported Ca concentration (Figure 8.9) masking Ca lost from the soil. However, such small losses of Ca may have been sufficient to induce a reduction in Ca concentration in the biomass. The author suggests that further investigation of the effect of KCl application on Ca in the biomass in organic soils is required to determine the mechanism for the reduction in Ca in the biomass observed.

The reduction in the concentration of Cu in the interstitial water was limited to the Thornholme East site. The effect of the application on the concentration of Cu, which could be extracted using EDTA, was a reduction in concentration at Thornholme East and Corney Fell North sites. These sites represented the sites where the soil had the greatest amount of organic matter. In 1977 Aubert and Pinta showed that the plant availability of Cu could decrease when the pH of an organic soil increased. Thornholme East showed a significant increase in soil pH as a result of KCl application which may have caused the lowering of Cu concentration in the soil. At Corney Fell North such a decrease in Cu may have been due attributable to the exchange of ions between the interstitial soil water and nutrients lost from the soil via mass flow. However, at both sites such reductions were not detected to result in any change in the concentration of Cu in the plant biomass, and therefore of no consequence to the nutrition of grazing animals. At Thornholme West, the application of KCl to the soil did reduce the concentration of Cu in the plant biomass, this effect was likely to be the result of dilution of Cu ions in the biomass due to greater biomass production (see Figure 9.1), and may have implications on the health of grazing animals. Such health implications are likely to be restricted to male rams where the demand for Cu is high and may be averted by the use of copper needles of salt licks.

At both the Thornholme sites changes in the concentration of Mg in the interstitial soil water only significantly affected Mg in the plant biomass of plots which were treated with 200 kg K ha^{-1}. At both Corney Fell sites effects of the potash application on Mg in the biomass were observed for both potash treatments, yet these sites showed no overall effect of treatment on the concentration of Mg in the interstitial soil water. This suggests that the effect of the potash was more complex than a simple displacement of ions. Hovland and Caldwell (1960) suggested that KCl may affect Mg uptake by two methods; a) adding K increases the loss of Mg from the soil system, and b) K 'out-competes' Mg for exchangeable sites on the plant roots. Since the potash treatments had no effect on Mg in the interstitial water, the lowering of Mg in the biomass could be attributable to competition between the K and Mg ions for plant uptake and a dilution effect of the Mg in the soil via an increase in the concentration of K. Jacob (1958) determined that an increased concentration of K in a soil decreased the speed of diffusion of Mg from the interstitial water into the plant. This increased the concentration of Mg in the interstitial water observed at all four sites. Stewart and Holmes (1953) reported that the addition of K to grassland increased the production of biomass though the concentration of Mg in this biomass decreased. However, it is also possible that the high variability between replicate treatment plots at Corney Fell compared with the Thornholme sites may have meant that the sampling programme undertaken failed to detect changes in interstitial water which were observed at the Thornholme sites (Figure 7.5).

Figures 7.7 and 7.9 have shown that the concentration of Mg and Ca in the soil at Thornholme East was far greater in plots established in June 1998 than any of the other treatment plots. The likely cause of these greater concentrations is unclear, as there was no effect on the biomass sampled.

10.5 Longevity of application

The application of KCl as a countermeasure for reducing the transfer of ^{137}Cs from soil to plant in organic upland soils should only be recommended if two criteria are met: a) the treatment is sufficiently effective, and b) the reduction in transfer is of sufficient duration to warrant the total cost of application. Nisbet (1995) defined that a countermeasure was effective if the reduction factor was greater than 1 and a countermeasure could be considered as highly effective if it generated a reduction factor greater than 5. In this report the countermeasure is considered effective if it either induced a significant ($p < 0.05$) reduction in the transfer and/or it generated a reduction factor greater than 1. The discussion in Chapter 6 demonstrated that the application of KCl was effective at each of the four sites. The duration of the effectiveness is more difficult to quantify. At Thornholme East and Corney Fell South the countermeasure was effective for at least one year producing significant reductions in the transfer of ^{137}Cs from soil to plant. The site at Corney Fell North was destroyed in February/March 1998 preventing a direct assessment of countermeasure longevity. As this site was the first to show an effect of the potash application, it can be assumed that it would also be the first to show a decrease in effectiveness due to the higher throughput of water and associated leaching of K. However, Paul and Jones (1995) demonstrated that an application of KCl to a bog site on Corney Fell was effective for over two years, hence it is likely that the countermeasure would have been effective at Corney Fell North for at least one year.

The longevity of the countermeasure at Thornholme West, was also difficult to determine since the KCl application was only effective in the winter period. One year after application in June 1998, the countermeasure was no longer effective. However, if sampling had continued until November or December in 1998, it may have been possible to demonstrate that the elevated concentrations of K within the interstitial soil water could still induce a negative effect on the transfer of ^{137}Cs into the biomass.

It can be concluded that at three of the four sites selected for this study the application of KCl as a countermeasure for ^{137}Cs was effective for at least one year. Both potash treatments increased the K concentration in the soil and caused a reduction in ^{137}Cs transfer which persisted for at least one year. However, had this study continued then it is likely that the effectiveness of the 100 kg K ha^{-1} treatment would have decreased sooner than that of the 200 kg K ha^{-1} treatment. According to the work of Jones et al. (1999), five years following KCl application at a rate of 200 kg K ha^{-1} the treatment was still effective. Thus, if sampling had continued it is likely that the countermeasure would have been effective for more than one year, validating hypothesis 4.

10.6 Units of measurement

Throughout this thesis the author expressed data in a range of formats including unit mass, unit area and unit volume. Literature generally publishes data in terms of units of mass. However, a concentration expressed as per unit mass has no direct relationship to a spatial area as it does not consider biomass production. Thus, to express relative differences between treatments relative to the ecosystem as a whole allowing ecosystems to be compared, values of biomass must also be considered to obtain a full comprehension of any effects. For example, WS Atkins (1996) did not identify any change in the K status of vegetation on Corney Fell five years following K application. In October 1995, five years after application the concentration of K in vegetation had a mean concentration of 6700 in the control plots and 6433 mg kg^{-1} in the plots treated with 200 kg K ha^{-1}. If this data is expressed per unit area this generates values of 409 mg K m^{-2} for the control treatment and 589 mg K m^{-2} for the potash treatment. This re-analysis of the data suggests that an actual effect of the KCl application enhancing K in the biomass, in the WS Atkins study was not reported.

The author suggests that the format of data presentation should be carefully considered and a unit of measurement chosen which reflects the aims of the study. For example Figure 4.3 shows that all four sites have a similar distribution size of soil particles, however, the same data when expressed as surface area or volume show an observable difference between the four sites. Figure 4.16 indicated that the greatest concentration of K in the soil extracted by NH_4Ac was at Thornholme East when expressed as per unit mass, yet when this data is expressed as per unit volume Figure 4.18 shows that Thornholme West had the greatest concentration of K. If the study is designed to examine the potential for change in nutrient concentration in an ecosystem then concentration per unit area or volume should be used. Alternatively if a study aims to examine changes in concentration of nutrients in the biomass then a concentration per unit mass should be adopted. In this study the author has attempted to determine changes induced by KCl application on the ecosystem and in grazing animals thus both formats of data presentation were considered.

10.7 Recommendations for the use of K as a countermeasure

The deployment of a countermeasure in upland environments in the UK is more problematic than in arable or lowland grassland systems due to physical limitations, costs and the unacceptability of many available countermeasure options to farmers, environmentalists and members of the general public (Nisbet, 1995). However, some of the potential countermeasures suitable for deployment on such upland areas include AFCF, bentonite, clinoptilolite and K (International Atomic Energy Agency, 1994).

Nisbet (1995) considered two countermeasures as potentially suitable for deployment on rough grazing land with semi-natural habitats: AFCF boli and K application. In the review, Nisbet concluded that AFCF administration was highly practical and discounted K application due to difficulties with administration of the treatments and ecological consequences.

This study has shown that an application of KCl in the form of a potash salt is an effective countermeasure to reduce the transfer of ^{137}Cs from soil to plant. The countermeasure is cheap and easily applied in comparison with other countermeasures which are currently available. The countermeasure also has several advantages over alternatives such as AFCF in that it is a low technology option which would be likely to have greater acceptability to farmers, members of the general public, and environmental groups as the countermeasure would be seen to be a familiar treatment which was of 'natural' origins. Problems with application of the countermeasure could be overcome if deployment were restricted to areas subjected to the greatest grazing pressure. These tend to occur on drier areas of land and as such mechanical methods of application may be used.

The application of AFCF has specific advantages over K application as it is directed at the individual animal rather than the foodstuffs such that the variability in reduction is likely to be more easily predicted. However, potential reductions in ^{137}Cs activity concentration may only reach a maximum of 50 % and with a longevity of 3 to 8 weeks (Beresford et al., 1999). The application of KCl can achieve reductions in ^{137}Cs concentrations of greater than 50 % and has a greater longevity. The author concludes that on areas where a reduction factor in the ^{137}Cs concentration of between 1 and 3 is required the application of K is a viable and appropriate option.

In an upland environment the application of any soil-based countermeasure is unlikely to occur over large swathes of land in the UK, due to application costs and availability of KCl salt. The application could be targeted at specific areas of land. In the UK countermeasures in upland environments have been developed for grazing animals which are principally sheep and cattle. Intervention prevents the movement of animals that contain concentrations of ^{137}Cs above threshold levels to market and thereby into the food chain. Monitoring of such animals generally occurs in restricted areas and requires the animals to be retained on land for a period of time. This land is typically freely draining where vehicular access is possible. If the animals were retained on such lands for a greater period of time prior to monitoring and subsequent movement to market it is possible that an application of KCl would reduce the concentration of ^{137}Cs in the animals. As the land represents a small spatial area the costs of materials and application time are minimised and, as all animals must graze on such treated land, the treatment is ensured to be delivered to all of the animals. Mechanical application is possible as the land is easily accessible and the animals can be monitored for any indication of nutrient deficiency induced by the application.

10.8 Summary and further investigation

This study determined the effects of applying K as a countermeasure against radiocaesium in organic soils. It is one of the first field investigations to be undertaken which has attempted to determine the effects of an application. It has shown that the countermeasure is effective in producing a reduction in the transfer of ^{137}Cs from soil to plant. However, the study has also identified that the application may also cause a disruption in the transfer of other nutrients from soil to plant such as Cu, Mn and Mg. This study has been limited in its scope to determine the exact cause or quantification of the effects on these nutrients and has identified that further research is necessary before the specific effects of the application are known. The study has shown that at each site the variability in the transfer of nutrients from soil to plant is large and that there is a need to conduct comparable studies where the number of samples collected is greater to reduce the sampling errors. Only when such sampling errors are reduced can accurate comparisons between sites be undertaken and definitive conclusions drawn.

This study has only examined the effect of the application on a few elements in the soil and biomass. The literature review identified nutrients that were likely to be effected by the countermeasure, however to ensure that the nutrition of grazing animals would not be deleteriously affected by the countermeasure further work is required. The author considers that in any subsequent analysis work the researcher should ensure that the effects on Mo and Co are quantified as these elements are vital for sheep nutrition.

The study showed that the effect of the KCl application at Thornholme West is complex and that further sampling work and analysis is required before the effect of the application is determined at that site. If the effect of the KCl application at Thornholme West is confirmed to be related to that of Ca concentration in the soil it may require detailed investigation. The application of Ca to soils has been identified as a suitable countermeasure for ^{90}Sr (International Atomic Energy Agency, 1994). If an increase in Ca concentration in the soil can induce an increase in ^{137}Cs transfer in vegetation this may pose management problems for organic soil that have been contaminated with both ^{137}Cs and ^{90}Sr.

Since this study began a slow release salt containing higher concentrations of Mg and trace elements has been marketed by Cleveland Potash Ltd. The author considers that an application of this countermeasure should be undertaken to determine if the longevity of the K in the soil system can be prolonged, the effectiveness of the application increased and the possible effects of nutrient deficiencies minimised. The author considers that potential negative effects of the countermeasure application may be removed by applying such a salt and that such a countermeasure could induce a significant reduction in ^{137}Cs transfer with few or no negative impacts on the grazing animals.

10.9 Conclusions

At the four Cumbrian upland sites studied the application of potash was effective at reducing the transfer of ^{137}Cs from soil to plant.

The study provides field evidence to support the observations of Shaw (1991) who demonstrated that the best method of predicting the reduction in ^{137}Cs transfer from soil to plant was by measuring the increase in K concentration in the interstitial soil water following K application.

The apparent effectiveness of the countermeasure was dependent on the method of calculation. When concentration ratios or Tag values were used to quantify transfer, the effects of KCl appeared to vary greatly between the four sites and between successive years. However, when the flux was quantified instead, the countermeasure effectiveness was more consistent between sites. The latter method showed a reduction in the transfer of ^{137}Cs by approximately 50 to 70 % at all four sites with only small differences between the use of 100 or 200 kg K ha^{-1}. The data generated by the flux methodology approach also indicated that the countermeasure was equally effective following an application in two successive years.

The countermeasure appears to have a delayed effect on the activity concentration of ^{137}Cs within the vegetation since there was a gap of two to three months between application and effect of the treatment. This is probably due to the time required for dissolution of the KCl salt to occur and the initially large fraction of standing biomass produced prior to countermeasure application. As a consequence, it is possible that the countermeasure initially had a greater effect than observed because the sampling of biomass encompassed material produced both prior to, and following KCl application.

The results for the Thornholme West site indicated that the concentration of Ca within the soil may need to be considered with respect to the effects of the countermeasure on organic soils that have developed on calcium rich bedrock. The change in Ca concentration in the winter months was the most likely dominant factor of the changes in the ^{137}Cs concentration in the vegetation.

The application of KCl raised the pH of the soil, but this effect was short lived and appeared to have little effect on any of the other variables measured.

The application of potash to the four study sites reduced the concentration of Mg in the soil through increased leaching. However, the total amount of Mg lost from the soil was relatively small relative to the remaining Mg concentration within the interstitial soil water, and that which could be extracted with NH_4Ac and restricted to the first few months following application. Furthermore, there was no significant loss of Mg from the soil following reapplication. Thus, only on soils where the concentration of Mg is bordering on deficiency prior to treatment could the countermeasure result in Mg deficiency in plants. The KCl application may also affect the concentration of available Mn and Cu in the soil for plant uptake. However, the effect was site specific and no general conclusions can be drawn from this study.

Overall this study has demonstrated that an application of KCl as a countermeasure for ^{137}Cs is effective and that the side effects of its application are limited and appear to pose no risk to the nutrition of sheep. Both application rates used in this study have been proven to be capable of producing a significant reduction in the transfer of ^{137}Cs from soil to plant. It is the recommendation of this study that as the countermeasure is relatively inexpensive, easy to apply and widely available, it should be broadly utilised as a countermeasure wherever practical application is possible and a reduction in the transfer of ^{137}Cs from soil to vegetation is desirable. The study also suggests that reapplication of potassium every one to two years will maintain the effectiveness of the countermeasure. An application rate of 200 kg K

ha^{-1} is recommended to ensure the greatest reduction in ^{137}Cs transfer possible and where suitable resources are available. If resources are limited, or the soil has been identified as bordering on deficient in Mg, Ca, Mn or Cu, an application rate of 100 kg K ha^{-1} is recommended.

Chapter 1 identified a number of hypotheses which have been tested in Chapters 6 to 9. These hypotheses have been tested and validated, or rejected in conclusions and summaries of Chapters 5 to 9.

1) The countermeasure significantly reduces the transfer of ^{137}Cs from soil to plant in a range of organic upland soils – thus validating hypothesis 1.
2) The depth of the organic horizon did not effect the reduction in ^{137}Cs. The author acknowledges that once the depth of the horizon is zero and the soil is mineral the effectiveness of the application will change, thus hypothesis 2 is validated.
3) The application of 200 kg K ha^{-1} has been shown to have a significantly greater effect on reducing the ^{137}Cs concentration than an application of 100 kg K ha^{-1} at some of the experimental sites thus hypothesis 3 is validated.
4) Thornholme East was the only site where sample collection continued for a period of greater than one year, however, as application was repeated on these plots hypothesis 4 has not been fully tested.
5) Hypothesis 5 aimed to test is there was any difference in the effectiveness of the countermeasure applied in two successive years. This study has shown that the format of the data presented is critical in determining if this hypothesis is valid. If the data is examined as activity concentrations, CR's or Tag values then the

hypothesis is invalid. If the data is presented as flux values the hypothesis is valid.

6) It has been shown that the effect of the potash application on other nutrients does differ between sites and as the site properties are likely to be dependent on the underlying geology hypothesis 6 is accepted.
7) The pH of the soil was significantly raised due to the application of KCl at both Thornholme sites, thus hypothesis 7 is also accepted.
8) Hypothesis 8 aimed to determine if the application of KCl was able to cause a significant increase in biomass production which was recorded at Corney Fell North for a treatment of 200 kg K ha^{-1}. However as the application also appeared to reduce biomass production at some sites, therefore the hypothesis is not accepted as the general effect is unclear.

This study has shown that an application of KCl at 100 or 200 kg K ha^{-1} is an effective countermeasure for ^{137}Cs in a field application in a range of organic upland soils. However, further studies into the effect of the application on the soil and plant nutrition are required to determine the effects on the ecosystem as a whole. The study has shown that there are few side-effects of application. However, it has also identified that spatial variation in upland soils is large and that potential effects of application may not have been identified due to sampling error.

This thesis has shown that further scientific research is required to determine the exact mechanism whereby KCl reduces ^{137}Cs concentration in the vegetation and to quantify the effect on soils which have high concentrations of Ca. The study has also shown that the measures employed to quantify the effect of the countermeasure need to be carefully examined such that true effects of the application may be identified.

This study has shown that in a practical field application KCl can significantly reduce the transfer of ^{137}Cs from soil to plant with few significant side-effects on the biomass.

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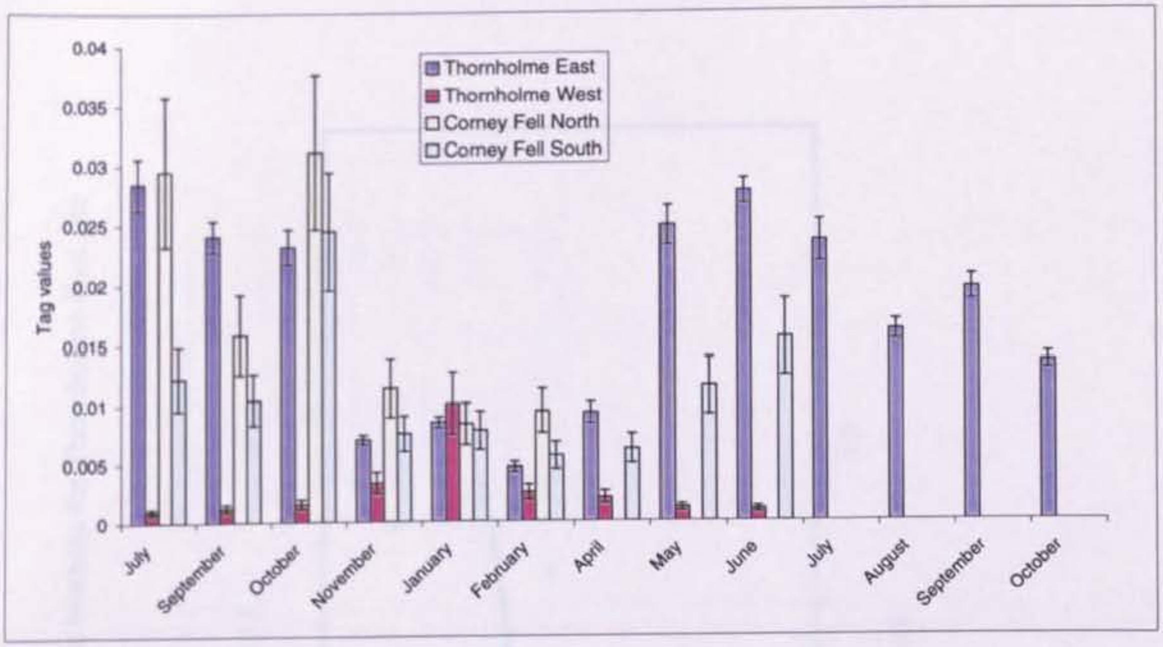
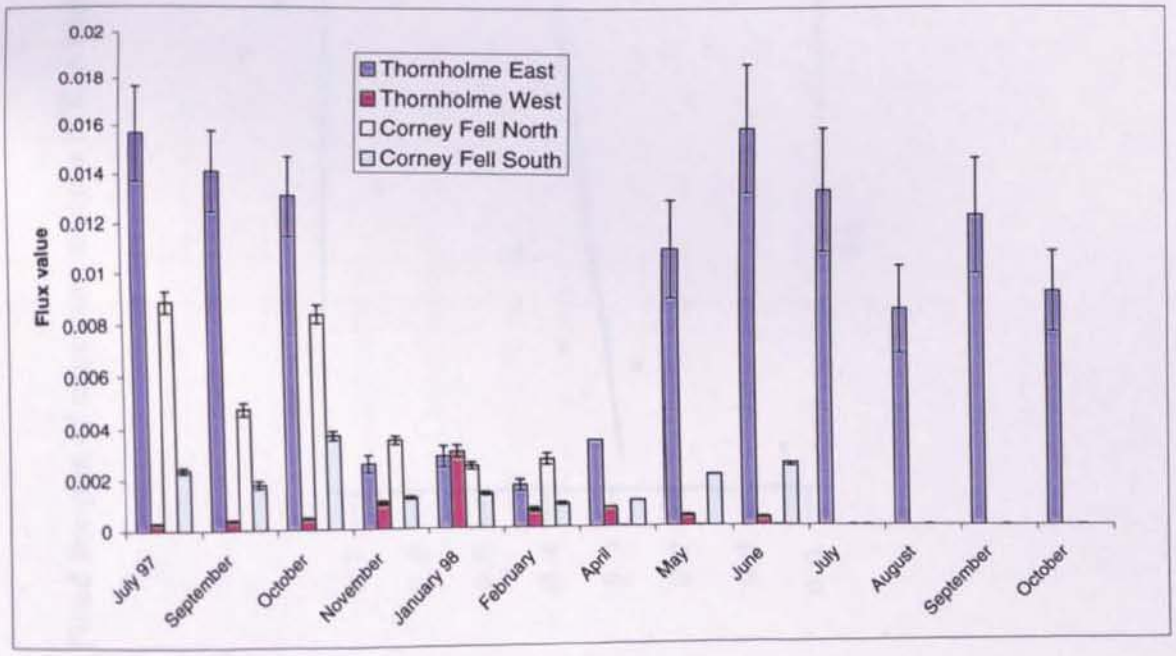
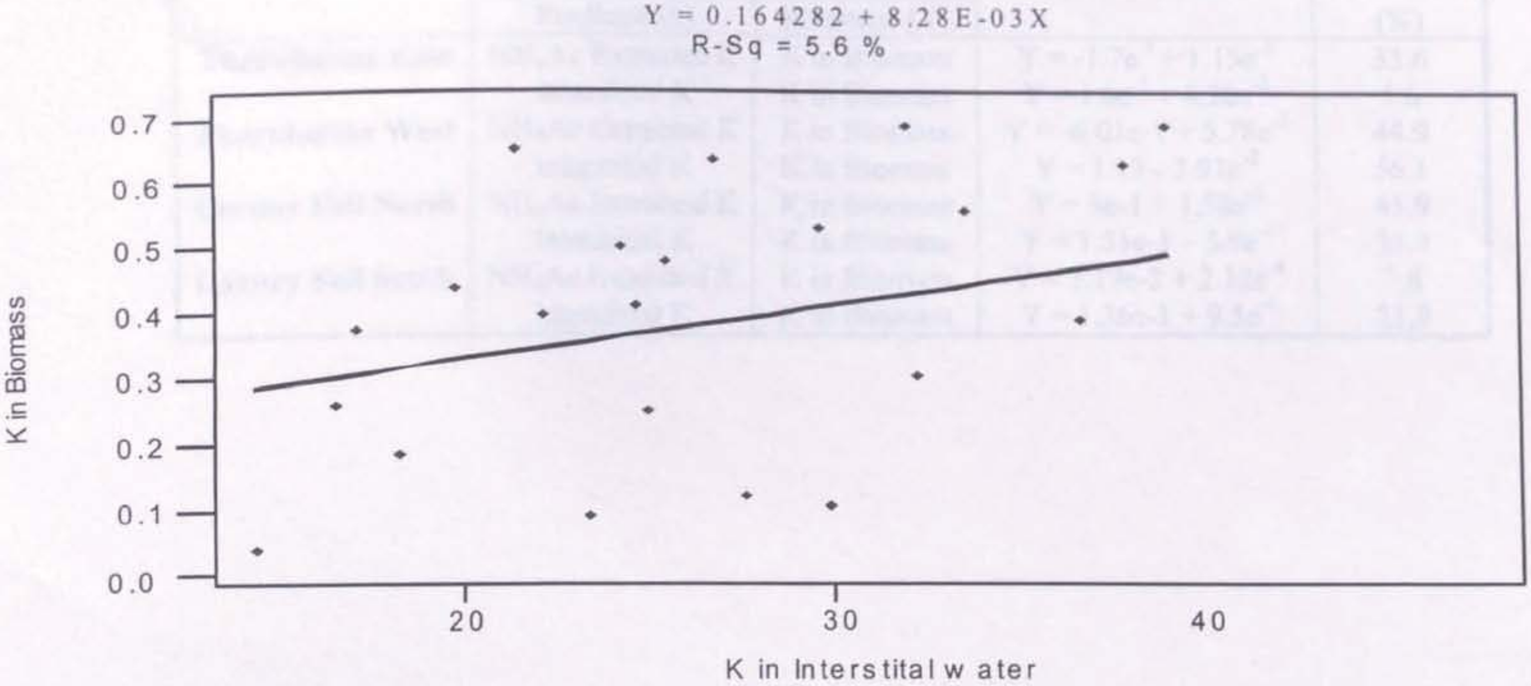


Appendix 1a. Tag values at each of the experimental sites.
(mean and one standard deviation)



Appendix 1b Flux of ^{137}Cs from soil to plant
(mean and one standard deviation)

Appendix 2 Fitted line plot of regression analysis of K in interstitial water against K in biomass for Thornholme East site



Appendix 3. Regression analysis data from regressing K in biomass to that extracted from the soil using NH$_4$Ac and interstitial soil water

Site	Regression		Equation of Line	R^2 Value (%)
	Predictor (x)	Response (Y)		
Thornholme East	NH$_4$Ac Extracted K	K in Biomass	$Y = -1.7e^{-3} + 1.15e^{-3}$	33.6
	Interstitial K	K in Biomass	$Y = 1.6e^{-1} + 8.28e^{-3}$	5.6
Thornholme West	NH$_4$Ac Extracted K	K in Biomass	$Y = -6.01e\text{-}1 + 5.78e^{-3}$	44.9
	Interstitial K	K in Biomass	$Y = 1.13 - 3.91e^{-2}$	56.1
Corney Fell North	NH$_4$Ac Extracted K	K in Biomass	$Y = 3e\text{-}1 + 1.58e^{-3}$	45.9
	Interstitial K	K in Biomass	$Y = 1.51e\text{-}1 - 3.9e^{-4}$	31.9
Corney Fell South	NH$_4$Ac Extracted K	K in Biomass	$Y = 5.19e\text{-}2 + 2.12e^{-4}$	7.8
	Interstitial K	K in Biomass	$Y = 1.36e\text{-}1 + 9.5e^{-4}$	21.9