Quantifying Mineral Sources of Potassium in Agricultural Soils

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Abstract

Soil potassium (K) reserves are crucial for crop quality and yield in low input agricultural systems. Soils contain varying amounts of K-bearing minerals and differ in their inherent K supply capacity. This thesis presents mineralogical methods for characterising and quantifying different K-bearing phases in soil and compares the results with K determined by common soil K extraction methods using 2 M HCl (K_{HCl}) or *aqua regia* (K_{AqReg}). The aim was to improve evaluations of potential long-term K supply of soils with different parent materials, particularly in grass/clover leys. Mineralogical budgeting based on X-ray powder diffraction was used to determine K distribution in K-bearing minerals in 20 Swedish and Scottish soils. K_{HCl} and K_{AqReg} were then tested against the concentrations of different mineral K pools and HCl effects on mineralogy were assessed through differential X-ray diffraction. Long-term Swedish cropping systems and soil fertility experiments were used to assess field K balances and long-term trends in exchangeable K (K_{ex}) and K_{HCl} and to estimate soil K delivery capacity. The K distribution between K-feldspar and different phyllosilicates varied significantly among soils, with Scottish soils showing greater variation in total K concentrations and K speciation than Swedish soils. HCl and *aqua regia* solubilised 1-17% and 4-60% of total K, respectively, depending on soil type and mineralogy, most derived from Fe-bearing di- and trioctahedral phyllosilicates. Conventional and organic cropping systems both demonstrated negative field K balances averaging 20-70 kg ha^{-1} yr^{-1} over 18 years, indicating a reliance on soil K delivery. This resulted in significantly decreased K_{ex} and K_{HCl} in two soils. Potassium weathering rates were 35-65 kg ha^{-1} yr^{-1} in silty clays and sandy loams, and 8 kg ha^{-1} yr^{-1} in loamy sands in insufficiently or non-K fertilised experimental plots. To compensate for net K output at field scale, the K_{HCl} soil pool would have to be totally replenished within 30-300 years, depending on site. Although K_{HCl} is a dynamic pool that is not exhausted until the least soluble K-bearing mineral has dissolved, replenishment rate kinetics ultimately limit K delivery from soil reserves. This demonstrates the significance of considering the size and properties of soil nutrient pools when using element balances to assess cropping system sustainability.

Keywords: Potassium, soil, agriculture, field balance, mineralogy, grass, ley, organic farming, weathering, HCl, *aqua regia*, XRPD, differential XRD, XRF

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Dedication

Till Gigi

Soils are as essential to human society as air and water. They are the basis for the production of 90% of our food, fibre and livestock food.
European Environment Agency 2005

Contents

Supplementary data

List of Publications

This thesis is based on the work contained in the following papers, which are referred to in the text by their Roman numeral:

I Andrist-Rangel, Y., Simonsson, M., Andersson, S., Öborn, I & Hillier, S. 2006. Mineralogical budgeting of potassium in soil: A basis for understanding standard measures of reserve potassium. *Journal of Plant Nutrition and Soil Science* 169, 605-615.

II Andrist-Rangel, Y., Edwards, A.C., Hillier, S. & Öborn, I. 2007. Long-term K dynamics in organic and conventional mixed cropping systems as related to management and soil properties. *Agriculture, Ecosystems and Environment* 122, 413-426.

III Simonsson, M., Andersson, S., Andrist-Rangel, Y., Hillier, S., Mattsson, L. & Öborn, I. 2007. Potassium release and fixation as a function of fertilizer application rate and soil parent material. *Geoderma* 140, 188-198.

IV Andrist Rangel, Y., Simonsson, M., Öborn, I & Hillier, S. Sources of HCl-extractable potassium in agricultural soils - insights from full pattern quantitative and differential X-ray powder diffraction. (Manuscript).

V Andrist Rangel, Y., Hillier, S., Öborn, I., Lilly, A., Towers, W., Edwards, A. C. & Paterson, E. Assessing long-term potassium supply in grassland soils: A regional perspective based on quantitative mineralogy and *aqua regia*-extractable K. (Manuscript).

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Abbreviations

K	Potassium
K_{sol}	Potassium in solution
K_{ex}	Exchangeable potassium
$K_{non\text{-}ex}$	Non-exchangeable potassium
K_{latt}	Structural potassium in the crystal lattice
K_{HCl}	2 M HCl-extractable potassium
${}_{corr}K_{HCl}$	2 M HCl-extractable potassium minus exchangeable potassium
K_{AqReg}	*Aqua regia*-extractable potassium
$K_{biotite}$	Potassium held in the form of biotite and phlogopite
K_{illite}	Potassium held in the form of illite
$K_{ML\ dioct}$	Potassium held in the form of mixed-layer dioctahedral phyllosilicates
K_{phyllo}	Potassium held in the form of phyllosilicates
$K_{K\text{-}feldspar}$	Potassium held in the form of potassium feldspar
K_{tot}	Total potassium
Dioct	Dioctahedral
Trioct	Trioctahedral
ML	Mixed-layer
XRF	X-ray fluorescence
XRD	X-ray diffraction
XRPD	X-ray powder diffraction
DXRD	Differential X-ray diffraction

1 Introduction

Potassium (K) is an essential element for plants and animals that is needed to sustain fundamental cell functions. In plants, the pathway for uptake is through the roots. The underlying reason for this strong K dependence is the evolution of life in sea-water. In this K-rich environment, K could be utilised in numerous life-supporting biochemical processes. Retaining its high reliance on K, terrestrial life had to adapt to an environment in which the availability of K was much scarcer (Rodriguez-Navarro & Rubio 2006). Nevertheless, K is the seventh most common element in the lithosphere and in the upper 20 cm of a hectare of soil the total reserves usually range between 3000 and 100 000 kg (Sparks 1987). Two of the obstacles to K availability to land-living plants and animals are K speciation in the solid phase and the kinetics governing K release rates. In contrast to the other macronutrients, K is primarily present in inorganic forms, while nitrogen (N) is primarily organic and phosphorus (P) and sulphur (S) occur in both inorganic and organic forms. Potassium contained in minerals, comprising both structural and non-exchangeable K, constitutes 98% of total soil K (Sparks 1987). Exchangeable K, although a relatively small K pool, can be associated with both mineral and organic material. Potassium in its solute state, K^+, is the form in which K is primarily taken up by plants, but constitutes less than 1% of total soil K. While there are a number of studies on the kinetic reactions of K in the soil–plant system, very few have evaluated the long-term effects of management and site-specific properties on the release potential of K from different soil pools.

Potassium is regularly applied to agricultural land in many areas. Recent decades of reduction in the use of P fertilisers have caused a parallel reduction in the amount of K applied (Foy *et al.* 2002; Öborn *et al.* 2005a). In combination with other factors, such as an increased demand for products grown under low input conditions, the general decrease in K application rates has resulted in negative field K balances being reported from a range of different cropping systems, under conventional and organic management (Fagerberg *et al.* 1996; Askegaard & Eriksen 2000; Watson *et al.* 2002; Askegaard *et al.* 2003; Bengtsson *et al.* 2003; Berry *et al.* 2003; Öborn *et al.* 2005b). Grass systems are especially prone to K imbalances, as the grasses can take up large quantities of K from the soil (Whitehead 2000). This K is often removed from the system at harvest or through grazing. However, reports on actual observed K deficiencies in plants are much less frequent (Skinner & Todd 1998; Pal *et al.* 1999; Askegaard & Eriksen 2000; Askegaard & Eriksen 2002; Foy *et al.* 2002). One explanation for this could be contributions of plant-available K from soil mineral weathering. This is the least understood component of the K balance (Robert 1992; Foy *et al.* 2002) and is often not included in mass balance calculations (Öborn *et al.* 2005a). Hence, an increased knowledge of the size of the soil K pool, its mineralogical speciation, the fluxes associated with it and hence its overall dynamics is a key requirement for the further adaptation of analytical procedures and prediction methods (Robert 1992; Holmqvist *et al.* 2003) needed by managers and policy-makers.

Data from the literature show that soils vary widely in their capacity to supply K to plants, in which soil mineralogy and particle size distribution are important explanatory factors, yet soil mineralogy is seldom part of the advisory system (Holmqvist *et al.* 2003). The methods used for quantitative mineralogical analysis have improved significantly during recent decades and can now be described as fully quantitative rather than qualitative or semi-quantitative, as was long the case. Omotoso *et al.* (2006) describe some of the state-of-the-art techniques within mineralogical analysis. Although mineralogical methods are often too expensive and time-consuming to be widely applied to soils, they can be used as tools to understand the results of more routine analytical methods, such as acid extraction, and hence how such measures may reflect and relate to soil mineralogy. Indeed, the amount of data available on several acid-extractable forms of K makes these methods especially interesting, as the potential use of such data could increase significantly if they could be interpreted in a mineralogical context.

2 Objectives

The overall aim of this thesis was to demonstrate mineralogical methods for characterising and quantifying different K-bearing phases in soil and compare the results with K determined by common soil K extraction methods using 2 M HCl or *aqua regia*. The practical application was to increase the ability to evaluate the potential long-term K supply of soils in a wide range of parent materials.

The general hypothesis for the research was that the potential K delivery capacity of a soil and its sustainability can be estimated from its mineralogy, the chemical composition of soil minerals, particle size distribution and knowledge of key factors that affect K dynamics in the soil-plant system.

Specific objectives were to:

- Determine how total soil K is distributed among K-feldspars and different types of phyllosilicates by using quantitative X-ray powder diffraction and assumed mineral formulae – effectively a mineralogical budgeting approach to K speciation (Papers I and V)

- Investigate long-term trends (18-40 years) in soil exchangeable K, HCl-extractable K and crop K concentrations, and combine these trends with calculated field K balances in grass cropping systems, in order to estimate K release and fixation in soils on a range of parent materials and under different management regimes (Papers II and III)

- Investigate how different soil particle size fractions and mineral phases contribute to HCl-extractable K; *i.e.* increase the understanding of how this operationally defined form of K is related to soil mineralogy and geochemistry (Paper IV)

- Assess how *aqua regia*-extractable K is related to a number of soil chemical, physical and mineralogical properties (Papers I and V)

- Rank long-term K delivery capacity of a range of Scottish grassland soils based on the size of mineralogical and chemically defined pools of soil K (Paper V)

3 Background

3.1 Physiological Functions of Potassium

Potassium is an essential element for plants and animals and can be regarded as a macronutrient, together with nitrogen (N), phosphorus (P), calcium (Ca), magnesium (Mg), and sulphur (S) (Evans & Sorger 1966). In plants, K^+ is the most abundant cation (Leonard 1985) and in human and animal cells it is the dominant mineral ion (Preston & Linsner 1985). This explains why the element is needed in such large quantities for plant uptake and dietary intake. Similarly, as for most other mineral nutrients, a deficiency or a surplus of K can lead to complications. The mean range of K concentrations in normal and K-deficient plant leaves has been reported to be 1.7-2.8% and 0.75-1.2% of dry weight, respectively, in a variety of species (Evans & Sorger 1966).

3.1.1 Cell Functions

In solution, K^+ is a cation required for fundamental cell functions common to all living organisms. Potassium is involved in the ATPase pumps of cell membranes, which maintain cell electric potential, and is essential for a number of plant and body functions, *e.g.* turgour build-up (Zeiger 1983), osmotic balance between cells and body fluids (*e.g.* Preston & Linsner 1985), cell pH regulation (Preston & Linsner 1985; Huber 1985) and nerve activation and muscle contractions (Preston & Linsner 1985). Potassium also acts as the driving force for the transport of organic compounds and other nutrients in and out through the cell membranes. Another universal function of K is its activation of a large number of enzymes, which have key roles in for example metabolic processes (Preston & Linsner 1985) and protein synthesis (*e.g.* Blevins 1985).

3.1.2 Plants

In plants, K regulates the opening and closing of stomata, a process driven by the osmotic potential and turgour of the guard cells (*e.g.* Hopkins 1995). Therefore, K-deficient plants are especially susceptible to drought (Beringer & Nothdurft 1985; Whitehead 2000). Potassium is also responsible for plant tissue structure through its effects on turgour pressure and cell extension (Beringer & Nothdurft 1985). Visual effects of K deficiency include chlorosis (yellowing of leaf tissue due to a lack of chlorophyll), leaf necrosis (death of living cells or tissues) and lodging of cereals (Beringer & Nothdurft 1985). However, through its negative effect on cell elongation, slight K deficiency can result in darker coloured leaves, as the relative concentration of chloroplasts increases with decreased cell size (Beringer & Nothdurft 1985). Potassium is involved in the uptake of NO_3^- and xylem and phloem transport of several nitrogenous compounds to and from roots and sites of protein synthesis. It also plays a key role in photosynthesis (Huber 1985). The negative effects that K deficiency imposes on growth and development, structure and mechanical strength, metabolic profile and defence mechanisms lead to an increased susceptibility of the plant to attacks by fungi, other pathogens and herbivorous insects (Beringer & Nothdurft 1985; Marschner 1995; Amtmann *et al.* 2008).

3.1.3 Animals

In animals and humans, hyperkalaemia and hypokalaemia are terms used to describe elevated or lowered levels of K in the plasma or serum (Preston & Linsner 1985). Both conditions can lead to serious consequences if not treated. A recent review showed that increased consumption of processed food, low in K, and decreased consumption of fruits and vegetables have led to a significant reduction in K intake in the developed world (He & MacGregor 2008). Current levels correspond to half the recommended daily intake of 4700 mg (USDA 2005). Symptoms of hypokalaemia include abnormal cardiovascular function, muscle weakness and paralysis (Preston & Linsner 1985). Symptoms of hyperkalaemia, on the other hand, are diverse and can involve multiple organ systems (Whang 1985). A potential risk of high dietary intake of K (and N) by ruminant animals is hypomagnesaemia, or abnormally low Mg concentration in the blood. This can have serious effects on the animal if left untreated (Whitehead 2000). To avoid hypomagnesaemia, the K/Mg ratio of swards is often monitored in grass systems prone to high ratios (Preston & Linsner 1985). Hence, a balanced uptake or intake of K in relation to the element's species-specific concentration optimum and in relation to the concentrations of other nutrients is fundamental for the maintenance, and indeed the development, of life in most of its forms.

3.2 Potassium in Agriculture

The K status of European soils, as estimated by routine soil analysis, varies widely. According to Johnston (2003), 25% of soils in many countries test 'very low' and 'low' in readily available K. In Swedish agricultural soils, the corresponding value is 35% (Swedish Environmental Protection Agency 2007). However, only a few studies (*e.g.* Singh & Goulding 1997; Skinner & Todd 1998; Blake *et al.* 1999; Andersson *et al.* 2007) report on long-term trends in soil K. To avoid K deficiency and to sustain long-term productivity, a continuous delivery of K from the soil's internal K reserves (through weathering of phyllosilicates and K-feldspars), in addition to applied mineral fertilisers and manure, can be crucial. This is especially the case in low-input systems containing a significant proportion of ley (grass/clover crops) in the rotation, such as certain organically managed systems (Öborn 2004), since grass/clover crops remove large quantities of K. Singh *et al.* (2002) stressed that more attempts are needed to quantify temporal changes in the K supply capacity of soil over time under different crop and soil management practices.

3.2.1 Natural Resource Perspective

Total global reserves of K from salt deposits are in the region of 9-20 x10^9 tonnes K_2O (potash), which represent amounts large enough to supply the total current demand for K for at least another 350 years (Johnston 2003). However, these reserves are not evenly distributed around the world. Long-distance transportation, which requires additional energy inputs, is needed to deliver the final product to the end-users. The cost of mining the K-bearing salts and refining the product depends on the quality and availability of the K-bearing deposit. This is reflected in the final price of mineral fertilisers, which in many cases is unaffordable to small-scale farmers. For example, Chinese authors (Wang *et al.* 2000a) report that the country has to import fertiliser K at great expense, due to a lack of natural K resources, and therefore it has been a considerable burden to supply crops with sufficient K.

3.2.2 Trends

As the wider environmental aspects mentioned above are most often not considered, the decline in research on K during the past few decades is probably due to the absence of any problems associated with the use of mineral K fertiliser. During the same period, a reduction in application rates has been observed in Europe as a whole (Öborn *et al.* 2005a) including Sweden (SCB 2008; Figure 1) and the UK (BSFP 2007). Since K is most often applied in the form of compound NPK fertiliser or as farmyard manure, the decline in K, sometimes to undesirable levels, might be the result of attempts to reduce the use of P (Foy *et al.* 2002) and N fertilisers (Öborn *et al.* 2005a) (Figure 1), which by way of contrast may have environmental effects in terms of eutrophication of surface waters and groundwater.

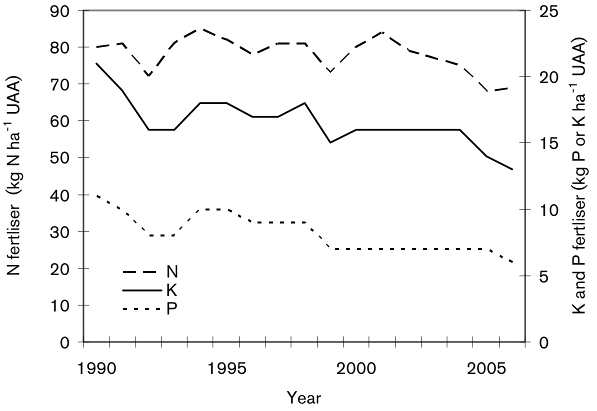

Figure 1. Mineral N, P and K fertilisers sold in Sweden 1990-2006 in relation to the utilised agricultural area (UAA); derived from data from SCB (2008).

In the industrialised world, increasing demand for locally produced farm products, often grown with a low input of mineral fertilisers, will lead to an increased reliance on the inherent capacity of soils to supply plant nutrients. This is even more significant in organic farming systems, which rely to a large extent on on-farm nutrient recycling and which commonly include grass and herbage crops. In EU-25[1], 5.7 Mha or 3.6% of the Utilised Agricultural Area[2] (UAA) was under certified organic production or in-conversion in 2003 (EC 2005). In 2005, the corresponding values for Sweden and UK were 7.0% and 3.8%, respectively (Eurostat 2008). In developing countries, limited access to fertilisers due to a combination of factors related to market forces and to the economic situation of farmers has

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[1] EU-25 refers to the 25 Member States of the European Union.

[2] The utilised agricultural area (UAA) is the total of arable land, permanent pasture and meadow, land used for permanent crops and kitchen gardens. The UAA excludes unutilised agricultural land, woodland and land occupied by buildings, farmyards, tracks, ponds, *etc.* (EC 2007).

also resulted in a greater dependence on soil mineral weathering for nutrient supply. Although organic agriculture is practised in almost all countries of the world (EC 2005), organic farming in its strict sense has been demonstrated to be unsuitable as a model for crop production in many developing countries not least in sub-Saharan Africa, where nutrient-poor soils are common (Vanlauwe & Giller 2006).

3.2.3 Current Application Rates in the UK and in Sweden

In the UK the overall application rate, or total use, of K mineral fertiliser ($K_{\text{min fert}}$) to all crops including grass decreased from 39 kg K ha^{-1} yr^{-1} for the period 1983-1987 to 30 kg K ha^{-1} yr^{-1} for the years 2002-2006 (BSFP 2007). The overall application rates were higher on tillage crops than on grass, as for example tillage crops in 2006 received on average 41 kg ha^{-1}, whereas grass received only 17 kg ha^{-1} yr^{-1} (BSFP 2007). In Sweden, the corresponding overall application rate of $K_{\text{min fert}}$ to all crops and grass was 12 kg K ha^{-1} in 2005 (SCB 2006). Swedish statistics also show that only one-fifth of the total K applied was in the form of mineral fertilisers. Hence, K in the form of animal manure (K_{manure}) was applied at an overall rate of 43 kg K ha^{-1} yr^{-1} (SCB 2006). However, $K_{\text{min fert}}$ and K_{manure} are not added to all agricultural land. Application rates to the area of land actually receiving $K_{\text{min fert}}$ and/or K_{manure} demonstrate the typical doses applied. In Sweden, 62% of the total agricultural land area received mineral fertiliser and/or manure and the average K application in 2003 was 89 kg ha^{-1} yr^{-1} (SCB 2005b). In organic production the corresponding figure was 76 kg ha^{-1} yr^{-1}, applied to the 41% of organically managed area that received fertiliser or manure (SCB 2005a).

3.2.4 Reasons for Imbalance

The reasons for negative K balances and K deficiency relate to fertiliser application strategies and processes within the soil–plant system. From a crop production perspective, the rate and timing of fertiliser and manure application are often based on the optimal N rate (Askegaard & Eriksen 2002) and not on K requirements (Alfaro *et al.* 2003). This can lead to excesses or shortages of K depending on crop and rotation choices (Alfaro *et al.* 2003; Bengtsson *et al.* 2003) and on the capacity of the soil to absorb K (Pal *et al.* 1999; Askegaard *et al.* 2004). For example, the timing of K fertilisation may cause problems, as it is commonly applied quite infrequently. Plant uptake is by far the largest output of K in arable systems, and has been reported to account for 93% of total export (Alfaro *et al.* 2003). Several plant species, especially grasses, have the ability to take up K in excess of their physiological requirements, a process known as luxury consumption (Whitehead 2000). Potassium may also be fixed in some soils if the K concentration in the soil solution is high (Sparks & Huang 1985). This may lead to the risk of late-season K deficiency, as K is taken up early in the season or becomes unavailable for the plant through fixation in the soil or through leaching to groundwater. Therefore, K fertilisation could be more effective if applied in smaller doses during the growing season (Pal *et al.* 1999). Another problem observed is that the size of fertiliser applications may be excessive due to underestimation of the K supply from the soil (Øgaard *et al.* 2002).

3.2.5 Grass Systems

Grassland systems provide essential environmental and economic services. For instance, they offer forage for livestock, habitats for flora and fauna, and are a net carbon sink (Soussana *et al.* 2007; Lindborg *et al.* 2008; Andren *et al.* 2008). Permanent grassland occupies 30% of the UAA in the European Union (EU-27) (EC 2007) and it sustains 15% of the global livestock population (FAOSTAT data 2004, *cit.* Soussana *et al.* 2007). Grass and other forage crops are also grown in rotation with other crops on arable land, *i.e.* temporary grassland, which represents 10% of the UAA in EU-27 (EC 2007). In the UK, 11 600 000 ha was used for fodder production (hay/silage) or grazing in 2006 (EC 2007; Defra 2008). Permanent grassland covered 63% of the UAA, constituting grass leys more than 5 years old (36%) and land used for rough grazing (27%). Temporary grassland constituted another 7% of UAA (Defra 2008). In the UK, the terms 'improved grassland' or 'improved pasture' are commonly used and are defined as agricultural land used for fodder production (*i.e.* temporary grassland plus grass leys more than 5 years old) and land used for grazing but excluding rough grazing. In Sweden, 1 100 000 ha or 35% of agricultural land was used for ley (hay/silage and grazing) and green forage crops in 2006, the highest value since records began in 1981 (SJV 2007; SCB 2007). Rough grazing constituted an additional 500 000 ha or 16% of agricultural land (SJV 2007).

In the EU-15, the production of grass and fodder accounts for the dominant use (60%) of organically managed land (EC 2005). In the UK it is even more significant, where permanent and temporary grassland account for 85% of fully organic or in-conversion land (Defra 2007). Many intensive ley-based organic systems show negative field balances (K inputs<K outputs) (Fagerberg *et al.* 1996; Askegaard & Eriksen 2000; Watson *et al.* 2002; Askegaard *et al.* 2003; Bengtsson *et al.* 2003; Berry *et al.* 2003; Öborn *et al.*

2005b). These livestock farms tend to rely on internal recycling of K together with inputs from purchased feed and K release from the soil. It is therefore important to quantify soil K delivery capacity (Øgaard & Krogstad 2005) and to evaluate its likely long-term contribution to on-farm nutrient cycling. Despite several studies of farm-gate and field K balances, few examples combine detailed information on pools and fluxes of soil K (Øgaard & Krogstad 2005; Öborn *et al.* 2005b; Hoa *et al.* 2006). Krauss (2003) concluded that there is a clear need to investigate the impact of negative nutrient balances on the long-term status of different soil K fractions.

Grass systems, or mixed systems including a period of ley in the crop rotation, are especially prone to K imbalances, such that K can become a critical nutrient in these types of systems (Öborn *et al.* 2005a). Grassland herbage in temperate regions including Swedish ley fodder (hay and silage) has a typical K concentration of 2.5% (Whitehead 2000; Spörndly 2001). Due to the large biomass export that is associated with the cutting of grass leys, considerable amounts of K are removed from the field. Critical K concentrations in young grasses growing in temperate areas have been reported to fall within the range 1.2-1.6% (dry matter) compared with 1.0-2.3% for white clover (Whitehead 2000). However, nutrient deficiencies that affect the health, or growth rate, of ruminants are generally more widespread than those affecting the grass itself (Whitehead 2000). Low K availability may for example lead to imbalance with other nutrients and/or pollutants. A critical example is that of radiocesium, of which the uptake in grass has been shown to be closely related to the soil K status (Delvaux *et al.* 2000).

3.3 Potassium-bearing Minerals

Potassium is a major element in the lithosphere but there is a large variation in composition within the main rock types (Robert 1992). For instance, igneous rocks tend to have higher K concentrations than sedimentary rocks. In igneous rocks, granites and syenites tend to have the highest values, around 46-54 g kg^{-1}, whilst 7 g kg^{-1} is an average for basalt and 2 g kg^{-1} or less is characteristic for peridotites. Among the sedimentary rocks, clayey shale has a K content of approx. 30 g kg^{-1} whilst limestone is amongst the most K deficient, at around 6 g kg^{-1} (Malavolta 1985).

Soils contain varying amounts of K-bearing minerals that constitute a major K reserve. The aluminosilicates are the most abundant K-bearing minerals. They include primary minerals, namely K-feldspars, biotite and muscovite mica. They also include the secondary aluminosilicates, comprising hydrous mica (illite) as well as a continuum of micaceous weathered or inherited products (Bertsch & Thomas 1985), including mixed layer phyllosilicates. The primary soil minerals are inherited from the parent material, whereas the secondary minerals are either inherited from sedimentary rocks or formed in soils during the weathering process.

3.3.1 Feldspars

Feldspars are tecto- (or framework-) silicates that consist of SiO_4 and AlO_4 tetrahedra. The structure includes openings that contain Ca^{2+}, Na^+ or K^+ to maintain electroneutrality (Barth 1969). Plagioclase is the term for the isomorphous series of feldspars ranging in composition between $NaAlSi_3O_8$ (albite) and $CaAl_2Si_2O_8$ (anorthite). These feldspars, if pure, do not contain K. For the K-bearing feldspar, a complete solid solution series exists of alkali feldspars, of which the end members are $KAlSi_3O_8$ and $NaAlSi_3O_8$ (albite). For pure $KAlSi_3O_8$, there are four main species: sanidine, orthoclase and microcline, and adularia. Together with the other alkali feldspars they constitute 31% of the Earth's crust (Barth 1969). Feldspars are commonly found in the silt and sand fractions of young to moderately developed soils representing various parent materials and soil-forming conditions (Somasiri *et al.* 1971; Sparks & Huang 1985). In unweathered soils of glacial rock-flour origin, feldspars may constitute up to 40% of the clay fraction, but are generally <5% of the clay fraction in most soils (McLean & Watson 1985).

3.3.2 Micas

All micas are 2:1 phyllo- (or layer-) silicates usually containing Al, Mg, or Fe in their octahedral sheet. The 2:1 layers are held together by their strong attraction to cations, especially K, that occur in the interlayer (Thompson & Ukrainczyk 2002). Primary micas have a negative layer charge of 1 mol per formula unit, whereas in secondary micas, such as illite and glauconite, the negative layer charge varies between 0.6 and 0.8 mol per formula unit, due to less substitution of Al^{3+} for Si^{4+} (Thompson & Ukrainczyk 2002). Muscovite, which is dioctahedral, and biotite, which is trioctahedral, are the most common micas in igneous and metamorphic rocks. Micas are also present in sediments and sedimentary rocks, where they tend to be more abundant in fine-grained types such as clay and shale than in coarse-grained types such as sandstone. Illitic micas are extensively found in shale and slate and are important phyllosilicates in limestone (Sparks 1987).

Mica is most common in young, less weathered soils such as Entisols, Inceptisols, Mollisols, Andosols and Alfisols (Sparks 1987). Almost all past work has shown that K in trioctahedral micas, such as phlogopite and biotite, is more readily released on weathering than K in dioctahedral micas; for further details see the review by Wilson (2004). Therefore micas remaining in clay fractions of soils are predominantly of the dioctahedral kind (Sparks 1987), which is more resistant to alteration. In clay fractions of Swedish soils, illitic phases are especially common among the micaceous minerals and constitute the dominant phyllosilicate in a number of soils (Wiklander 1950; Wiklander & Lotse 1966; Ghorayashi & Öborn 1993). Micas are important for plant nutrition because they represent a major source of K. It is well-established that K in biotite is useful to plants and that the mineral is quite a good fertiliser (Arnold 1963).

3.3.3 Potential K-bearing Minerals

This is a group of minerals that potentially may contain K. It includes mixed layer phyllosilicates, vermiculites, smectites and hydroxy-interlayered vermiculites. These are secondary minerals, which may originate from primary or other secondary minerals that contained K in their lattice structure or interlayers. Depending on the stage of weathering and the concentration of K in the soil solution, these minerals may act either as sources or sinks for K. Vermiculites play an important role in natural environments (Malla 2002); their high layer charge gives them a high CEC and a high affinity for weakly hydrated cations such as K^+, NH_4^+, and Cs^+ (Schulze 2002). Through selective sorption, fixation and release of these ions, vermiculites play a role in their availability to plants and in their retention in soil or leaching to groundwater (Malla 2002).

3.4 Potassium in Soil

3.4.1 Forms and Processes - Some Basic Concepts

Total K concentrations in mineral soils typically range between 0.4 and 30 g kg^{-1}, and total pools in the upper 0.2 m of a soil profile are generally between 3000 and 100 000 kg ha^{-1} depending on soil type and mineralogy (Sparks 1987). Traditionally, four pools of soil K have been recognised (Figure 2): structural K (K_{latt}), non-exchangeable K (K_{non-ex}, also referred to as fixed K), exchangeable K (K_{ex}), and K in soil solution (K_{sol}) (Hoagland & Martin 1933). Together, K_{ex} and K_{sol} constitute approx. 2% of total K and are often considered readily available to plants (Sparks 1987), whereas K_{latt} and K_{non-ex} constitute 98% of total K and are described as slowly (Pal *et al.* 1999) or potentially available to plants. The definitions of K_{ex} and K_{sol} are relatively precise and easily understood. In contrast, a strict differentiation between the definitions of K_{latt} and $K_{non\text{-}ex}$ is lacking in the literature and has perhaps clouded thinking in relation to K in soil. One way to tackle this issue is by recalling that in practice, when thinking about K_{latt}, only two mineral groups have to be considered, namely the feldspars and the phyllosilicates. In both groups structural K is held in crystallographically well-defined cation sites in a mineral lattice where it has always been since the mineral was formed. The K in K-feldspar very clearly falls into the K_{latt} category and cannot be placed in any other. Pristine K in interlayer positions in unweathered micaceous phyllosilicates also falls into this category. However with phyllosilicates a continuum exists between K_{latt}, $K_{non\text{-}ex}$ and K_{ex}. For example it has been demonstrated that all interlayer K can be removed from micas by cation exchange processes provided the activity of K_{sol} is kept below a certain critical value (Scott & Smith 1966). Furthermore, although micas can be destroyed by weathering they can also be partially reconstituted by the process of K fixation, whereupon K is relocated into crystallographic sites that for all intents and purposes may be indistinguishable from K that is occupying K_{latt} sites.

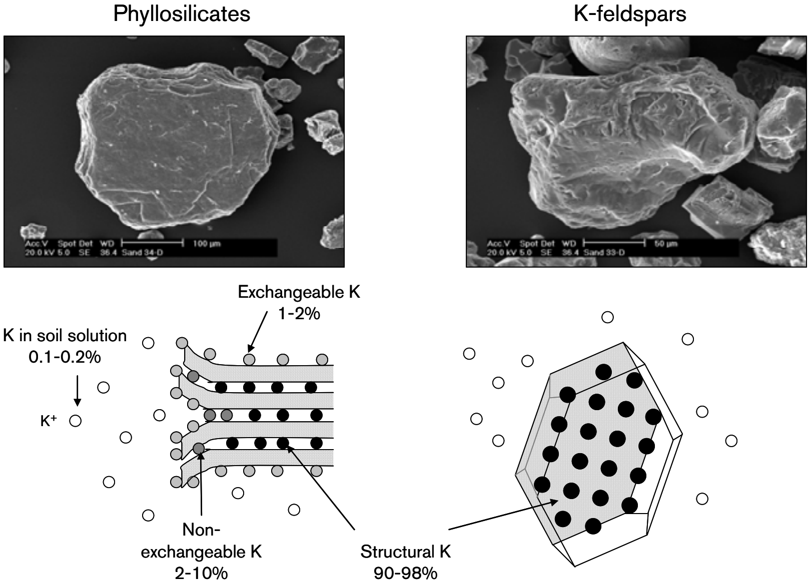

Figure 2. The four forms of K and their location in phyllosilicates and K feldspars with corresponding SEM images. (SEM images: A. Tharande)

This puts a slightly different perspective on the definitions of structural, non-exchangeable and exchangeable K with respect to phyllosilicates, as it highlights the fact that all of these definitions are operational and depend on the test conditions. Therefore, further clarity would be achieved by splitting K_{latt} into two distinct groups, *i.e.* K_{latt} in feldspars and K_{latt} in micas. The K_{latt} in feldspars will always be a distinctive and unambiguous category. Structural K in micas and other phyllosilicates only includes K that is pristine in the sense that it has always been in the structural site it now occupies. Non-exchangeable K is a category that is only related to phyllosilicates and includes K that may be in interlayer positions or otherwise fixed on former wedges and frayed edges of phyllosilicates. This K occupies its particular site by virtue of the process of fixation, which implies that at some prior time the K in question was exchangeable or in solution. What needs to be established is whether techniques (and plants) are able to distinguish between K_{latt} and K_{non-ex} in relation to phyllosilicates, *i.e.* if and when these categories show different characteristics or behaviour *e.g.* with respect to their availability to plants. Exchangeable K is well understood and requires no clarification. Likewise, there is no ambiguity in the definition of K_{sol}. In this thesis, when reference is made to 'K_{non-ex}', this implies that it also includes K_{latt} unless specially stated otherwise.

Dynamic equilibrium reactions exist between the pools of soil K (Sparks 1987). Hence, all the factors that affect these reversible reactions indirectly affect the size of the different K pools. Figure 3 (with references in Table 1) provides a schematic illustration of different interrelated pools and processes and lists some of the key factors controlling the reactions.

Chemical weathering is the release of elements due to chemical dissolution and transformation of specific minerals in the soil matrix and in the bedrock (Holmqvist 2001). It plays a central role in controlling the inherent capacity of a soil to supply nutrients for plant growth (Wilson 2004). Weathering rates of primary minerals depend on both their relative stability and the amount of exposed surface area of the mineral particles (Marshall 1977). When discussing K, the term weathering is used hereafter for all processes that release K from the soil, except for release from the exchangeable pool. In contrast, fixation is defined as the conversion of either K_{sol} or K_{ex} into K_{non-ex} (Malavolta 1985) and/or K_{latt}. It occurs through selective sorption of ions in favour of others such that if an ion is held tightly and resists replacement by other ions, it is defined as fixed (Malla 2002).

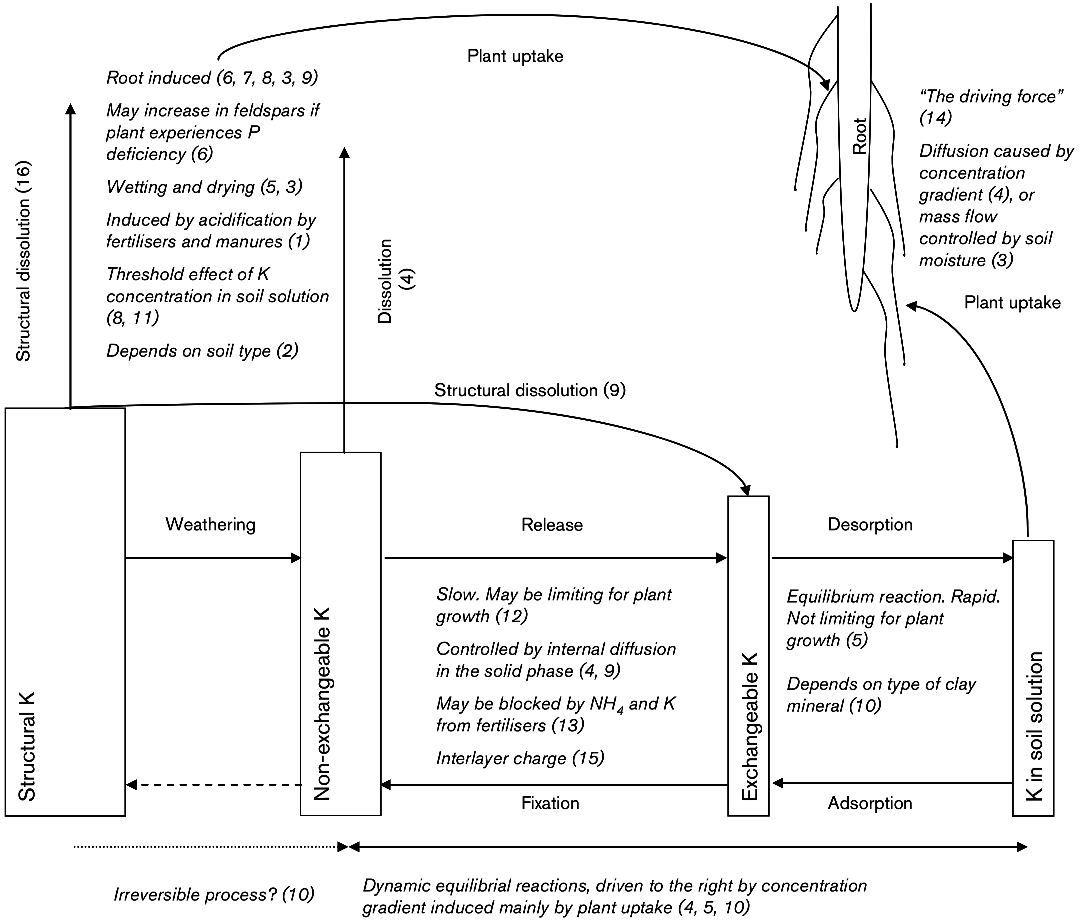

Figure 3. The different forms of K pools, reactions between them, and factors controlling these reactions. Numbers refer to references listed in Table 1.

Table 1. *Reference list for Figure 3*

1	(Singh *et al.* 2002)
2	(de la Horra *et al.* 2000)
3	(Askegaard *et al.* 2004)
4	(Pal *et al.* 1999)
5	(Robert 1992)
6	(Wang *et al.* 2000b)
7	(Hinsinger & Jaillard 1993)
8	(Hinsinger *et al.* 1993)
9	(Schneider 1997)
10	(Sparks 1987)
11	(Wilson 1992)
12	(Grimme 1985)
13	(Welch & Scott 1961)
14	(Jungk & Claassen 1997)
15	(Feng *et al.* 2003)
16	(Wang *et al.* 2000a)

3.4.2 Weathering and Fixation of K

Under conditions of soil K depletion, the ability of soil minerals to release K generally follows the sequence: trioctahedral micas > dioctahedral micas > K-feldspars (Sparks & Huang 1985; Thompson & Ukrainczyk 2002). The release of K occurs either stoichiometrically (proportionally) or non-stochiometrically. Stoichiometric dissolution may be an important mechanism for K release from trioctahedral micas at low pH, but a selective loss of interlayer K, part of a process known as vermiculisation, accounts for most of the K release from micas and illites in soil (Feigenbaum *et al.* 1981). Partial release of interlayer K from phyllosilicates seems to proceed near equilibrium and switches to fixation if K concentration in the ambient solution exceeds a critical value (Sparks & Huang 1985; Fanning *et al.* 1989). Thus, ample application of K fertiliser is expected to replenish phyllosilicates in fixed K (Huang 2005). Some authors report changes in clay mineral composition, as observed using X-ray diffraction, after long-term cropping or fertilisation (Møberg & Dissing Nielsen 1983; Tributh *et al.* 1987; Liu *et al.* 1997; Velde & Peck 2002), although other authors have reported no change (Singh & Goulding 1997).

The driving forces for K release from soil and its transport to roots are diffusion and mass flow. The diffusion rate depends on the concentration gradient of K_{sol} caused by plant uptake, whereas mass flow is caused by root uptake of water and is affected by soil moisture content (Barber 1968; Jungk & Claassen 1997) (Figure 3). Several studies have shown that the release of K from the structural and/or non-exchangeable pools (Figure 3) can contribute significantly to plant uptake (Gholston & Dale Hoover 1948; Becket & Clement 1973; Tributh *et al.* 1987; Badraoui *et al.* 1992; Hinsinger & Jaillard 1993; Schneider 1997; Wang *et al.* 2000a; Rupa *et al.* 2001; Øgaard & Krogstad 2005). Some studies have also demonstrated the direct importance of weathering on K supply to crops. For example Wang (2000a) reported that freshly broken rocks of gneiss had been successfully used by farmers as fertilisers, while Zhu *et al.* (2008) showed that a significant proportion of the total K from parent rocks was released within 2 years and concluded that weathering was the key to soil fertility in the region studied.

In addition to the dynamic equilibrium reactions where the exchange equilibrium shifts due to plant uptake of K, alternative mechanisms for release of K from K-bearing minerals may exist (Wang *et al.* 2000b), such as root-induced plant uptake from non-exchangeable and mineral pools (Hinsinger *et al.* 1993) and through the activities of mycorrhizal fungi (Jongman *et al.* 1997; van Scholl *et al.* 2008). Recently, Barre *et al.* (2007) have been able to quantitatively determine the effect of plant K uptake on 2:1 phyllosilicates.

Research on weathering and fixation rates in agricultural soil is scarce. The great majority of weathering studies have been made on forest soils. Of the few studies carried out on agricultural soils, various approaches have been applied, such as controlled experiments in pots and greenhouses (Sinclair 1979a; Goulding & Loveland 1986; Ghorayshi & Lotse 1986a; Ghorayshi & Lotse 1986b), field studies using element balances (Ulén & Snäll 1998) and modelling (Holmqvist 2001; Öborn *et al.* 2005b). Holmqvist *et al.* (2003) used the biogeochemical model PROFILE to estimate K release from mineral weathering in agricultural soil and specifically highlighted the importance of obtaining information on total K distribution between the various K-bearing minerals, in order to make reliable estimates of K weathering rates.

3.5 Methods of Determination

3.5.1 Chemical Extractions

Exchangeable K

For practical agronomic purposes, the most common measure of soil K status is the concentration of 'available K', generally the sum of K_{sol} and K_{ex}, which often forms the basis for K fertiliser recommendations. This K form is determined and actually defined by chemical extraction of the soil using a solution usually containing ammonium as the exchanging cation. Since K_{sol} usually only constitutes a minute fraction of extracted K, available K is often used as a synonym for K_{ex}. In Sweden, the K fertilisation recommendations are based on the level of ammonium acetate + ammonium lactate (AL-solution)-extractable K (Egnér *et al.* 1960). Under some circumstances, the K application is adjusted to a lower level if the soil has a high clay content (SJV 2006). In England and Wales, K fertiliser recommendations are based on ammonium nitrate extraction (Ministry of Agriculture, Fisheries and Food 2000), whereas acetic acid has been used in Scotland (SAC 1983).

Potentially available K

A wide range of different methods are used in the analysis of less soluble forms of K. The methods often involve extraction with an acid and, depending on the extractant, they represent a varying proportion of the total soil K reserve. In the literature, the terms used for the extracted K include expressions such as 'potentially available K' or 'slowly available K', 'reserve K', and 'acid-extractable K'. Reitemeier *et al.* (1948) suggested a 10 min boiling of soil in 1 M HNO_3^- (soil:acid = 1:10) and concluded that K extracted by this method correlates well with the uptake of K in clover. Using the same method, Mortland *et al.* (1957) also found a good correlation between extracted K and uptake in wheat. Ståhlberg (1958) suggested a modified extraction, using 1 M HCl, and claimed that he obtained similar amounts of K compared with the 1 M HNO_3 method. Subsequently, Egnér *et al.* (1960) adapted the HCl method into a more practical procedure, which also gave more reproducible results, and suggested a 2 M concentration for the extractant. Øgaard *et al.* (2001) found 'acid-soluble K' (K-HNO_3 minus K-AL) to be a good parameter for assessing the ability of a soil to supply ryegrass with reserve K. Other methods that have been tried include electro ultra filtration (EUF) (Nemeth 1979) and exchange resins (Goulding & Loveland 1986). In addition, environmental geochemical surveys of soils often utilise *aqua regia* digestion (*e.g.* McGrath & Loveland 1992; Reimann *et al.* 2003; Salminen 2005) for estimations of pseudo-total metal concentrations in soil, including those of K. The true total K concentration can be obtained by fusion with alkali salts (*e.g.* lithium metaborate, $LiBO_2$), or acid digestion with hydrofluoric acid (HF) (Sawhney & Stilwell 1994), or from X-ray fluorescence (XRF) analysis after decomposition by fusion or homogenisation by grinding (Amonette & Sanders 1994). However, with little exception (Güzel & Wilson 1978), there is virtually no direct information on the effect that acid extractions have on soil minerals. To my knowledge there is no published study on 2 M HCl that evaluates this extraction method from a mineralogical perspective with the aim of clarifying the phases that actually dissolve and release K.

Problems with the use of K pool measurements

There are two major constraints on attempts to estimate the amount of available and potentially available K in soils. Firstly, the ability of different soils to release and fix K is not fully understood. It has long been recognised that K_{ex} is not a very good index of available K for many soils (Bertsch & Thomas 1985; Bhonsle *et al.* 1992; Ghosh & Singh 2001; Askegaard & Eriksen 2002). Singh *et al.* (2002) suggested that chemical extractions of K_{ex} pools would provide a reasonable index of K availability in soils with low K fixation capacity, but not in soils containing vermiculite, illite or other highly K-fixing minerals. Secondly, the definitions of terms such as 'reserve K' and 'potentially available' K are not internationally standardised, and the wide range of analytical methods used (for a list of methods see McLean & Watson 1985; Sparks 1987) makes it difficult to compare data and hence to systematically evaluate the available knowledge.

3.5.2 Mineralogical Analysis by X-ray Diffraction

The single most useful analysis for identification and quantification of soil minerals is the determination of mineral structure (Amonette 2002). This is preferably done by X-ray diffraction (XRD), as it is a convenient and unambiguous non-destructive analytical method (Bish 1994). Since the Nobel Prize rewarded[3] pioneering work at the beginning of the last century by physicists Friedrich *et al.* (1912) and Bragg (1913; 1920), XRD has been extensively applied across a enormous range of scientific disciplines. The first studies on soil were carried out by Hendricks & Fry (1930) and Kelly *et al.*

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[3] The Nobel Prize in Physics. 1914: Max von Laue, 'for his discovery of the diffraction of X-rays by crystals' and 1915: William Lawrence Bragg and Sir William Henry Bragg 'for their services in the analysis of crystal structure by means of X-rays'

(1931). The determination of mineralogical composition of the samples is based on Bragg's Law (Bragg 1913; see *e.g.* Brown & Brindley 1984):

$$n\lambda = 2d\sin\theta \qquad \text{Eq. 1}$$

where

n is an integer that denotes the order of reflection,
λ is the wavelength of the incident X-radiation (nm),
d is the spacing, or distance, between successive scattering planes in the atomic lattice (nm), and
θ is the angle between the incident X-radiation and the scattering plane (°).

The analytical output from XRD experiments consists of reflection intensities at different angles, 2θ, which can be graphed as a diffraction pattern with peak intensities along the y-axis and θ along the x-axis (see Figure 12 in Section 5.2.2). Through Eq. 1, θ can be converted into d-spacings (both nm and Å are used as units of distance in the literature), which are then compared with reference databases of know peak positions for individual minerals (*e.g.* ICDD 2007). Due to the difficulties involved in quantitative mineralogical analysis (Bish 1994), the vast majority of publications on the mineralogical composition of soils are qualitative or semi-quantitative only. However, recent methodological advances in sample preparation, instrumentation and computational procedures, including full pattern fitting and modelling of diffraction patterns, have significantly increased both the precision and the accuracy of quantitative analysis (Bish & Post 1989; Hillier 1999; Hillier 2003; Omotoso *et al.* 2006).

Differential XRD

Differential XRD (DXRD) analysis is another technique that can be used for the comparison of diffraction data before and after applying a treatment to the sample. The treatment is often chemical; *e.g.* an acid extraction. A DXRD pattern is generated by computing the difference between two patterns, one recorded before treatment and one after. Although original XRD patterns of untreated and treated samples can be compared directly, changes in the sample are often more clearly visualised in a differential pattern. Its peaks represent the mineralogical composition of the part dissolved, destroyed or altered by the extraction. DXRD has been widely used for identification of minerals and for quantification of specific minerals.

However, the approach is also very useful for evaluating selective-dissolution procedures *per se* (Schulze 1994). Reproducibility of results is fundamental for DXRD, as any differences observed should be attributable solely to the treatment applied.

Obstacles in quantitative mineralogical analysis

Quantitative mineralogical analysis is most often performed using X-ray powder diffraction (XRPD). The method is based on the assumption, and hence prerequisite, that the sample is randomly orientated before analysis. One of the greatest difficulties in the development of reliable methods for analysis of powder samples is the problem of preferred orientation (Chipera & Bish 2002), which occurs when the powdered samples are packed into sample holders, as even the slightest pressure can cause some degree of orientation of most particles because their shapes are anisotropic. Problems with reproducibility can also arise here, as it is unlikely that exactly the same degree of preferred orientation will be achieved on different occasions (Hillier 2003). This is especially a problem for phyllosilicates because of their platy shape. However, the problem also exists for other minerals with one or more good cleavages, for example the feldspars (Hillier 2003). In a sample with a mixture of unknown phases, platy minerals are overrepresented in the XRPD patterns compared with phases that are less susceptible to preferred orientation. Therefore, sample preparation is one of the most crucial steps in XRPD. To overcome the problem of preferred orientation, different sample preparation procedures are used, one of which is spray-drying. A spray-drying technique developed by Hillier (1999; 2003), based on ideas by Smith *et al.* (1979), has proven successful in avoiding both preferred orientation and low sample recovery (Hillier 1999; Hillier 2003; Omotoso *et al.* 2006). For further details on spray-drying see Section 4.4.1.

3.6 Available Data and Maps

3.6.1 Sweden

A vast amount of data has been collected on K_{ex} and K_{HCl} in agricultural soils in Sweden. From 1965 onwards, the Egnér methods for exchangeable K (K-AL) and K_{HCl} (Egnér *et al.* 1960) have been used within the Swedish agricultural advisory system (KLS 1965). Exchangeable K and K_{HCl} are also components of the Swedish Environmental Monitoring of Agricultural Soils and Crops. Maps with data from the first phase of the monitoring, mainly 1994-1995, have been published by Eriksson *et al.* (1997). They contain a wide range of soil properties including K_{ex}, soil texture, *etc.* These data are also available in the form of digital maps and processed data, which are available on-line from an open-access database that also includes data from the second phase of the monitoring, 2001-2007 (SLU 2008). At present, the database includes more than 5000 records, with a sample density of one sample per 10 km^2. For the second phase of the monitoring, K_{HCl} was added to the analytical scheme. General soil survey maps are not available in Sweden and the most soil relevant maps available with a reasonable national coverage are the 1:50 000 Quaternary geology maps with adjacent descriptions published by the Geological Survey from 1967 to 2003 (Lantmäteriet, SGU, SMHI, Sjöfartsverket 2008).

3.6.2 Scotland

A comprehensive survey and sampling of Scottish soils has been carried out using free survey techniques during the mapping phase (Soil Survey of Scotland, completed 1984). Between 1978 and 1988 a systematic, objective grid sampling covering all of Scotland except the Orkney Isles was undertaken within the National Soils Inventory of Scotland (NSIS) and this grid is currently (2007-) being partially re-sampled. Soil samples to characterise map units were taken, as were samples along transects and localised grids to be used in geostatistical investigations. All samples were analysed for a range of soil properties, including K_{ex}. For a subset of samples, which represent surface soil from the NSIS 10 km grid, data on K_{AqReg} are also available. The collected data and soil samples comprise the Scottish Soils Database and the National Soils Archive of Scotland (Towers *et al.* 2006). Together, the database and the soil archive comprise approx. 44 000 records from more than 13 000 geo-referenced soil profiles and are held by The Macaulay Institute, Aberdeen. There is a complete national coverage of soil maps at the 1:250 000 scale, with accompanying handbooks, which were completed in 1984 (Macaulay Institute for Soil Research 1984). In addition, there is almost 95% coverage of the cultivated land at 1:25 000 scale, including accompanying memoirs and handbooks for much of the area surveyed. Scotland also has digitised land cover data for the whole country at the 1:25 000 scale (MLURI 1992). This information resource represents one of the most complete collations of national scale soil data in Europe (Lilly *et al.* 2004; Towers *et al.* 2006).

3.6.3 Geochemical atlases

Data on K_{AqReg} and/or K_{totXRF} are available in several geochemical atlases, of which some are listed in Table 2. The publications range from less available monographs to highly available on-line publications, which include databases with open access to raw data as well as processed data in the form of statistical tables and maps.

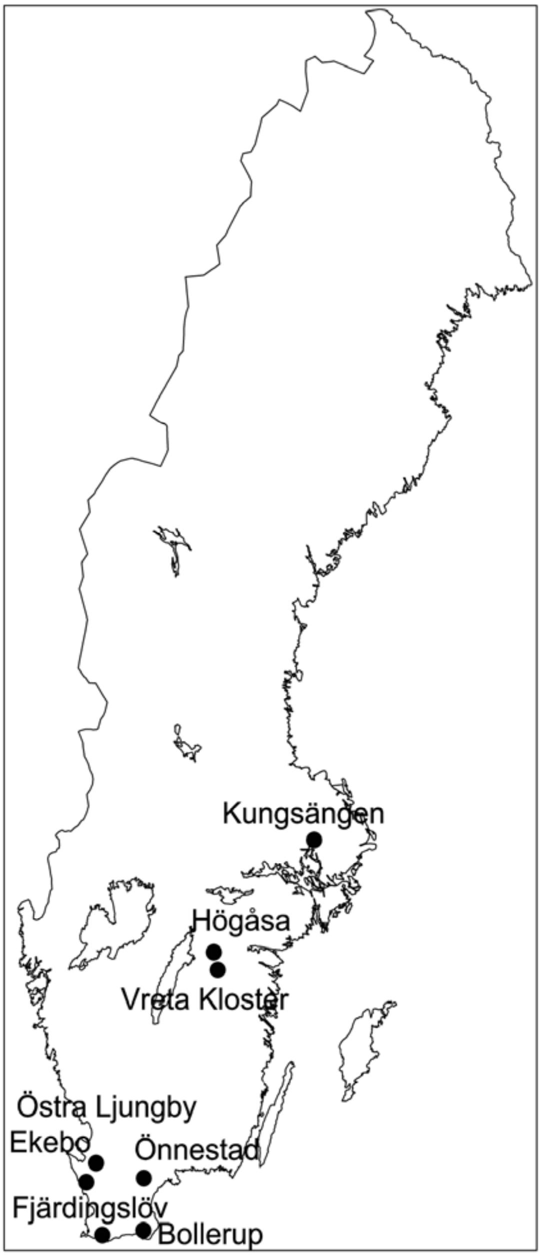
Table 2. *Selection of geochemical atlases and their K-related attributes*

Title	K_{ex}	K_{AqReg}	K_{XRF}	Sampling density (km^2 $sample^{-1}$)	No. of points	No. of countries	Reference
Geochemical Atlas of Europe			x	4700	850	26	Part 1: (Salminen 2005); Part 2: (De Vos & Tarvainen 2006)
Geochemical Atlas of England and Wales		x		25	6000	2	(McGrath & Loveland 1992)
Geochemical Atlas of Scottish top soils		x		100	705	1	(Paterson, unpublished)
Environmental Geochemical Atlas of the Central Barents Region	x		x	300	650	3	(Reimann *et al.* 1998)
Agricultural Soils in Northern Europe - a Geochemical Atlas	x	x	x	2500		10	(Reimann *et al.* 2003)
Geochemical Atlas of Eastern Barents Region		x	x	1000	1373	2	(Salminen *et al.* 2004)

4 Materials and Methods

4.1 Selection of Study Sites and Soils

Soils from eight agricultural experimental sites in Sweden (Figure 4) and from twelve agricultural sites in Scotland (Figure 5) are included in this thesis (Table 3). Three of the Swedish sites, Bollerup (Boll), Önnestad (Önn), and Ö Ljungby (ÖLj), belong to the programme 'Long-term Field Experiments with Environmentally-Friendly and Sustainable Cropping Systems' (Ivarson & Gunnarsson 2001; Gissén & Larsson 2008), which started in 1987. The other five, Fjärdingslöv (Fjä), Ekebo (Eke), Högåsa (Hög), Vreta Kloster (Vre) and Kungsängen (Kun), were selected from among the 'Swedish Long-term Soil Fertility Experiments' established in 1957-1966 (Carlgren & Mattsson 2001). The Scottish soils were selected from sites under improved grassland. In the Scottish soil classification, soils are organised into soil associations based on parent material (Figure 5) and soil series based on drainage class. In order to have a large representative proportion of the land area under improved grassland and to cover a wide range of soil parent materials, eight of the fourteen most extensive soil associations were selected. Acidic parent materials were represented by soils from three soil associations, namely Strichen (ST), Arkaig (AK) and Countesswells (CW); intermediate parent materials by four soil associations, Thurso (TH), Ettrick (ER), Foudland (FD) and Sourhope (SH), and basic parent materials by the Darleith (DL) soil association. The freely drained soil series of each of these eight soil associations were selected since they were the most extensive. For four soil associations, however, both a freely drained (f) and a poorly drained (p) soil series were selected because they had a similar extent of land cover.



The overall aim of the selection of sites was to include a wide range of soils in terms of parent material and soil fertility in general and K status in particular. The Swedish sites had a wider range of textures than the Scottish soils. On the other hand, the Scottish soils were more diverse in terms of the geochemistry of the soil parent material compared with the Swedish soils. In the following, Swedish and Scottish soils used in this thesis are referred to by their abbreviated site names and soil association names, respectively.

Figure 4. Location of the Swedish experimental sites.

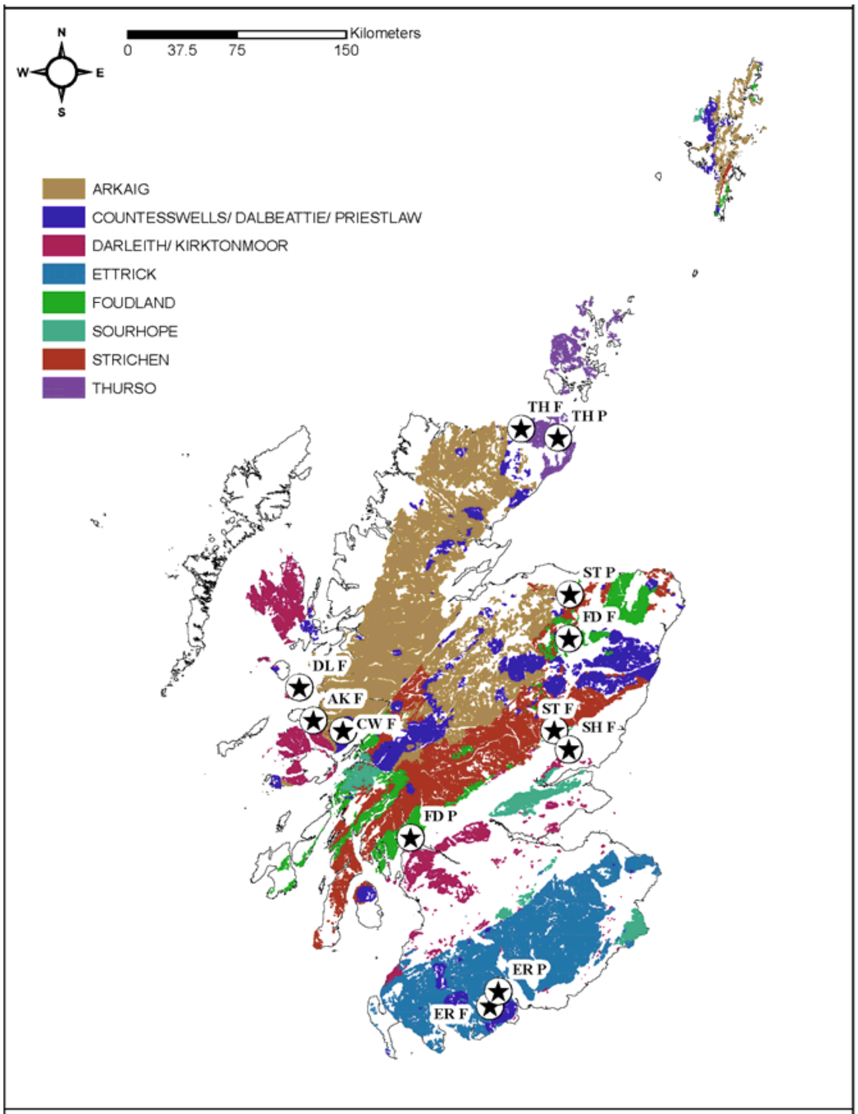


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Figure 5. Location of the Scottish profiles and distribution of Soil Associations based on information from the Scottish Soils Database (Towers *et al*., 2006). 'F' and 'P' refer to freely and poorly drained, respectively.

Table 3a. *Site and soil characteristics of the Swedish field experiments*

Site	Site abbr.	Coord.	Altit. (m)	Prec. (mm)	Soil temp (°C)	Quaternary deposit[a]	Bedrock[a]	Soil texture[b] (subsoil)	Moist. regime	Soil type[c] (WRB)
Bollerup[d]	Boll	55° 28'N, 14° 03'E	45	656	8.6	Clayey till[b1]	Ordovician clay slate	Sandy loam	Udic	Orthoeutric Cambisol
Önnestad[d]	Önn	56° 03'N, 14° 02'E	10	551	8.6	Post glacial sand[b2]	Cretaceous limestone, sandstone	Sandy loam	Udic	Hypereutric Regosol
Östra Ljungby[d]	ÖLj	56° 12'N, 13° 03'E	35	742	8.2	Post glacial sand[b3]	Gneiss, granite	Loamy sand	Udic	Orthidystric Regosol
Fjärdingslöv[e]	Fjä	55° 24'N, 13° 14'E	30	660	8.5	Silty to sandy glacial till[b4]	Danian limestone rich in chert	Sandy loam	Udic	Haplic Phaeozem
Ekebo[e]	Eke	55° 59'N, 12° 52'E	59	800	8.4	Clayey till[b5]	Sediments Upper Trias	Sandy loam	Udic	Haplic Phaeozem
Högåsa[f]	Hög	58° 30'N, 15° 27'E	77	517	7.1	Post glacial reworked sandy deposit[b6]	Ordovician limestone	Loamy sand	Udic	Arenic Umbrisol
Vreta Kloster[f]	Vre	58° 29'N, 15° 30'E	55	517	7.1	Varved clay[b6]	Lower Ordovician shales	Silty clay	Udic	Haplic Phaeozem
Kungsängen[g]	Kun	59° 50'N, 17° 41'E	4	660	5.4	Lacustrine postglacial gyttja clay[b7]	Precambrian gneissic granites and leptites	Silty clay	Aquic	Gleyic Cambisol

[a] Quaternary maps 1:50 000:

[1] Daniel (1986), [2] Ringberg (1991), [3] Daniel (1980), [4] Daniel (1977); [5] Adrielsson *et al.*(1981); [6] Fromm (1976); [7] Möller (1993).

[b] Based on particle size distribution in the B horizon, 25-40/50 cm depths.

[c] Food and Agriculture Organization (FAO 2001).

[d] Ivarson & Gunnarsson (2001), Paper I; [e] Kirchmann *et al.*(1999); [f] Kirchmann *et al.*(2005); [g] Kirchmann (1991).

Table 3b. *Site and soil characteristics of the Scottish (UK) soils*

SA	N.D.	Soil abbr.	Coord.[a]	Altit.[a] (m)	Parent material[a]	Texture[b] (subsoil)	Soil type[c] (WRB)
Strichen	Free	ST_f	56° 41’N; 3° 14’E	291	Till; undifferentiated schist	Sandy loam	Fragic mollic dystric cambisol
Strichen	Poor	ST_p	57° 32’N; 3° 5’E	126	Till; undifferentiated schist and gneiss	Loam	Epigleyic mollic eutric stagnosol
Arkaig	Free	AK_f	56° 41’N; 5° 56’E	76	Colluvium; Moine schist and gneiss	Sandy loam	Dystric mollic cambisol
Countesswells	Free	CW_f	56° 38’N; 5° 36’E	185	Moraine; granite	Loamy sand	Umbric podzol
Thurso	Free	TH_f	58° 33’N; 3° 41’E	107	Till; M.O.R.S.A. flagstones	Silt loam	Fragic leptic dystric cambisol
Thurso	Poor	TH_p	58° 30’N; 3° 15’E	47	Till; M.O.R.S.A. sandstone and shale	Loam	Epigleyic mollic eutric stagnosol
Ettrick	Free	ER_f	54° 58’N; 3° 52’E	35	Till; greywacke	Loam	Mollic dystric cambisol
Ettrick	Poor	ER_p	55° 4’N; 3° 47’E	130	Water-modified till; greywackes	Sandy loam	Mollic eutric gleysol
Foudland	Free	FD_f	57° 15’N; 3° 5’E	396	Till; argillaceous schist	Sandy loam	Haplic dystric cambisol
Foudland	Poor	FD_p	56° 0’N; 4° 48’E	44	Till; phyllite	Sandy loam	Gleyic mollic hypereutric stagnosol
Sourhope	Free	SH_f	56° 34’N; 3° 4’E	244	Colluvium; andesite	Sandy loam	Mollic leptic eutric cambisol
Darleith	Free	DL_f	56° 53’N; 6° 7’E	55	Residual drift; basalt	Silt loam	Dystric mollic cambisol

[a] Data from the Scottish Soils Database (Towers *et al.* 2006).

[b] Based on particle size distribution in the shallowest B horizon.

[c] Reference Soil Group (IUSS Working Group WRB 2007).

N.D.=natural drainage; M.O.R.S.A.= Middle Old Red Sandstone Age

4.1.1 Experimental Design of Swedish Long-term Field Experiments

The Swedish soils were taken from agricultural field experiments. At Boll, Önn and ÖLj, mixed conventional (Conv) and organic (Org) systems, consisting of 6-year crop rotations, were studied (Table 2 in Paper II). Each experimental cropping system had six plots, one for each crop in the rotation. This enabled sampling of all crops in the rotation during a single season. At Fjä, Eke, Hög, Vre and Kun, the experimental design included treatments that were arranged in blocks in a split-split plot design with crop rotation systems on main plots, P and K application rates on subplots (PK subplots), and N application rates on sub-subplots (Table 2 in Paper III). All four PK subplots (A–D) in the mixed arable/livestock crop rotation were studied. Within these subplots, the sub-subplots receiving the highest N application rate were selected. For details on applications of mineral fertilisers and manures in the two experiments, see Papers II and III respectively.

4.2 Sampling and Sample Preparation

4.2.1 Repeated Sampling in Long-term Field Experiments

From the start of the experiments at Boll, Önn and ÖLj, surface soil (0-20 cm) was sampled annually after the crop had been harvested in the autumn. At Fjä, Eke, Hög, Vre, and Kun, surface soil (0-20 cm) and subsoil (40-60 cm) were sampled approximately once per crop rotation period throughout the experiment. Crop samples for biomass yield and chemical analysis were collected and treated according to Papers II and III.

Sampling for detailed investigation of soils

Soil profile sampling at the Swedish sites was carried out during the summers of 2002 (Fjä, Eke, Kun, Boll, Önn, ÖLj) and 2003 (Hög, Vre) in the plots with grass/clover ley. Surface soil was taken from three depths within the plough layer (Ap-horizon): 0-5 cm, 5-10 cm, and 10-25 cm. Subsoil samples were taken from 25-40, 40-70, 70-110 cm; 70-110 cm was omitted at Boll, Önn and ÖLj. In addition to the plot-wise samples, one composite sample from each soil layer and site was created by pooling equal weights of the fine earth fraction from all sampled plots of the site in order to obtain 'site-representative' samples for each experimental site.

In addition, a soil pit was excavated inside the buffer area of one of the plots with grass/clover ley at each experimental site. Root distribution to 1 m depth was estimated using the same methodology at all eight sites (Papers II and III). At Boll, Önn and ÖLj, a soil profile description (FAO, 1990) was carried out in the soil pits (Supplementary Data), and samples for determination of bulk density were taken. Soil profile descriptions and information on bulk densities for the other five Swedish sites had already been published (see corresponding reference in Table 3).

Within the twelve selected Scottish soil series, suitable soil profiles were systematically selected from the Scottish Soils Database (Towers *et al.* 2006) using a series of selection criteria. Subsequently, the corresponding air-dried fine earth (<2 mm) samples were collected from the National Soils Archive of Scotland; the uppermost Ap, uppermost B and deepest C horizon samples were chosen (Paper V). Data on a wide range of standard chemical and physical analyses were already available from the Scottish Soils Database (Table 4). Soil profile descriptions corresponding to the selected soils were also available from the Scottish Soils Database (Supplementary Data).

4.2.2 Sample Preparation

Swedish soil samples were air-dried at 30 °C and sieved to separate gravel and stones (>2 mm) from the fine earth fraction (<2 mm). For the 2002/2003 profile samplings, the two fractions were weighed.

In Paper IV, the study focused on the Hög, Fjä, and Kun profiles. Soil particle size separation was performed on samples from the 5-10 cm layer within the Ap horizon. The fractions were obtained after ultrasonic dispersion (600 W, Amp 100%, 25 mm probe), using a combination of wet sieving (2000-200 and 200-60 μm fractions) and sedimentation in Atterberg cylinders (60-20, 20-2 and <2 μm fractions). Sand fractions were concentrated by drying (105 °C) and the silt and clay fractions by freeze-drying.

Reproducibility is one of the most important methodological aspects in quantitative analysis. Sub-sampling is therefore a critical step of the sample preparation. In this thesis, several analyses were performed on each of the individual samples (i.e. the composite Swedish soil samples and the archived Scottish soil samples). Furthermore, in Paper IV, where the effects of a certain extraction procedure were to be assessed, it was fundamental that any detected differences between treated and untreated samples could be ascribed solely to the treatment and not to any pre-existing differences between pairs of sub-samples. Samples were therefore split into aliquots of required weights, using a spinning riffler for all site-representative fine earth samples (Figure 6) or so-called 'coning and cloning' for the particle size fractions of Paper IV. Whole splits prepared accordingly were used in all quantitative work involving site-representative samples or size-fractionated samples. When an analysis required very small sample weights (*e.g.* total C and N analysis) or a standardised sample weight (*e.g.* *aqua regia* digestion), whole splits were finely ground prior to further sub-sampling.

4.3 Chemical Analyses

For the standard chemical and physical analyses performed on the site-representative samples, see Table 4. For the K-related analyses, the methods used were as follows:

4.3.1 Exchangeable and HCl-extractable K

Exchangeable K (K_{ex})[4] and 2 M HCl-extractable K (K_{HCl}) followed standard procedures (Egnér *et al.* 1960; SIS 1993). The method for K_{ex} involved extraction in 0.1 M ammonium lactate + 0.4 M acetic acid (pH 3.75) at room temperature (20-25 °C). For K_{HCl}, the soil was extracted by 2 M HCl in a boiling water bath (100 °C) for 2 h. Extracts were analysed by flame atomic emission spectroscopy (flame-AES), inductively coupled plasma atomic emission spectrophotometry (ICP-AES), or flame atomic absorption spectroscopy (flame-AAS).

4.3.2 *Aqua regia*-Extractable K

For K_{AqReg}, 0.5 g of ground sample (<200 µm) was digested using the procedure of McGrath and Cunliffe (1985) as modified by McGrath (1987) (3:1 of 50% HCl:concentrated HNO_3, by volume), with the digest being made up into 100 mL of 12.5% HNO_3 prior to analysis by ICP-AES.

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[4] Ståhlberg (1980) made a comparison between ammonium lactate and ammonium sulphate extractable K and concluded that a similar amount of K; i.e., the exchangeable K fraction (K_{ex}), was extracted from mineral soils using the two methods.

Table 4a. *Selected properties of the eight Swedish soils*

Site	Depth (cm)	CEC[a]$_{pH8.2}$ (cmol$_c$ kg^{-1})	BS[b] (%)	pH[c] (CaCl$_2$)	C$_{org}$[d] (%)	C$_{org}$:N	Particle size distribution (%)[e]				
							<2	2-20	20-60	60-200	200-2000
Boll	0-25	13	66	5.6	1.4	10	16	18	11	24	31
	25-50	9	62	5.5	0.5	7	13	19	11	25	33
	50-70	9	64	5.2	0.3	9	13	17	13	25	32
Önn	0-25	18	100	6.4	3.4	10	9	7	14	42	28
	25-50	6	100	7.3	0.3	7	7	10	17	48	18
	50-70	5	100	7.5	0.2	6	3	10	22	48	16
ÖLj	0-25	15	55	5.6	3.4	15	10	8	12	17	53
	25-50	5	29	5.4	0.7	15	4	5	8	15	69
	50-70	3	25	5.4	0.3	11	2	2	5	11	81
Fjä	0-25	15	n.a.	6.7	2.1	18	18	14	13	26	30
	25-40	16	n.a.	7.2	1.1	16	18	15	13	24	30
	40-70	13	n.a.	7.5	0.7	31	17	16	15	22	30
	70-110	7	n.a.	7.7	0.8	26	16	17	12	24	32
Eke	0-25	14	n.a.	5.2	3.2	17	14	17	18	27	25
	25-40	10	n.a.	5.0	1.7	24	13	17	17	26	27
	40-70	9	n.a.	5.7	0.3	11	16	16	14	25	29
	70-110	9	n.a.	5.0	0.2	6	17	17	16	24	26
Hög	0-25	9	n.a.	5.8	2.5	16	7	7	12	43	31
	25-40	7	n.a.	5.4	1.4	25	5	7	14	47	28
	40-70	3	n.a.	5.3	0.3	11	2	4	12	52	31
	70-110	3	n.a.	5.4	0.2	5	2	3	13	53	30
Vre	0-25	25	n.a.	6.3	2.3	13	46	19	26	5	4
	25-40	26	n.a.	6.6	1.4	15	50	19	25	4	3
	40-70	23	n.a.	7.3	0.9	21	53	25	16	4	4
	70-110	22	n.a.	7.4	0.7	24	59	23	8	4	6
Kun	0-25	24	n.a.	5.8	2.8	13	52	30	14	3	2
	25-40	22	n.a.	6.0	1.6	15	51	29	15	3	1
	40-70	20	n.a.	6.0	1.4	14	53	31	11	3	2
	70-110	19	n.a.	4.5	1.7	11	55	31	10	3	1

n.a.=not analysed, [a] Cation exchange capacity after Na-saturation (Polemio & Rhoades 1977), [b] Base saturation at pH 8.2 (%), [c] In 0.01 M CaCl$_2$ (McLean 1982; Sumner 1994), [d] Organic carbon (see Paper I), [e] Gravimetric particle size distribution of the <2000μm fraction. Wet sieving (2000-60 μm) and sedimentation by pipette method (<60 μm) (Ljung 1987).

Table 4b. *Selected properties of the twelve Scottish soils*

Site	Horiz.	CEC_{pH7}[a] ($cmol_c$ kg^{-1})	BS[a] (%)	pH[a] ($CaCl_2$)	C_{org}[a] (%)	C_{org}:N	Particle size distribution (%)[b]				
							<2	2-20	20-60	60-200	200-2000
ST_f	Ap	18	56	5.2	4.1	16	14	22	19	22	23
	B(s)	7	36	5.2	1.0	50	8	19	20	23	30
	C(x)	5	28	5.2	0.1	n.d.	8	25	13	16	39
ST_p	Ap	13	67	5.7	4.3	14	14	24	21	24	17
	Bg	6	65	5.5	0.7	24	13	20	20	30	18
	Cg	7	63	5.3	0.8	26	17	25	19	22	18
AK_f	Ap	19	52	5.6	4.6	6	14	14	15	35	21
	Bs	13	31	5.0	1.7	9	8	14	16	38	24
	C	6	4	4.9	0.8	7	1	12	19	36	31
CW_f	Ap	18	19	4.1	3.7	12	7	10	6	11	66
	Bs	14	3	4.3	1.0	12	3	7	7	10	73
	BC	3	2	4.5	n.d.	n.d.	2	4	6	17	71
TH_f	Ap	17	37	5.2	4.7	11	19	25	27	19	11
	Bx	8	24	5.2	0.4	9	11	26	25	19	20
	C	25	59	5.8	3.6	13	12	25	12	8	43
TH_p	Apg	15	65	5.7	3.4	19	19	28	21	21	11
	Bg	9	77	5.5	0.3	n.d.	17	23	17	21	22
	Cg	10	86	5.9	0.2	n.d.	18	23	16	21	21
ER_f	Ap	19	56	5.0	5.9	11	22	27	18	14	20
	B	8	46	5.1	2.7	11	12	25	12	13	38
	C	7	23	5.2	1.5	12	8	28	11	16	37
ER_p	Ap	25	50	5.1	7.2	13	19	26	21	20	15
	Bg	3	42	5.5	n.d.	n.d.	4	26	23	19	29
	C	4	89	5.4	n.d.	n.d.	11	24	20	21	24
FD_f	Ap	20	48	5.0	4.3	14	n.a	n.a	n.a	n.a	n.a
	Bw	10	35	5.0	1.4	16	6	17	28	30	20
	C	3	32	4.9	0.3	7	3	10	25	34	29
FD_p	Ap	11	88	5.6	4.4	12	12	31	18	19	20
	Bg	2	100	5.4	n.d.	n.d.	7	24	22	25	23
	BCg	1	100	5.4	n.d.	n.d.	7	31	20	17	25

Cont. Table 4b

Site	Horiz.	CEC$_{pH7}$[a] (cmol$_c$ kg^{-1})	BS[a] (%)	pH[a] (CaCl$_2$)	C$_{org}$[a] (%)	C$_{org}$:N	Particle size distribution (%)[b]				
							<2	2-20	20-60	60-200	200-2000
SH$_f$	Ap	37	69	5.3	5.6	11	18	19	19	21	23
	B	26	76	5.5	0.6	n.d	3	13	18	32	34
	C	43	91	5.9	0.0	n.d	2	10	17	30	41
DL$_f$	Ap	29	72	5.1	8.1	10	26	36	16	10	13
	B	29	25	4.7	7.4	11	23	38	17	10	13
	C	41	47	4.4	1.8	12	6	18	17	20	39

n.d.=not detected, n.a.=not analysed.

[a] Data derived from the Scottish Soils Database (Towers *et al.* 2006);

[e] Gravimetric particle size distribution of <2000µm fraction. Method as in SWE soils.

4.3.3 Total K

Total geochemical analysis was performed on finely ground samples by X-ray fluorescence (XRF) under contract at the University of Southampton. The ground samples were prepared as fused glass beads using Spectroflux® 100B (80% $LiBO_2$ + 20% $Li_2B_4O_7$, weight percentages). The instrument used was a Philips® MAGIX-PRO with SuperQ4 software and a 4kW Rh end-window X-ray tube.

Before this could be done, grinding procedures had to be developed to obtain samples with particle diameter smaller than 75 µm, using a TEMA disc mill. This comprehensive methodological study showed that sample weight, grinding time and grinding agent all had an effect on the particle size distribution in the ground soil samples. Dry grinding of 3 g soil for 6 min resulted in a sample with 99.9% of the particles smaller than 75 µm, which was very satisfactory in terms of particle size, sample consumption and practicality. The procedure was applied to all samples submitted for total geochemical analysis.

4.4 Mineralogical Analyses by X-ray Diffraction

In all papers, X-ray powder diffraction (XRPD) was used to identify and quantify the mineralogical composition of the soils. In Paper IV, parallel orientated XRD was also used for identification.

4.4.1 Sample Preparation

Random powders

For qualitative and quantitative mineralogical analysis, XRPD, weighed samples plus a 20% addition of an internal standard were ground in a polyvinyl alcohol water solution. Following the spray-drying procedure by Hillier (1999; 2003), the slurry was poured directly into a small glass bottle, onto which an artistic air-brush was fitted. The sample was then spray-dried down through a specially designed oven with an exit air temperature of 130 °C (Figure 6c).

Figure 6. a) *above left*: Use of a spinning riffler for sub-sampling of fine earth, b) *above right*: Aliquots of sub-samples with desired weight, c) *left*: Sample preparation for XRPD by spray-drying of samples with an air-brush, d) *above*: The result of spray-drying: spherical granules with a diameter of approx. 50 µm, SEM image.

The spray droplets dried during the process were collected as spherical granules of approx. 50 μm diameter (Figure 6d) on a sheet of sample paper at the bottom of the oven. Due to the spherical shape of the granules, the sample could easily be poured into a sample container and subsequently into the cavity of the sample holders. Truly random powder samples for XRPD were thereby obtained, which ensured highly reproducible diffraction patterns (Hillier 2003).

Parallel orientated slides

In Paper IV, the clay fractions (<2 μm) were also prepared as orientated mounts on glass slides using the Millipore™ transfer method (Moore & Reynolds Jr 1997). Samples were analysed air-dried (AD), glycolated (G), and after heating to 300 °C for 1h (H300).

4.4.2 Diffraction Patterns and Identification of Minerals

All samples were run on a Siemens D5000 diffractometer, using Co Kα radiation selected by a diffracted beam monochromator. Random powders were scanned from 2 to 75° 2θ in 0.02° steps and counting for 2-5 seconds per step, depending on the level of detail required. Parallel orientated samples were scanned from 2 to 45° 2θ in 0.02° steps and counting for 1 second per step. Diffraction patterns were evaluated visually using the software EVA DIFFRAC^{plus} (Brucker 2006). For an overview of the K-bearing mineral phases identified in the different papers, see Table 5.

4.4.3 Quantification of Mineralogical Composition

Quantitative estimates (weight-percent) of spray-dried soil minerals were obtained using the single peak Reference Intensity Ratio methodology of Hillier (2003) (Papers I-III) and a full pattern fitting procedure as outlined in Omotoso *et al.* (2006) (Papers IV and V). However, for comparison, all XRD patterns included in Papers I and II were re-evaluated for this thesis summary using the full pattern method. Using a similar full pattern method, differential XRPD patterns were derived for Paper IV by subtracting XRPD patterns of HCl-treated samples from those of untreated samples.

Table 5. *Nomenclature of K-bearing feldspar and phyllosilicate phases and groups of phases, identified by XRPD and used in Papers I-V*

Paper	Feldspars			Phyllosilicates							Method
	Number of phases		Term used for K-bearing phase	Number of phases		Terms used for K-bearing phases					
	Total	K-bearing		Total	K-bearing[a]						
I-III	2	1[b]	K-feldspar	3	2	Illitic dioct[c]		M-L dioct			Single peak/ RIR
						“Dioct phyllo’					
IV	5	1[b]	K-feldspar	10	5	Muscovite	Illite	M-L dioct	Biotite[d]	Hydro-biotite	Full pattern fitting/RIR
V	6	2[e]	K-feldspar	9	4	Muscovite	Illite	M-L dioct	Biotite[d]		Full pattern fitting/RIR
							“Fe-containing K-bearing phyllo’				

Dioct = dioctahedral; M-L = mixed-layer; phyllo=phyllosilicates; RIR=reference intensity ratio. For detailed information about the identified phases, see Supplementary Data. [a] Includes both K-bearing and potentially K-bearing minerals. However, according the assumed mineral formulae used in this thesis work (Supplementary Data), all phases in this group contain K to some degree. [b] Includes orthoclase and microcline, but counted as one phase as they have the same K content. [c] Includes dioctahedral illite and muscovite. [d] Includes biotite and phlogopite (=trioctahedral mica, as termed in Paper IV). [e] Includes orthoclase, microcline and sanidine, but counted as two phases since orthoclase and microcline have the same K content.

4.5 Data Evaluation

4.5.1 Normative Calculations

The partitioning of K between different mineral phases was estimated by normative calculations. The term 'normative' is borrowed from the igneous petrology literature where chemical data are commonly recast in terms of a hypothetical mineral composition. The method advanced in the present work is direct rather than hypothetical in that the results from quantitative XRPD are combined with assumed mineral formulae. In Paper II, eight different phases were included in the calculations, whereas 22 phases were considered in Paper V and in this thesis summary (Supplementary Data). The agreement between the total element concentrations derived in this way and those obtained by the XRF analysis was used as a validation of the accuracy of the mineralogical analyses and the general applicability of the mineral formulae used.

4.5.2 Field K Balances

Field K mass balances were calculated differently in the different papers. In Paper II, the primary aim was to assess the sustainability of cropping systems while in Paper III it was to estimate the release and fixation of $K_{non\text{-}ex}$. However, for this thesis summary (Section 5.4.2), balances similar to those of Paper III were also assessed for the agricultural systems of Paper II, in order to provide comparable estimates of the release of $K_{non\text{-}ex}$ for all Swedish soils.

In general terms, the major input and output flows of an element (E) that are typically included in a field or soil surface balance are given in Eq. 2:

$$\Delta E_{soil} = E_{seeds} + E_{fertiliser} + E_{deposition} + E_{other\ inputs} - (E_{harvest} + E_{leaching} + E_{runoff} + E_{other\ outputs}) \qquad \text{Eq. 2}$$

where ΔE_{soil} is the net change in soil storage of the element, in our case K.

In Paper II, only $K_{fertiliser}$ and $K_{harvest}$ were measured and included in the K balance calculation (Eq. 3). Hence, data on inputs of fertiliser, consisting of mineral fertiliser ($K_{min\ fert}$) and slurry (K_{slurry}), and outputs through crop off-take ($K_{harvest}$), including harvest and removed crop residues, were used to calculate average annual field balances for K:

$$K_{balance} = K_{min\ fert} + K_{slurry} - K_{harvest} \qquad \text{Eq. 3}$$

In Paper III, on the other hand, $K_{leaching}$ and $K_{deposition}$ were included in addition to $K_{fertiliser}$ and $K_{harvest}$, and ΔK_{soil} was divided into the respective changes in K_{ex} and $K_{non\text{-}ex}$ (Eq. 4). Of the latter two, changes in K_{ex} were established from time series of K_{ex}. Changes in $K_{non\text{-}ex}$ could then be calculated from the following balance, which corresponds to the rate of K release or fixation:

$$\Delta K_{non\text{-}ex} = K_{min\ fert} + K_{manure} + K_{deposition} - (K_{harvest} + K_{leaching} + \Delta K_{ex}) \qquad \text{Eq. 4}$$

4.5.3 Statistical Analysis

Simple linear regression was used to validate total K by XRPD ($K_{totXRPD}$) versus that by XRF (K_{totXRF}) (Papers I and V, Section 5.1.3) and for modelling the relationships between all the other variables tested (Paper V). In Paper II, simple linear regression with groups was used for modelling the relationships between the x-variate as K present in dioctahedral phyllosilicates and the y-variates K_{ex}, K_{HCl} or K_{AqReg}. For the long-term data, simple linear (Papers II and III) and non-linear (Paper II) regression techniques were used to fit models to the long-term herbage yield (Paper II), herbage K concentration (Paper II) and soil K_{ex} (Papers II and III) and K_{HCl} (Paper II) data. The regression equations were used to calculate the total change in K_{ex} (Papers II and III) and ${}_{corr}K_{HCl}$ (Paper II) since the start of the experiment, corresponding to a period of 18 and 30 years in Papers II and III, respectively. In Paper I, Principal Component Analysis (PCA) was used to visualise how K_{HCl} and K_{AqReg} were related to a number of soil chemical, physical and mineralogical properties. In Paper II, Residual Maximum Likelihood (REML) was used to analyse crop data from four growing seasons (2001-2004) on ley herbage yields and herbage K concentrations from individual cuts. Within the REML analysis, least significant difference was used to determine significant differences between pairs of means. All data analysis was performed in GenStat, using either the 8.1 (2005) or 10.1 (2008) release, except for in Paper III, where Excel was used. For a more detailed description of the statistical analysis used in the different papers, see the respective papers.

5 Results and Discussion

5.1 The Mineralogical Budgeting Approach

The total K concentration obtained by XRF (K_{totXRF}) gives an overview of the range of soils included in this study. The Swedish soils had K_{totXRF} concentrations ranging from 17-31 g kg^{-1} (Figure 7), representing the middle to uppermost part of the range of total K concentrations generally reported for soils globally, which is 0.4-30 g kg^{-1} (Sparks 1987). The Scottish soils showed a wider range of concentrations, 4.6-39 g kg^{-1}, covering nearly the entire typical global span (Figure 7).

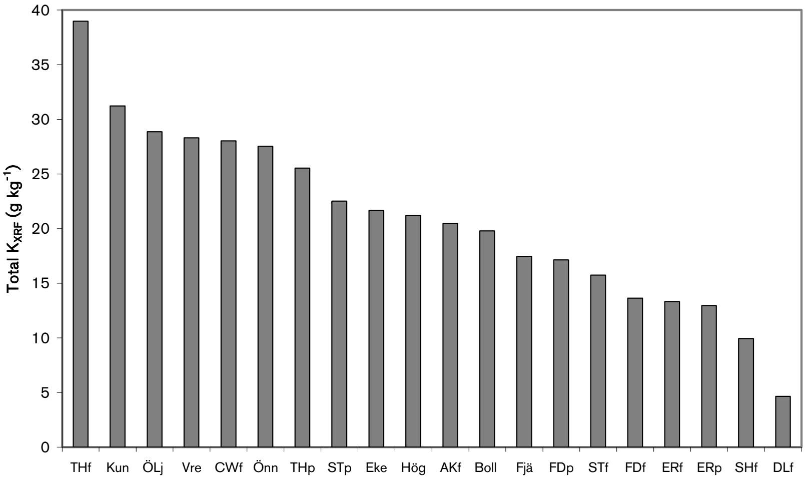

Figure 7. Concentration of total K by XRF (g kg^{-1}) in Ap-horizons of Scottish and Swedish agricultural soils.

In the majority of studies, K status is reported and evaluated in terms of concentrations or pools or different chemically (operationally) defined forms of K, only occasionally with reference to the mineralogical composition of the soil. To my knowledge, a complete quantitative mineralogical budget of K, showing the speciation of K among different K-bearing mineral phases (Papers I and V), has not been presented previously. The procedure was first developed and tested on the Swedish soils (Paper I) and was thereafter applied to the Scottish soils (Paper V). The results presented in Papers I and V show that the soils varied considerably in terms of the apportionment of K between the mineral phases identified.

5.1.1 Speciation of Mineral K in Soils

The results from the quantitative mineralogical analysis are presented in Table 6 and the subsequent K speciation in Figure 8. In the coarse-textured soils ÖLj, Önn, Hög, CW_f and SH_f, almost all K was present in the form of K-feldspar. The texture ranged from sandy loam to loamy sand. The soils had $K_{K\text{-feldspar}}$ concentrations above 14 g kg^{-1} and total K concentrations of phyllosilicates (K_{phyllo}) below 6 g kg^{-1} in the entire profiles (Table 6 and Figure 8). In the loams and sandy loams of Eke, Boll, Fjä, TH_f, TH_p and DL_f, phyllosilicates contributed on average more K, 4-11 g K kg^{-1}, although K-feldspar was still the dominant K form. The sandy loam AK_f had approximately equal contributions of K from K-feldspars and phyllosilicates, 11-14 g kg^{-1} of each. Both the freely and the poorly drained soils of the ER, FD and ST soil associations had the majority of their K allocated into phyllosilicates, which contributed K at 7-14, 14-27 and 17-37 g kg^{-1}, respectively. The high value of 37 g kg^{-1} in the ST_f soil only occurred in the C-horizon, whereas both the Ap and the B horizon had 17 g kg^{-1}. The texture of the B horizons was loam to sandy loam. Vre and Kun were the only soils classified as silty clays. In Vre there was a slight dominance of $K_{K\text{-feldspar}}$ over K_{phyllo} while in Kun the converse occurred. Potassium in phyllosilicates contributed 11-15 and 17-20 g kg^{-1} in the two soils, respectively.

Table 6. *Mineralogical composition (weight %) including organic matter (OM) of the fine earth (<2 mm) in Swedish and Scottish soil profiles. Dioct.=dioctahedral phyllosilicates; ML=mixed-layer; Trioct.=trioctahedral phyllosilicates; exp.=expandable; -=not detected. Uncertainties at 95% confidence according to Hillier (2003)*

Site	Horizon	Quartz	Plagioclase	Kfeldspar	Amphi-bole	Pyroxene	Calcite	Muscovite	Illitic-dioct.	ML-dioct	Dioct exp.	Kaolinte	Chlorite	Biotite	Trioct-exp.	Fe,Ti oxides	OM
Boll	0-25	65±4	8±2	8±2	1±1	-	-	-	-	-	-	1±1	1±1	1±1	1±1	1±1	2
	25-50	65±4	9±2	8±2	2±1	-	-	4±2	4±2	3±1	-	-	1±1	1±1	1±1	1±1	1
	50-70	64±4	9±2	8±2	1±1	-	-	6±2	6±2	1±1	-	1±1	1±1	1±1	1±1	2±1	0
Önn	0-25	48±4	19±3	18±3	3±1	-	-	-	-	-	-	1±1	1±1	1±1	1±1	1±1	6
	25-50	49±4	20±3	18±3	3±1	-	1±1	2±1	1±1	-	-	2±1	-	1±1	2±1	1±1	0
	50-70	48±4	21±3	17±3	3±1	-	5±2	2±1	1±1	-	-	1±1	1±1	1±1	-	1±1	0
ÖLj	0-25	41±4	23±3	19±3	3±1	-	-	-	-	-	-	-	1±1	-	1±1	2±1	6
	25-50	41±4	26±3	20±3	3±2	-	-	2±1	1±1	-	-	1±1	-	-	2±1	1±1	1
	50-70	44±4	28±3	19±3	1±1	-	-	1±1	1±1	1±1	-	-	1±1	1±1	-	2±1	1
Fjä	0-25	65±4	8±2	7±2	1±1	-	-	-	-	-	-	1±1	-	1±1	3±1	1±1	4
	25-40	64±4	8±2	8±2	1±1	-	-	3±1	3±2	4±2	2±1	1±1	-	-	3±1	1±1	2
	40-70	60±4	8±2	7±2	1±1	-	4±2	2±1	4±2	6±2	1±1	1±1	-	-	4±2	1±1	1
	70-110	55±4	7±2	7±2	1±1	-	14±3	3±1	3±2	3±1	-	1±1	-	-	3±1	1±1	1
Eke	0-25	56±4	14±3	13±2	1±1	-	-	-	-	-	-	1±1	-	1±1	-	1±1	6
	25-40	54±4	14±3	13±2	1±1	-	-	2±1	-	6±2	-	2±1	1±1	1±1	1±1	2±1	3
	40-70	55±4	14±3	12±2	1±1	-	-	3±1	5±2	3±1	-	2±1	-	1±1	1±1	1±1	1
	70-110	50±4	14±3	13±2	3±1	-	-	4±2	4±2	3±1	-	5±2	-	-	3±1	2±1	0
Hög	0-25	58±4	18±3	12±2	1±1	-	-	-	-	-	-	-	1±1	1±1	-	1±1	4
	25-40	57±4	19±3	13±2	1±1	-	-	3±1	-	1±1	-	-	1±1	2±1	-	1±1	2
	40-70	60±4	20±3	12±2	1±1	-	-	-	-	2±1	-	-	1±1	2±1	-	1±1	1
	70-110	60±4	20±3	12±2	2±1	-	-	1±1	-	1±1	-	-	1±1	1±1	-	1±1	0

Cont. Table 6

Site	Horizon	Quartz	Plagioclase	Kfeldspar	Amphi-bole	Pyroxene	Cal-cite	Musc-ovite	Illitic-dioct.	ML-dioct	Dioct exp.	Kaol-inte	Chlo-rite	Bio-tite	Trioct-exp.	Fe,Ti oxides	OM
Vre	0-25	37±4	15±3	12±2	2±1	-	-	-	-	-	-	3±1	-	2±1	8±2	2±1	4
	25-40	37±4	15±3	12±2	2±1	-	-	-	6±2	10±	-	2±1	1±1	3±1	7±2	3±1	2
	40-70	30±3	15±3	12±2	2±1	-	1±1	3±1	5±2	11±	-	2±1	1±1	4±2	9±2	2±1	2
	70-110	26±3	15±3	13±2	2±1	-	2±1	4±2	8±2	9±2	-	2±1	1±1	3±1	11±2	3±1	1
Kun	0-25	24±3	17±3	12±2	4±2	-	-	-	-	-	-	1±1	2±1	3±2	10±2	2±1	4
	25-40	24±3	17±3	12±2	4±2	-	-	3±2	14±3	4±2	-	1±1	2±1	4±2	10±2	3±1	3
	40-70	22±3	17±3	12±2	4±2	-	1±1	5±2	10±2	7±2	-	1±1	3±1	6±2	7±2	3±2	2
	70-110	22±3	17±3	12±2	4±2	-	1±1	4±2	8±2	10±	-	2±1	2±1	6±2	8±2	2±1	3
STf	Ap	39±4	15±3	2±1	5±2	-	-	16±3	-	2±1	-	2±1	3±2	1±1	2±1	4±2	7
	B(s)	41±4	15±3	2±1	5±2	-	-	15±3	1±1	3±1	-	3±1	4±2	1±1	3±1	4±2	2
	C(x)	27±3	13±2	2±1	3±1	-	-	33±3	4±2	1±1	-	6±2	4±2	1±1	1±1	5±2	0
STp	Ap	46±4	7±2	4±2	-	-	-	18±3	2±1	5±2	-	4±2	2±1	1±1	2±1	2±1	7
	Bg	50±4	9±2	5±2	1±1	-	-	13±2	2±1	5±2	-	3±2	2±1	3±1	3±1	3±1	1
	Cg	49±4	8±2	6±2	1±1	-	-	12±2	5±2	4±2	-	3±2	2±1	4±2	2±1	3±1	1
CW	A p	22±3	42±4	11±2	6±2	-	-	3±2	-	-	-	-	1±1	1±1	6±2	2±1	6
	Bs	24±3	38±4	15±3	7±2	-	-	3±2	-	-	-	-	2±1	2±1	4±2	2±1	2
	BC	24±3	42±4	14±3	7±2	-	-	3±1	-	-	-	-	1±1	1±1	6±2	1±1	0
AKf	Ap	41±4	22±3	8±2	2±1	-	-	8±2	3±1	2±1	-	-	-	2±1	1±1	2±1	8
	Bs	45±4	23±3	8±2	2±1	-	-	8±2	5±2	2±1	-	-	1±1	2±1	-	2±1	3
	C	45±4	26±3	9±2	2±1	-	-	7±2	3±1	-	-	-	1±1	2±1	3±1	1±1	1
THf	Ap	42±4	15±3	18±3	-	-	-	3±2	7±2	1±1	-	-	1±1	1±1	1±1	2±1	8
	Bx	42±4	17±3	20±3	-	-	-	5±2	3±1	5±2	-	1±1	2±1	3±1	-	2±1	1
	C	26±3	14±3	19±3	-	-	-	7±2	5±2	3±1	-	2±1	5±2	3±2	5±2	4±2	6

Cont. Table 6

Site	Horizon	Quartz	Plagioclase	Kfeldspar	Amphi-bole	Pyroxene	Cal-cite	Musc-ovite	Illitic-dioct.	ML-dioct	Dioct exp.	Kao-linte	Chlo-rite	Bio-tite	Trioct-exp.	Fe,Ti oxides	OM
THp	Apg	43±4	20±3	15±3	-	-	-	5±2	3±1	3±1	-	1±1	1±1	1±1	-	2±1	6
	Bg	41±4	23±3	15±3	1±1	-	-	7±2	2±1	3±1	-	1±1	1±1	3±1	-	4±2	1
	Cg	45±4	19±3	14±3	-	-	-	4±2	2±1	6±2	-	1±1	2±1	4±2	1±1	3±1	0
ERf	Ap	49±4	10±2	3±1	-	-	-	5±2	4±2	8±2	2±1	1±1	3±1	2±1	-	3±1	10
	B	47±4	10±2	2±1	-	-	-	4±2	5±2	12±	-	3±1	7±2	3±1	-	3±2	5
	C	43±4	11±2	3±1	1±1	-	-	7±2	5±2	6±2	-	3±1	8±2	2±1	4±2	3±1	3
ERp	Ap	54±4	11±2	3±1	-	-	-	3±1	1±1	11±	-	-	2±1	1±1	-	2±1	12
	Bg	58±4	15±3	4±2	-	-	-	6±2	4±2	4±2	-	1±1	6±2	1±1	1±1	1±1	0
	C	54±4	14±3	4±2	-	-	-	6±2	4±2	7±2	-	2±1	6±2	1±1	2±1	1±1	0
FDf	Ap	30±3	16±3	3±1	8±2	-	-	9±2	1±1	3±2	-	5±2	2±1	3±2	7±2	6±2	7
	Bw	30±3	18±3	4±2	8±2	-	-	10±2	1±1	1±1	-	5±2	2±1	4±2	10±2	5±2	2
	C	27±3	20±3	2±1	7±2	-	-	7±2	3±1	1±1	-	8±2	2±1	7±2	9±2	5±2	1
FDp	Ap	42±4	16±3	1±1	-	-	-	11±2	3±1	11±	-	1±1	7±2	1±1	-	1±1	8
	Bg	45±4	17±3	1±1	1±1	-	-	16±3	6±2	1±1	-	2±1	10±2	-	-	1±1	0
	BCg	39±4	16±3	1±1	1±1	-	-	22±3	5±2	2±1	-	1±1	10±2	1±1	-	1±1	0
SHf	Ap	8±2	22±3	11±2	-	12±2	-	1±1	3±1	-	-	5±2	1±1	1±1	22±3	4±2	10
	B	1±1	28±3	12±2	-	18±3	-	1±1	-	-	-	7±2	1±1	1±1	24±3	5±2	1
	C	-	34±3	13±2	-	17±3	1±1	-	-	-	4±2	5±2	-	1±1	21±3	4±2	0
DLf	Ap	7±2	8±2	7±2	-	11±2	-	-	4±2	2±1	1±1	6±2	-	2±1	30±3	7±2	14
	B	6±2	7±2	6±2	-	10±2	-	-	4±2	1±1	2±1	7±2	-	2±1	34±3	8±2	13
	C	2±1	1±1	1±1	1±1	4±2	-	1±1	6±2	2±1	11±2	7±2	-	2±1	52±4	8±2	3

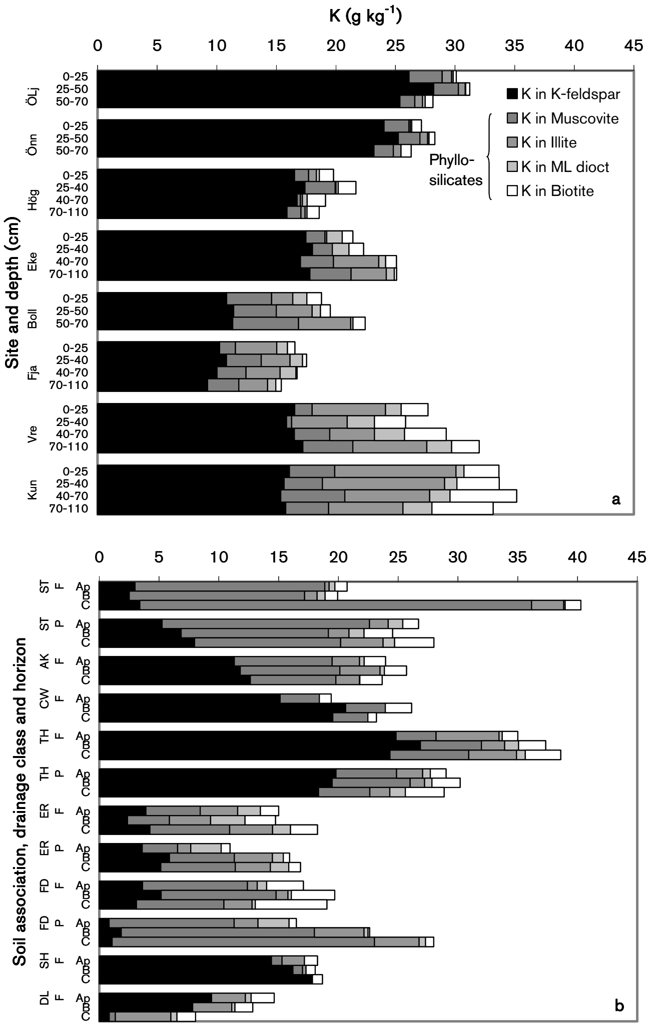

Figure 8. Speciation of total K_{XRPD} (g kg^{-1}) among K held in K-feldspars, muscovite, illite, mixed-layer (ML) dioctahedral phyllosilicates and biotite in a) Swedish and b) Scottish soil profiles.

The full pattern fitting approach enabled an estimate of the contribution of K from individual phyllosilicates as shown in Table 6 and Figure 8. Muscovite contributed uniform concentrations of K in the Swedish soils, around 5 g kg^{-1} down to trace amounts, whereas in the Scottish soils the range was from 0 to 33 g kg^{-1}. Because muscovite is always a primary mineral inherited from the parent material (*e.g.*, Thompson & Ukrainczyk 2002), this demonstrates the much wider range of parent materials in the Scottish soils.

Biotite, also a primary mica, varied both between the soils and within the soil profiles, although its contribution of K was less than 6 g kg^{-1} in all soils. In more than half the soils, there was a trend of lower K_{biotite} concentrations in the Ap horizons compared with the subsoil and in several cases the concentration was highest in the deepest horizon sampled. This suggests that K from biotite may have been released from the shallower part of the soils through weathering, possibly both through abiotic weathering (*e.g.*, Boyle & Voigt 1967) and as a result of biological processes such as plant uptake (Mortland *et al.* 1956; Boyle & Voigt 1967; Hinsinger & Jaillard 1993).

Illite contributed K in all soils except CW. In the Swedish soils, the concentration of illite (Table 6), and consequently of K_{illite} (Figure 8), was higher in soils with a fine texture. Thus, in the postglacial sands of ÖLj, Önn, and Hög, the concentration of K_{illite} was <1 g kg^{-1}, whereas in the clayey and silty to sandy tills (Boll, Eke, and Fjä) it was 2-4, and in the clays (Ver and Kun) 4-10 g kg^{-1}. This is in line with the general view that illites are concentrated in the finer soil particle fractions (*e.g.* Thompson & Ukrainczyk 2002). Mixed layer dioctahedral phyllosilicates (ML dioct) followed the same trend as illite in terms of site differences among the Swedish soils, but the concentration was lower than that of illite.

In four of the Scottish soils (ER_f, ER_p, FD_p and TH_p) and two of the Swedish soils (Vre and Kun), there were significant depth trends in ML dioct. For ER_p, FD_p and Kun, the trend was accompanied by an opposing trend in illite and/or muscovite, suggesting transformation in either direction: illite — ML dioct and/or muscovite — ML dioct. The reasons for this are probably site-specific, but are likely to be related to crop uptake, bio-circulation, K fertilisation and parent material.

All of the above-mentioned trends are the type that would be expected to occur as a result of weathering processes. Hence the fact that they are determined by the objective part of the full pattern fitting method is an encouraging sign of the utility of this approach in obtaining quantitative mineralogical data.

5.1.2 Sensitivity of Results to Method Development

Although the budgeting approach enables a mineralogical speciation of K to be calculated, it must always be borne in mind that the speciation of K inferred from XRD patterns, as presented in Papers I and V, is nonetheless based on judgments and on assumed mineral formulae. Hence, the speciation can change and also improve from time to time with developments in XRD pattern interpretation. Two years elapsed between Papers I and V and the methods were further developed during that time. In Paper I, the quantitative estimates of the mineral phases were based on single peak measurements and individual phyllosilicates were not quantified *per se*. In Paper V, on the other hand, a full pattern fitting approach was used for the quantification. This approach is less encumbered by potentially subjective interpretations, apart from the decision on which phases to include. Because more mineral phases were identified and quantified in the full pattern approach, especially feldspars and phyllosilicates, there was a larger range of phases used in the K budgeting in Paper V than in Paper I. Most of the changes, which are hopefully improvements, are related to the handling of phyllosilicates, which are undoubtedly the most complex group of K-bearing minerals to attempt to quantify in soil.

The apportionment of K between the two main groups K-feldspars and phyllosilicates did not change to any significant extent when the XRPD patterns from Paper I were re-evaluated with the full pattern fitting approach. For K-feldspars, this was partly due to the distinct peaks of microcline and orthoclase, which could easily be quantified with the single peak method (Figure 9). The chemical composition, especially the K content of K-feldspars, was also more easily standardised compared with the phyllosilicates. Hence, K-feldspar is probably the K-bearing mineral phase included in this study that is least likely to change as a result of method improvement and/or uncertainties in the method itself.

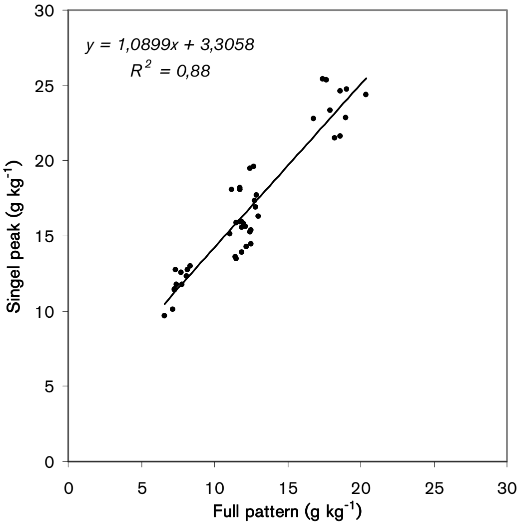

Figure 9. Comparison of the concentration of K feldspar determined with the single peak method and the full pattern fitting method in soil samples from eight Swedish sites and different soil depths.

It was more difficult to evaluate the speciation of K within the phyllosilicates, where Paper I has fewer K categories than Paper V in terms of mineral phases. The 10 Å peak in Paper I was interpreted as an illitic type dioctahedral phyllosilicate phase. With the full pattern fitting method in Paper V, however, it was possible to distinguish between muscovite and illitic type phases. The quantification of muscovite (2M1 polytype) is probably most comparable with that of feldspars, since it has a distinct X-ray pattern. Hence the estimated concentration is unlikely to change significantly with any further improvement of the full pattern fitting method. Illite, on the other hand, and the mixed layer phyllosilicates were much more difficult to estimate since the XRD patterns of these phases are less distinct and naturally more variable. Furthermore, it is difficult to allocate accurate chemical formulae to these phases and indeed for the greatest accuracy, this should be done on a case-by-case basis using all available information for the minerals in a particular soil. Hence, the apportionment of K into illites and mixed layer phyllosilicates is the most difficult judgment, and is likely to improve and change with complementary analyses or further method development. Nonetheless, all soils were quantified by exactly the same procedure, which should guarantee that results can be reasonably compared.

Biotite is probably intermediate between muscovite and illite in terms of sensitivity to method improvement. In Paper I, no biotite could be detected and the trioctahedral phases were interpreted as primarily chlorite and its weathering products. When the XRD patterns were re-evaluated using the method of Paper V, up to 6% of biotite was detected in the Swedish soils Vre and Kun (Table 6), which clearly shows the advantage and sensitivity of detection of this full pattern fitting method.

5.1.3 $Ktot_{XRPD}$ *versus* $Ktot_{XRF}$

Total K, calculated as the sum of K in minerals quantified with XRPD ($K_{totXRPD}$), was compared to K_{tot} measured by XRF (K_{totXRF}). This comparison was used to validate the mineralogical budgeting approach and its inherent assumptions; ideally, $K_{totXRPD}$ should equal K_{totXRF}. With the Swedish soils and the single peak method in Paper I, $K_{totXRPD}$ showed a close to 1:1 linear relationship with K_{totXRF} ($K_{totXRPD} = 0.976\ K_{totXRF} + 2.54$, $R^2=0.883$, S.E. = 1.85 g kg^{-1}, $p<0.001$; Figure 3 in Paper I). The correlation was slightly improved after re-evaluation of the XRPD patterns with the full pattern fitting method ($K_{totXRPD} = 1.0551 K_{totXRF} - 2.03$, $R^2=0.910$, S.E. = 1.76 g kg^{-1}, $p<0.001$).

When the mineralogical K budget was re-evaluated for all soils analysed, including the Scottish soils with their wide span of total K concentrations, there was still a close correlation between the two K totals, although there was more spread in the data and a significant intercept ($K_{totXRPD} = 0.7692\ K_{totXRF} + 6.10$, $R^2 = 0.755$, S.E. = 3.36 g kg^{-1}, $p<0.001$; Figure 10). The deviance from the 1:1 line and the intercept was primarily due to the two soils SH and DL. They had the lowest total K concentrations among the soils measured by XRF, <10 and 5 g kg^{-1}, respectively. In these soils, the K_{tot} concentrations estimated by XRPD were 2-6 times higher than those estimated by XRF. It is also notable that both soils are developed on intermediate and basic igneous volcanic rocks, and hence the generalised assumptions made for the composition of the phyllosilicates may need some revision in order to be able to cope with this type of parent material and better predict total K based on mineralogical analysis. It is also possible that uncertainties in relation to some of the other phases present in these soils affect the accuracy.

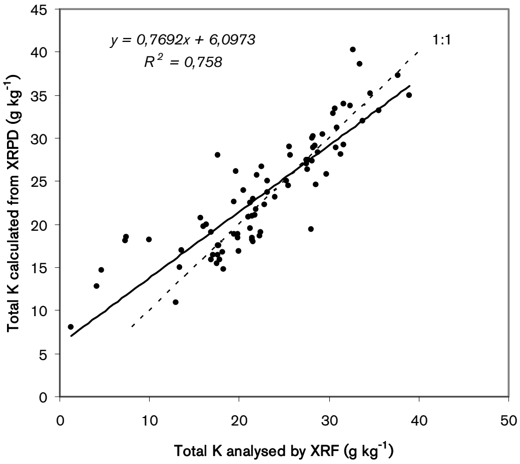

Figure 10. Comparison and validation of the total mineralogical budget of K derived from the normative calculations based on mineralogical analysis and a full pattern fitting method (XRPD) and total K measured by XRF of soil samples from twenty sites and different soil depths in Sweden and Scotland.

Nevertheless, the philosophy of the mineralogical budgeting approach is clearly validated by the degree of prediction obtained when exactly the same set of mineral formulae was applied in normative calculations performed on twenty different soil profiles, spanning a wide range of parent materials and located in three different climatic regions. The generalised mineral formulae can only be an approximation of the true chemical composition of a mineral in a specific soil. However, despite this approximation, there was very satisfactory overall agreement between $K_{totXRPD}$ and K_{totXRF}, confirming the general reliability of the mineralogical results and validating the budgeting approach and its assumptions.

5.2 Understanding Chemical Measurements of Soil K

To increase the understanding of some of the commonly used chemical measurements of soil K, K_{ex}, K_{HCl} and K_{AqReg} (*e.g.*, Egnér *et al.* 1960; McGrath & Loveland 1992), these were analysed in the soils and the results compared and analysed in the context of other soil chemical, physical, mineralogical, geochemical and agronomic properties. The ratios of K_{HCl} and K_{AqReg} to K_{totXRF} were also assessed and used as a measure of the extractability of the two fractions.

5.2.1 Exchangeable K

The range of exchangeable K (K_{ex}) measured in the eight Swedish soil profiles was 0.014-0.34 g kg^{-1}. In surface soil the concentrations ranged from 0.034 to 0.34 g kg^{-1}, which covered all the Swedish K status indices[5] I-V, from 'very low' to 'very high'. Surface soil was generally enriched in K_{ex} compared with subsoil (Figure 11). For the soil studied, no relationship was found between K_{ex} and any of the soil variables tested (Paper I).

5.2.2 HCl-extractable K

Range and extractability

HCl-extractable K varied between 0.25 and 6.2 g kg^{-1} in the Swedish soils. The concentrations in the surface soil ranged from 0.34 to 4.9 g kg^{-1} and, as for K_{ex}, this corresponded to the K status indices 1–5, or 'very low' to 'very high'. At most sites K_{HCl} showed the opposite pattern to K_{ex}, with lower concentrations in surface horizons compared with the subsoil (Figure 11). HCl-extractable K corrected for the concentration of exchangeable K (${}_{corr}K_{HCl}=K_{HCl}$ minus K_{ex}) differed between soil groups in the order clays >> tills > sands (Figure 1a in Paper I). The ability of 2 M HCl to solubilise K varied between soil textural groups. This extraction ability was calculated in terms of an extractability ratio, K_{HCl}/K_{totXRF}. In the sands, the extractability was 1-3%, in the tills 3-8%, and in the clays 11-17% (Paper I). Reported data on K_{HCl} and K_{tot} in three typical Swedish soils (Öborn *et al.* 2001) from textural groups similar to those in Paper I show corresponding levels of extractability by HCl of 3-16%.

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[5] Swedish indices for K_{ex} (Roman numbers) and K_{HCl} (Arabic numbers) status for agricultural soils: I, 1 = very low; II, 2 = low; III, 3 = moderate; IV, 4 = high; and V, 5 = very high (SJV 2006).

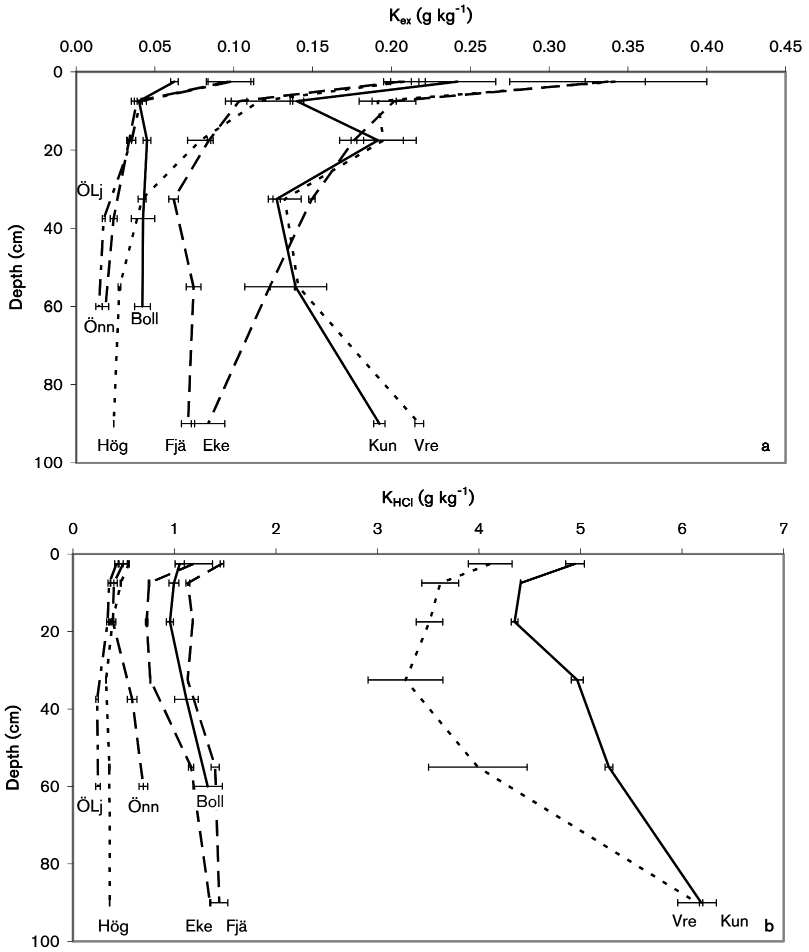

Figure 11. Concentrations of a) exchangeable K (K_{ex}) and b) HCl-extractable K (K_{HCl}) in eight soil profiles in Sweden. For Fjä, Eke, Hög, Vre, Kun data is from plots with replacement fertilisation n=2; for Önn, Boll n=6, and for ÖLj n=11. Error bars represent ± 1 standard error of the means.

Relation to mineralogy

In Paper I, K_{HCl} was shown to be significantly correlated ($R^2 = 0.96$, S.E. 0.32, $p<0.001$) with the amount of K present in dioctahedral phyllosilicates (dioct phyllo) (Figure 4 in Paper I). The correlation coefficients were almost equally good when using only K in illitic dioctahedral phyllosilicates (illitic dioct) as the independent variable. In contrast, K in mixed layer dioctahedral phyllosilicates (ML dioct) alone was not significantly correlated with K_{HCl}. Using clay content as the independent variable resulted in a decrease in the explained variance and an increase in the standard error of the estimate.

The regression (Figure 4 in Paper I) indicated that HCl removed 12% of $K_{dioct\ phyllo}$ from sands and tills and 21% from clays. The group of clay soils had a positive intercept ($p<0.05$), which indicated a contribution of K from source(s) other than dioctahedral phyllosilicates in these soils.

There was no correlation between K_{HCl} and $K_{K\text{-}feldspar}$, suggesting that dissolution of feldspar did not contribute any significant amount of K, although a small contribution cannot be completely excluded. A more likely explanation, however, is a contribution of K from trioctahedral mica. As mentioned in the section on mineralogical budgeting above, the method used in Paper I did not detect any significant amounts of biotite in the soils. However, there was up to 6% of biotite or other trioctahedral micas present in the Swedish clay soils, as the later assessment by full pattern fitting revealed (Figure 8). This would have contributed up to 5.6 g K kg^{-1}, more than adequate to explain the positive intercept of only 1 g kg^{-1}. In addition, the multivariate analysis in Paper I, where the two variates Fe_{tot} and Mg_{tot} were located very close to K_{HCl} in the loading plot (Figure 5 in Paper I), suggested a contribution of K from a trioctahedral phase. Alternatively, the loading plot could also support an interpretation that the dioctahedral phyllosilicates that released K were rich in Fe, which would be in line with the general view that dioctahedral phyllosilicates are not affected to any significant degree by acids such as HCl (Hayashi & Oinuma 1964; Carroll & Starkey 1971), unless they are Fe-rich (MacEwan & Wilson 1980). However, the latter interpretation would not explain the significant intercept in the regression between K_{HCl} and K in dioct phyllo. The details are hard to tease out from the quantitative mineralogical analyses alone. Since dioctahedral Fe-rich phyllosilicates may be formed as weathering products of trioctahedral micas (Fordham 1990), the K-bearing mineral phases that correlated with K_{HCl} phases may be considered as members of some sort of continuum of Fe-rich micaceous weathering products.

5.2.3 Characterisation of the HCl-soluble Fraction

In Paper III it was found that the soil K balance resulting from the interplay of fertilisation and harvesting was a driving force for both fixation and release of $K_{non\text{-}ex}$. In line with that are the results by Barre *et al.* (2008) which show that soil clay mineralogy was strongly related to soil K balance. In Paper III it was shown that the soil K balance also affected the pool of K_{HCl}, suggesting that this pool is strongly influenced by fixation and release of K_{non-ex}. Thus, it appears that acid-extractable K may contain a large component of K that, although non-exchangeable, is nonetheless a dynamic pool of K in relation to availability to crops. A thorough study by Güzel & Wilson (1978) showed that repeated extractions of soil particle size fractions with 1 M HCl had the greatest effect in the clay fraction and that the main contribution to extracted K seemed to come from a dioctahedral mica-interlayered smectitic phase, whereas a separate micaceous [muscovite] phase was only insignificantly affected by the treatment. Except for these observations and the fact that K_{HCl} seems to be related to K in phyllosilicates (Paper I), there was little direct information available on the effect of the 2 M HCl extraction on soil minerals or soil particle size fractions of a sample. The role of K-feldspars as a source of K_{HCl} in soils was also unclear. Therefore, to determine the phases that actually dissolve and release K in 2 M HCl and whether or not there are any properties in common among the dissolved phases, a detailed study (Paper IV) was carried out where the approach was to analyse the soil physically, chemically and mineralogically, before and after extraction.

Distribution of K_{HCl} among particle size fractions

Both the weight loss due to the 2 M HCl treatment and the K concentration in the extracts showed an inverse relationship between particle size and solubility (Paper IV). There was an abrupt change in extractability at 20 µm, suggesting a significant difference in mineralogy and/or surface area between the two silt fractions. The 20-60 µm silt fraction behaved similarly to the sand fraction, with low weight loss and low K_{HCl}, whereas the fine silt fraction (2-20 µm) acted more like the clay fraction. However, coarser particles than the fine silt fraction may make a significant contribution to the K status in coarse-textured soils. In Hög for instance, the >20 µm fractions together accounted for more than one-third of total K_{HCl}. Results summarised by Bertsch & Thomas (1985) also show that a substantial proportion of total K release can be attributed to the coarser size fractions; 15-56% from the silt fraction and 2-21% from the sand fraction.

Geochemistry of the dissolved soil fraction

The geochemical composition of the dissolved soil fraction deviated substantially from the composition of untreated samples (Paper IV). This indicated congruent dissolution of certain phases that were attacked selectively by the HCl and/or incongruent dissolution of mineral phases. The solubility ratio derived from the geochemical analyses suggested that the dissolved mineral phases were rich in Fe, Mg and P, and/or that these elements were selectively dissolved. There was no strong evidence for selective dissolution of interlayer K, because the concentration of K in the dissolved soil fraction was always lower than the concentration in the untreated samples. However, a solubility ratio ≤1 cannot exclude selective interlayer K dissolution of certain mineral phases. For instance, a certain phyllosilicate may have lost all its interlayer K but this may have been concealed if this mineral was present in a soil dominated by K in feldspars that were not affected by the treatment at all.

Mineralogical characterisation of K_{HCl}

The trends in mass loss caused by the HCl treatment were supported by the mineralogical analyses. Differential XRD (DXRD) showed a significant decrease in several phyllosilicate phases in the 20-2 and <2 μm fractions upon treatment with 2 M HCl (Paper IV; Figure 12). There was no significant decrease in K-feldspars in any of the samples in the quantitative analysis (Paper IV). Even at Hög, where there was a significant contribution of total K_{HCl} from the coarser size fractions (35% came from the >20 μm fractions), the extracted K was probably mostly ascribed to phyllosilicates present in these fractions (Paper IV).

The treatment had its strongest effect on several 14 and 12 Å phases, including mixed layer dioctahedral phases (ML dioct), Fe-containing dioctahedral expandable phases (Fe dioct exp) and trioctahedral expandable phases (Trioct exp) (Paper IV; Figure 12). These are all potentially K-bearing phyllosilicates. With only one exception, the phases that were identified in the random powders as Fe-containing dioctahedral expandable and trioctahedral expandable phases in the 2–20 and >2 um fractions completely dissolved in the acid. These observations were further supported by parallel orientated XRD of the clay fractions, which revealed complete collapse of most of the 14 Å phases (Paper IV). The DXRD analysis combined with the quantitative evaluation of the original diffraction patterns demonstrated that the K-bearing minerals that had decreased significantly in concentration due to the acid treatment were trioctahedral micas, including biotite, phlogopite and hydro-biotite, and a micaceous dioctahedral mixed layer phase (Table 5 in Paper IV). Muscovite was much more resistant to the treatment, and with the sole and probably disparate exception for the Hög <2 μm fraction, there was no significant difference between treated and untreated samples with respect to muscovite content (Paper IV).

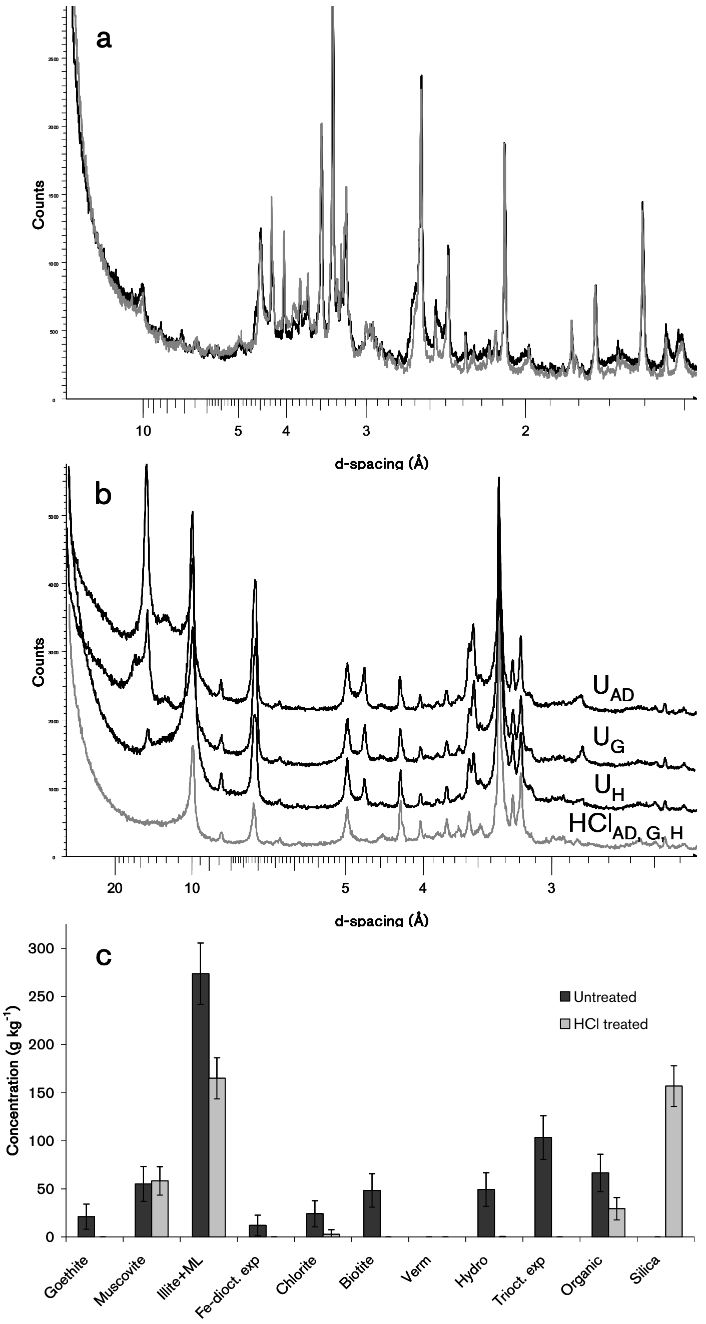

Figure 12. Effect of the 2 M HCl treatment on Kun clay fraction (<2um), 5-10 cm soil depth. Untreated (U, black) and HCl-treated (HCl, grey). a) Diffraction patterns of spray-dried random powders; b) parallel orientated: air dried (AD): glycolated (G), heated to 300°C (H) (HCl treated AD, G, H patterns looked similar); and c) histogram of identified phases.

These results are in line with the findings by Güzel & Wilson (1978) from their study on the effects of successive 1 M HCl extraction of four Turkish soils. In the clay fraction, the dissolved phase at Kun had a dominant trioctahedral character, whereas that at Fjä was mainly dioctahedral; Hög had about equally high peaks at the di- and trioctahedral positions, which was apparent from differential peaks at the non-basal 02,11 and 060 positions (Paper IV). These non-basal peaks also indicated that both the di- and trioctahedral phases that had dissolved in the acid were Fe-rich. This was revealed through the observed discrepancies between untreated and treated original patterns, especially at the 1.53 Å (Fe-rich trioctahedral) and 1.51 Å (Fe-rich dioctahedral) positions (Paper IV; Figure 12). Hence, both the visual interpretation of the differential patterns and the quantitative analysis indicated that Fe-richness seemed to be a shared property of all of the phases that were most affected by the HCl treatment. This is an interesting observation, since Fe-rich dioctahedral smectites are known to show a greater propensity to fix K relative to more aluminous dioctahedral varieties (Eberl *et al.* 1986). It has also previously been noted that the oxidation state of Fe in phyllosilicates may play an important role in relation to K fixation in soils (Stucki & Shen 1995; Stucki & Huo 1996 and references therein). Hence the fact that HCl appears to solubilise Fe-rich phyllosilicates may again be a basis for understanding why K_{HCl} is an effective indicator of long-term K status. Hence, Paper IV supports the hypothesis advanced in Paper III that K_{HCl} is a measure of the quality of the K held in the phyllosilicate pool with respect to its long- term availability to plants.

5.2.4 *Aqua regia*-extractable K

Range and extractability

Aqua regia-extractable K ranged from 0.5 to 9.2 g kg^{-1} in the Scottish soils and from 0.7 to 14 g kg^{-1} in the Swedish soils (Papers I and IV; Figure 13). This corresponds to 5-60% of K_{totXRF} in the Scottish soils, and 4–45% in the Swedish soils. Similarly to K_{HCl}, K_{AqReg} was generally lower in the Ap horizons than in the deepest horizons sampled. In the Swedish soils, K_{AqReg} differed between soil groups clays > tills > sands, whereas there was no relationship between K_{AqReg} and soil texture in the Scottish soils. Aqua regia solubilised 5-60% of K_{totXRF} in the Scottish soils and 4-45% in the Swedish soils. When the two data sets were combined, there were indications that the extractability (K_{AqReg}/K_{totXRF}) was negatively correlated with K in K-feldspars and positively correlated with K in Fe-phyllosilicates. Soil texture was not a satisfactory variable to explain the extractability.

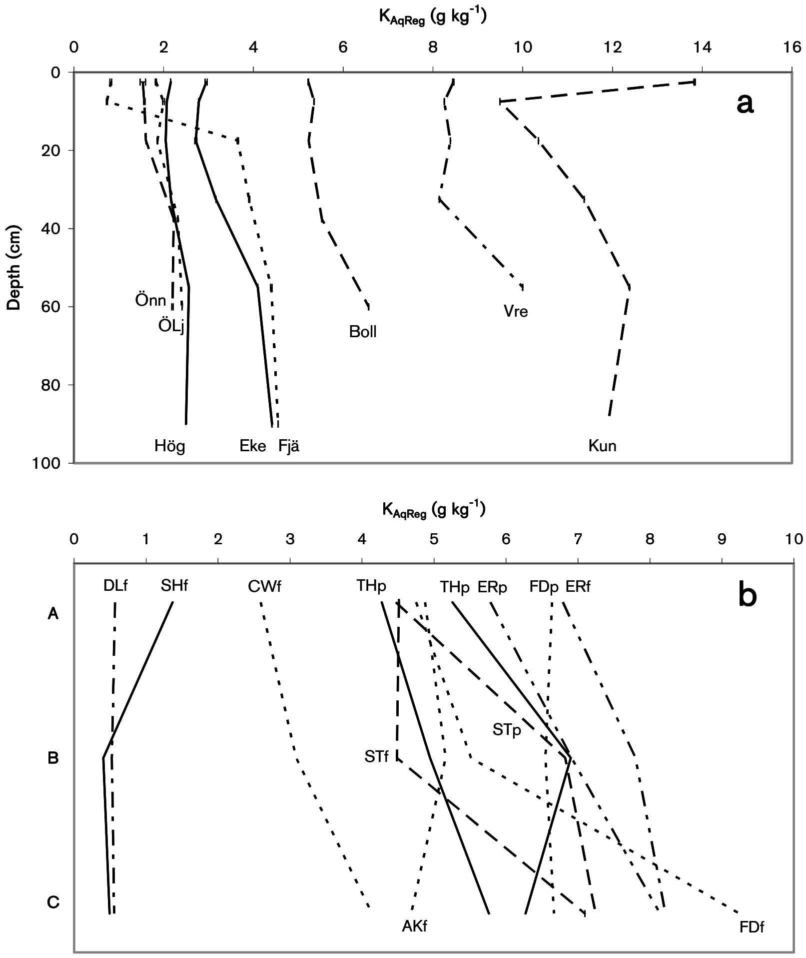

Figure 13. Concentrations of *aqua regia*-extractable K (K_{AqReg}), in a) Swedish and b) Scottish soil profiles.

Relationship to mineralogy

To further assess the relationship of K_{AqReg} to soil mineralogy and soil texture, the Swedish and Scottish data sets were combined and the mineralogical speciation based on the full pattern fitting method was applied. Among individual K-bearing phases and combinations of these, the sum of K in Fe-containing K-bearing phyllosilicates (K_{illite} + $K_{ML\ dioct}$ + $K_{biotite}$) could explain most of the variation in K_{AqReg}, (R^2 = 0.74, S.E. 1.6 g kg^{-1}, $p<0.001$; Figure

14). This observation lends further support to the hypothesis presented in the previous section, that it is Fe-rich di- or trioctahedral phases that are most affected by the acid treatment and thereby the key sources of K measured by this extraction. The slope of the regression shows that on average over all soils, *aqua regia* extracted 74% of the K in the form of Fe-phyllosilicates. Three of the four samples that fell far away from the regression line (they had high standardised residuals) belonged to the DL profile, showing a poor correlation between $K_{totXRDP}$ and K_{totXRF} (see Section 5.1.3) and hence the estimated speciation of K was not satisfactory in this particular soil.

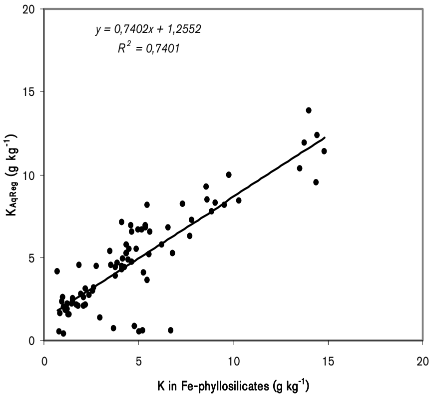

Figure 14. Linear regression of *aqua regia*-extractable K (g kg^{-1}) and K held in the form of Fe-bearing phyllosilicates (g kg^{-1}) in soils from eight Swedish and twelve Scottish sites and different soil depths.

The regression with K_{AqReg} including all soils had a positive intercept ($p<0.001$), indicating a dissolution/contribution of K from phases other than Fe-containing phyllosilicates. Similarly to HCl, there was no relationship between K_{AqReg} and $K_{K\text{-}feldspar,}$ suggesting that K-feldspars probably only made a limited contribution to K_{AqReg}. Using clay content as the independent variable resulted in a decrease in the explained variance, $R^2=0.46$, and an increase in the standard error of the estimate to 2.3 g kg^{-1} (data not shown). This demonstrates that clay content is a poor indicator of soil K status compared with mineralogical measures.

5.3 Long-term Trends in Mixed Cropping Systems

Recent concerns about the environmental effects of N and P have led to reduced application rates of fertiliser, and this seems to have been accompanied by often undesirable reductions in K (Foy *et al.* 2002; Öborn *et al.* 2005a). In Papers II and III, the long-term effects of land management, fertiliser application rate(s) and soil properties on K dynamics in mixed cropping systems were investigated. The main emphasis was on the ley herbage component of the crop rotations as it accounted for the greatest off-take of K.

5.3.1 Ley Herbage Yield and K Concentrations

Data from the three long-term field trials in southern Sweden (Paper II), including both conventional (Conv) and organic (Org) mixed cropping systems, showed no significant change in ley herbage yield over the 18 experimental years studied (Figure 15a). This excluded increased yields as a possible explanation for the significant decrease in herbage K concentration observed in both the Conv and Org systems and at all three sites (Figure 15b). For more recent years, the fitted regression lines were close to 2% K for all sites and systems except for the Conv system at Önn, where they were around 3%. Based on the existing 2.0-3.0% recommendation for optimal herbage K concentrations (Bergmann 1992), it can be argued that the most recent years provided a better fodder quality compared with the start of the experiment, when K concentrations were higher than recommended. However, there was no indication of a stabilisation of the decreasing trend in herbage K, and if the concentration continues to fall and reaches critical levels (1.2-1.6 for young temperate grasses and 1.0-2.3% for white clover (Whitehead 2000), there will be a risk of increased susceptibility of the crop to pathogens, herbivorous insects, drought and frost damage (Beringer & Nothdurft 1985; Marschner 1995; Whitehead 2000; Amtmann *et al.* 2008). The short-term decrease in herbage K concentration over the growing season suggested that the K_{ex} pool did not recover between herbage cuts (Paper II). By the time of the following season, however, K_{ex} in the soil could have been replenished to some extent due to release of previously non-exchangeable K. This highlights the importance of applications of K to each cut, a common practice in conventional production, rather than a single application to the ley crop (Paper II).

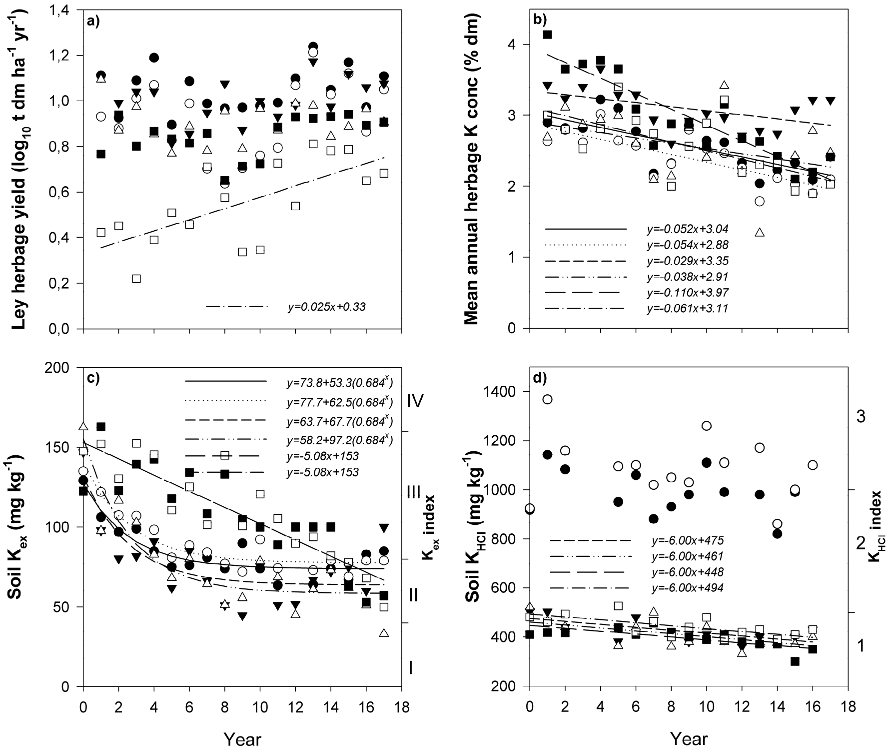

Figure 15. Observed and fitted relationship of ley crop and surface soil variables over the 18 experimental years, in conventional (Conv) and organic (Org) systems at the three sites. Linear trend lines are only shown when significant (slope $\neq 0$, $p<0.05$). a) Ley herbage yield, $R^2=0.57$, S.E.=0.14; b) mean annual herbage K concentrations, $R^2=0.52$, S.E.=0.37; c) soil exchangeable K (K_{ex}) Boll and Önn $R^2=0.75$, S.E.=12 (exponential), ÖLj $R^2=0.78$, S.E.=14 (linear); d) soil HCl-extractable K (K_{HCl}) (mg kg^{-1}), ÖLj and Önn $R^2=0.48$, S.E.=35. ● —— Boll Conv, ○ ········ Boll Org, ▼ ----- Önn Conv, Δ – · · – · · – Önn Org, ■ – – – ÖLj Conv, and □ – · – · – ÖLj Org.

Results presented by Andersson *et al.* (2007) for the same long-term field experiments as studied in Paper III (Fjä, Eke, Hög, Vre and Kun), showed a general trend of increasing ley herbage yields at all sites over the 40-year experimental period. The K (and P) fertilisation treatment had no significant effect on the herbage yield, indicating that it was probably the overall productivity of the sites that increased over time, possibly due to more effective management practices, and to the fact that K (and/or P) did not generally limit growth even at zero K (and P) applications (treatment A) (Andersson *et al.* 2007). However, similarly to Paper II (Figure 15b and c), Andersson *et al.* (2007) reported that herbage K concentrations, rather than total biomass yield, were sensitive to different K_{ex} levels.

5.3.2 K_{ex} and K_{HCl}

In both Conv and Org systems at all sites of the field trials (Paper II), the surface soil K_{ex} concentration decreased significantly over the 18 years. At Boll and Önn, the decrease was rapid during the initial part of the experiment, after which K_{ex} stabilised at a plateau (Figure 15c). At ÖLj the decrease was continuous during the whole course of the experiment. In all cases, the decrease represented a fall from Class III to II on the five-level scale used within the Swedish advisory system.

In the unfertilised plots (treatment A) of all the sites studied in Paper III, there was also a trend of decreasing surface soil K_{ex} over the 30 years studied (Table 3 in Paper III). In the plots fertilised with replacement K (treatment B), some of the soils still showed a decrease, whereas others showed an increase or no change in K_{ex} (Paper III).

Previous research has suggested that soils reach a limit for K_{ex} below which the K ions on the exchange complex are more strongly bound and therefore less available for crop uptake (Reitemeier 1951; Sinclair 1979b; Ghorayshi & Lotse 1986b). Askegaard & Eriksen (2002) observed that the critical level of K_{ex} for yield response to K fertiliser application in a barley/pea system appeared to be lower than the present minimum level of K_{ex} in their soil, which was about 40 mg kg^{-1}; although the K concentration in the crop increased significantly. Results from Paper II seem to agree with those of Askegaard & Eriksen (2002); K_{ex} stabilised at a minimum level of around 60-80 mg kg^{-1} and crop K concentrations decreased, but there was no effect on the yield (Figure 15a and c). The plateau suggests that K_{ex} was replenished by fertiliser K, subsoil K and/or K released from soil mineral weathering. The continuous decrease at ÖLj, on the other hand, indicated that the K_{ex} pool was not replenished at a sufficient rate to support the crop uptake.

The levels of K_{HCl} and the observed time trends in this parameter could partly explain some of the trends in K_{ex}. At both ÖLj and Önn, the K_{HCl} status was very low (K_{HCl} Class 1). A significant decrease in ${}_{corr}K_{HCl}$ at these sites (Paper II, data not shown), confirmed a contribution of K from the $K_{non\text{-}ex}$ pool, although it did not seem to be sufficient to keep K_{ex} on a steady level at ÖLj. At Bollerup, with the finer-textured soil, the K_{HCl} status was better than at Önn and ÖLj (Class 2/3) and no significant change over the experimental period was observed (Figure 15d). Although K_{ex} was most likely replenished from this relatively larger K pool, the contribution of K_{HCl} to K_{ex} may well be hidden in the large variations in the former parameter (Paper II).

At the other five sites, Hög and Vre were the only soils that had a significant decreases in K_{ex} in the A treatment. Somewhat puzzlingly, however, they were opposites in terms of K_{HCl} status. The loamy sand Hög, had very low K_{HCl} status (Class 1), and K_{ex} reached values as low as 25 and 60 mg kg^{-1} in treatment A and B, respectively (data not shown). These values are similar to those reported as representing the 'limiting' concentration for crop uptake in loamy sands to sandy loams, which ranged from 24 to 46 mg kg^{-1} (Sinclair 1979b). The silty clay Vre had a very good K_{HCl} status (Class 4–5), but still showed a significant decrease in $K_{ex..}$ In this soil, K_{ex} never reached below 150 g kg^{-1}, which is in range with the critical values of up to 144 g kg^{-1} reported for clay loams (Ghorayshi & Lotse 1986b).

5.4 K Field Balances Including K Release and Relation to Soil K Pools

In Papers II and III, field K balances were calculated and combined with long-term trends in soil K and with chemically and mineralogically defined soil K pools. This enabled the potential K delivery capacity of the soils to be assessed and provided an opportunity to address the sustainability of the current systems with respect to continued K supply.

5.4.1 Field K Balances

Data from all crops grown in 2002 showed that among the individual crops in the rotations, the ley herbage accounted for the largest outputs, 45-75% of the total crop off-take in the rotation (Paper II). Other crops with large K off-take were potato and sugar beet. Crop K concentrations at individual cuts varied significantly among sites and years and among cuts within the same year (Paper II). This demonstrated the potential risks of erratic estimates of crop K off-take if standard crop K concentrations are used in budget calculations. This was also highlighted in a study on nutrient budgets by Watson *et al.* (2002), where both actual and standard crop K concentrations were used and compared. The mean annual field K balances for the 18 experimental years of Paper II showed that the crop off-take was much larger than the inputs, resulting in negative field balances at all sites. Depending on site, the balance varied from -21 to -60 kg K ha^{-1} yr^{-1} in the conventional system and from -22 to -75 kg K ha^{-1} yr^{-1} in the organic system, This indicates that management systems relied to some extent on K from soil reserves (Paper II). In Paper III, on the other hand, the average soil K balance varied between sites but was more affected by fertiliser application rates, which were intentionally varied between treatments to provide both positive and negative soil K balances (Table 3 in Paper III).

The treatments applied to the plots in Paper III revealed clear differences between the soils in terms of K dynamics. Fjä, Vre, and Kun formed a group with little or no significant change in K_{ex} as a result of K imbalance, probably due to strong buffering by weathering and fixation (Figure 3 in Paper III). Eke and Hög, on the other hand, were more sensitive to imbalance in this respect (Paper III). In the two most buffering soils, Kun and Fjä, the treatment had very different effects on the yields. Fjä had a significant yield response due to the K (and P) fertilisation, indicating that there were few other site factors that seemed to limit the growth potential (Andersson *et al.* 2007). At Kun, on the other hand, K_{non-ex} seemed to compensate for the different levels of K applications and there were probably other sites factors that limited growth. Climate could be one of them.

5.4.2 Potassium Fluxes and Relation to Total Deficit and Soil K Pools

The total deficit of K (Eq. 3) over the experimental period at Boll, Önn and ÖLj, *i.e.* the K off-take not replenished by mineral fertiliser or slurry, ranged from 390 kg ha^{-1} (18 $years)^{-1}$ in both systems at ÖLj to 1350 kg ha^{-1} (18 $years)^{-1}$ in the Org system at Boll (Table 4 in Paper II). For the non-K fertilised plots (treatment A) at the five sites in Paper III, the total deficit for the 30 years ranged from 2040 to 750 kg ha^{-1}. In all cases, the deficit was larger than the detected decline in soil pools of $K_{ex.}$, indicating uptake of K_{non-ex} and/or a contribution from subsoil root uptake (Haak 1981; Kuhlmann 1990; Witter & Johansson 2001). The root distribution obtained from the root study carried out at the sites suggested that the conditions for nutrient uptake from the subsoil were favourable in the clay soils at Vre and Kun, less favourable in the till soils at Boll, Fjä and Eke and restricted in the sands at Önn, ÖLj and Hög (Papers II and III; Supplementary Data). In the cropping system trials, the K release/weathering rate, *i.e.* the change in K_{non-ex}, defined as the total deficit minus the change in K_{ex} (Eq. 4), was estimated at 50-60, 35-45, and 7-8 kg ha^{-1} yr^{-1} at Boll, Önn and ÖLj, respectively (Table 7). Of this, the decrease in ${}_{corr}K_{HCl}$ constituted approx. 15% at Önn and up to 75% at ÖLj. For the non-K fertilised plots at Fjä, Eke, Vre and Kun, the K weathering rate was 40-65 kg ha^{-1} yr^{-1}, whereas it was only 8 kg ha^{-1} at Hög (Paper III; Table 7). Hence, all soils delivered K from the soil reserve. It is worth mentioning, however, that there is no evidence within the present experiments that the maximum K delivery capacity of the soils has been reached.

Table 7a. *Changes in K over the experimental periods, b) surface soil reserves of chemically and mineralogically defined soil K pools, and c) duration of present K pools* $_{corr}K_{HCl}$ *and* K_{phyllo}*, calculated from the K pool sizes and current release rates of* $K_{non\text{-}ex}$*; all data refer to soils from eight experimental sites in Sweden*

	Boll		Önn		ÖLj		Fjä	Eke	Hög	Vre	Kun
	Con	Org	Con	Org	Con	Org	Non-K fertilised (treatment A)				
a) Changes (kg ha^{-1} yr^{-1})											
Mean annual deficit	60	75	56	55	21	22	68	54	25	58	48
Components											
Decrease in K_{ex} [a]	11	13	13	19	14	14	3	3	18	18	3
$_{cor}K_{HCl}$ [b]	n.d.	n.d.	6	6	5	5	n.a.	n.a.	n.a.	n.a.	n.a.
$K_{non\text{-}ex}$ [c]	49	62	43	36	7	8	65	51	8	40	45
b) K reserves surface soils (0-25 cm, kg ha^{-1})											
K_{ex}	163	187	196	137	134	144	195	211	105	601	451
$_{corr}K_{HCl}$	3110	3760	1540	1140	810	1010	4790	2140	1330	13200	14500
K_{phyllo}	29500		10900		11600		25200	13100	11200	39900	57700
c) Duration of present pool (years)											
$_{corr}K_{HCl}$	63	61	36	32	110	130	74	42	170	330	320
K_{phyllo}	600	480	250	300	1600	1500	390	260	1400	1000	1300

K_{ex} = exchangeable K, K_{HCl} = 2 M HCl-extractable K, $_{corr}K_{HCl}$ = K_{HCl} minus K_{ex}, K_{phyllo} = K in phyllosilicates, Conv = conventional, Org = organic.

[a] Measured changes in K_{ex} in the soil (0-25 cm at Boll, Önn, ÖLj; 0-60 cm at Fjä, Eke, Hög, Vre, Kun).

[b] Measured changes in $_{corr}K_{HCl}$ in the soil (0-25 cm).

[c] Calculated from field K balances (Eq. 4).

The above results are in line with those of other studies (Gholston & Dale Hoover 1948; Becket & Clement 1973; Ghorayshi & Lotse 1986b; Tributh *et al.* 1987; Badraoui *et al.* 1992; Hinsinger & Jaillard 1993; Schneider 1997; Wang *et al.* 2000a; Rupa *et al.* 2001; Øgaard & Krogstad 2005), which have demonstrated crop uptake of initially non-exchangeable K. Data from Papers II and III suggest that the K release was somehow related to the pool of ${}_{\mathrm{corr}}K_{\mathrm{HCl}}$, either to the absolute pool size (Paper II, data not shown), or to the ratio of ${}_{\mathrm{corr}}K_{\mathrm{HCl}}$ to total phyllosilicate K (Figure 6 in Paper III). Considering present day release rates of K, driven by the net K output from the fields studied under the current climate and management, the present ${}_{\mathrm{corr}}K_{\mathrm{HCl}}$ pool would hypothetically last for 30-300 year at the sites included in Paper II (insufficiently fertilised) and Paper III (non-K fertilised) (Table 7). If instead the whole pool of K in phyllosilicates were considered, of which ${}_{\mathrm{corr}}K_{\mathrm{HCl}}$ clearly is a component (Papers I and IV), the K reserve would last for 250-1600 years. However, under other climatic conditions (Holmqvist *et al.* 2003) and oher management strategies (Paper III), the weathering rates would change, which would affect how long the soil K reserves would last. Furthermore, if the crops have the potential to utilise subsoil K reserves, as the results from Papers II and III suggest, then calculated duration times of the K reserves will be longer than those presented in Table 7. Finally, although ${}_{\mathrm{corr}}K_{\mathrm{HCl}}$ is a dynamic pool that is not exhausted until the least soluble K-bearing mineral has dissolved, the kinetics governing the replenishment rates from different mineral phases will ultimately limit K delivery from soil reserves (section 3.4.1-2).

This way of presenting the size of K reserve pool(s) in relation to management, or more specifically to field K balance, can be an effective basis for discussions and assessments of long-term sustainability of cropping systems. The relatively short times calculated for some of the soils in this thesis in combination with the observed decrease in crop K concentrations emphasise the need for more attention to soil K status and the significance of quantifying flows of soil K in agricultural systems.

5.5 Ranking Scottish Soils - Potential Long-term K supply

Paper III concluded that management can impose a stronger effect on K release rates than inherent soil properties. However, within groups of soils under a similar type of management and especially in systems with low input of external K, the parent material has a significant influence on the K balance (Papers II and III). In Paper V, one of the aims was to evaluate the effect of soil parent material on K status and potential long-term K delivery capacity in a wide range of Scottish soils. The main emphasis was on soils under an improved grassland management system, one of the dominant types of land use in Scotland and in the EU as a whole. Furthermore, long-term sustainability of soil K in grass production systems has been identified as a potential concern (Öborn *et al.* 2005a; Paper II).

5.5.1 Ranking

Both the total K concentration and the mineralogical speciation of K varied considerably among carefully selected soils from different soil associations (Figures 8 and 9). Concentrations of *aqua regia*-extractable K clearly varied among the soils (Figure 13b), which also was demonstrated by data from the National Soil Inventory of Scotland (Figure 16). Based on the quantified soil K reserves, the soils were divided into four groups (I-IV) as regards their assumed potential long-term capacity to deliver K to plants (Table 8).

Group IV

Soils with large pools of K_{AqReg} (>15 000 kg K_{AqReg} ha^{-1}) and with a significant proportion of their K in the form of illite and biotite (Figure 8) were given the highest ranking (IV) (Table 8), since K in these two mineral forms is generally more readily available to plants than K in muscovite (Oenema *et al.* 1975). Two soils fell into this category: ER_F and TH_f, developed on greywackes and shales (ER_f) and flagstones (TH_f). The flagstone soil TH_f also had the highest concentration of K in the form of K-feldspar of all soils. However, this form of K did not seem to contribute to K_{AqReg} and, in the presence of K_{phyllo}, is possibly a less important source of K to plants (Rasmussen 1972).

Group III

The soils ranked as intermediate (III) in terms of potential K release had significant pools of K_{phyllo} but intermediate pools of K_{AqReg} (11 000-13 000 kg K_{AqReg} ha^{-1}) (Table 8). The group included three sandy loams: AK_f, ST_f (both schists), and FD_f (slates and phyllites). The low clay content (6-8%) in all three soils suggests that a significant proportion of the K must be allocated into coarser fractions, which is likely to result in a lower potential K weathering rate compared with more clay-rich soils. The K_{phyllo} pool in the ST_f soil was almost entirely made up of muscovite (Figure 8), a mineral phase that requires very low K concentration in the soil solution to release K (*e.g.*, Wilson 2004). Thus in addition to the low clay content, the mineralogical speciation of K could be the reason for the lower concentrations of K_{AqReg}, and probably also a lower K release rate, in these soils compared to the soils with the higher ranking (Paper V).

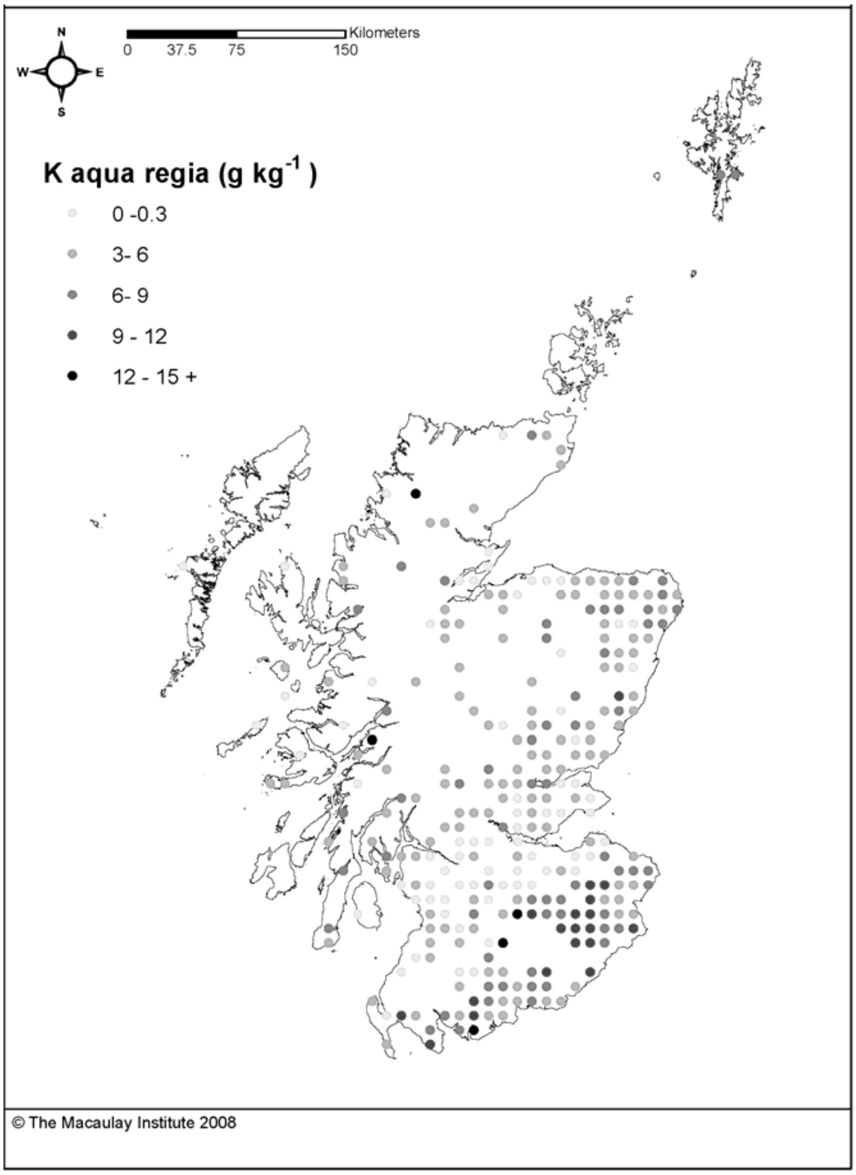

Figure 16. Levels of *aqua regia*-extractable K in Ap horizons in Scottish agricultural soils. Data from the National Soils Inventory of Scotland (NSIS) (Towers *et al.* 2006).

Table 8. *Surface soil (0-25 cm) reserves (kg ha^{-1}) of aqua regia-extractable K, K in phyllosilicates and K in feldspars; classes of K delivery capacity*[a] *and precence of roots in the subsoil*[b] *in freely drained soils from eight Scottish soil associations (SA)*

SA	K reserves in surface soil (0-25 cm, kg ha^{-1})			K delivery capacity[a]	Access to subsoil K[b]
	K_{AqReg}	K_{phyllo}	$K_{K\text{-}feldspar}$		
STf	12100	47500	7990	III	+
AKf	12700	32900	29400	III	++
CWf	7390	12200	43100	II	++
THf	15900	30800	75100	IV	+/++
ERf	20700	33900	11900	IV	++
FDf	10700	30200	8100	III	+
SHf	3450	9670	36400	I	+++
DLf	1650	15200	27300	I	+++

[a] Classes of K delivery capacity: Good IV; Intermediate III; Limited II; Poor I.

[b] Precence of roots in the subsoil: High +++; Intermediate ++; Low +.

Group II

The CW_f soil was ranked as Group II. It had a lower K_{AqReg} (7 000 kg ha^{-1}) and much lower K_{phyllo} compared with Group III (Table 8). The texture of the CW_f soil was very coarse (Table 4) and the parent material was granitic, with K allocated into K-feldspar, muscovite and biotite (Figure 8). The presence of the latter may be the main advantage of this soil in terms of K delivery capacity.

Group I

The lowest ranking group (I) included both of the soils developed on volcanic rocks (SH_f on intermediate lava and DL_f on basalts). They had only small reserves of K_{AqReg} in the Ap-horizon, 3 500 and 1 700 kg ha^{-1}, respectively (Table 8). SH_f had also very small K_{phyllo} pools.

5.5.2 Potential Long-term K Delivery Capacity

As mentioned above, weathering studies in agricultural soils are scarce, and the methods applied to estimate them vary considerably. In the work by Sinclair (1979a) the K supplying capacity of pairs of cultivated Scottish soils of low and satisfactory K status was investigated in intensive grass cropping glasshouse experiments. The weathering rates obtained were poorly correlated with the K status, *i.e.* initial level of K_{ex}, of the soils but depended on the soil parent material (Sinclair 1979a). The author concluded by grouping and ranking the soils based on their capacity to release initially non-exchangeable K. The two Strichen and the two Carpington soils formed a group of 'Good releasers'. The two Countesswells soils and the Insch soil of 'satisfactory K status' were ranked as 'Moderate' releasers. Finally, the two Foudland soils and the 'low status' Insch soil were classed as 'Poor releasers' (Sinclair 1979a). Goulding & Loveland (1986) classified soils according the size of their mica content and their capacity to release K to a Ca saturated exchange resin. They concluded that soil series could be used as a basis for mapping the K reserves in England and Wales. In the modelling study by Holmqvist (2003) of Scottish, Swedish and Norwegian soils the soils could be divided into three groups. A Countesswells soil and two other coarse textured soil had weathering rates of 3 kg K ha^{-1} yr^{-1}; two intermediates textured till soils delivered approx. 20 kg K ha^{-1} yr^{-1} and three clay soil, including Kungsängen (as in Paper III) had estimated weathering rates of 60-80 kg K ha^{-1} yr^{-1}. For the Swedish soils in Paper III the estimates ranged from 8-65 kg K ha^{-1} yr^{-1}. In a 30-year grass rotation experiment, the same Countesswells soil as in Holmqvist *et al.* (2003) delivered 35 kg K ha^{-1} yr^{-1} when no or low doses of K fertiliser were applied (Öborn *et al.* 2008). The main obstacle to comparing the cited references among themselves as well as with the ranking of the soils in Paper V, is the lack of shared variables or comparable units among the studies. Nonetheless, the combination of textures, geochemistry (K_{tot}, K_{AqReg}) and mineralogy (K_{phyllo}) of the Scottish soil studied in Paper V indicate that they cover a broader range of parent material than any of the other studies cited and hence, their weathering rates would be expected to be more variable as well. Furthermore, by establishing that measures such as *aqua regia*-extractable K can be translated into a mineralogical perspective on K delivery capacity there is now an opportunity for future work to clarify the range of regional variation that should be considered when looking to the long term.

6 General Discussion and Conclusions

Simple and relevant tools to estimate soil K reserves are becoming increasingly important for the development and management of sustainable cropping systems. By combining quantitative mineralogical methods with a novel mineralogical budgeting approach (based on assumed elemental composition of minerals) this thesis demonstrates a means of quantitatively determining the apportionment of soil reserve K into its different mineralogical forms. The K speciation is shown to be highly variable between soils, which under low or balanced K input conditions could explain a large part of the variation in the capacity of soils to release K to the crop. In a wider context, the mineralogical budgeting approach can easily be extended to other soil types and climatic regions than those studied here. It also has applications in relation to dynamic modelling of soil K release and K crop uptake, where the speciation of K is one of the key inputs.

The mineralogical speciation of the bulk soil combined with the differential analysis of particle size fractions also provided information that could be used to deepen the understanding of some commonly used operational measures of soil K status. The K extracted by 2 M HCl and by *aqua regia* from soils developed on a wide range of parent materials in the southern boreal and northern temperate regions is shown to be derived principally from phyllosilicates. In the soils studied, 2 M HCl and *aqua regia* solubilised 1-17% and 4-60% of total K, respectively, depending on soil type and mineralogy. More specifically, most of this K was derived from Fe-bearing di- and trioctahedral phyllosilicates. The Fe-richness, which characterised the soil fraction dissolved by 2 M HCl, could possibly explain previous empirical observations that the K_{HCl} is a predictor of K uptake in crops, since Fe-containing phyllosilicates are often more soluble than those containing aluminium. They are also expected to respond to redox cycles, which consequently may be relevant to K dynamics in soils. The differential study also revealed that most of the extracted K originated from the clay and fine silt fractions. Nevertheless, the coarser fractions contributed significantly to total K_{HCl} in a coarse-textured soil, demonstrating the significance of considering the non-clay fractions in the assessment of soil K status of some soils. Hence, the work increases our understanding of two common soil extraction methods and has direct applications from the perspective of potential plant available reserves of K, both in terms of routine assessment of agricultural soils and for the re-interpretation of existing environmental and geochemical soil data. Accordingly, the study lends support to the recent introduction of K_{HCl} in the Swedish national soil monitoring scheme.

The long-term field experiments used in this thesis enabled the analysis of long-term effects of different fertilisation treatments and management options on the K status in mixed cropping systems. The main emphasis was on the ley component, as it accounted for the greatest off-take of K. The response to different fertiliser treatments of the various components of the field K balance varied significantly among soils, demonstrating the importance of accounting for site-specific properties when a management scheme is designed for individual cropping systems and fields. For example, one of the clay soils had a very strong buffering capacity and showed hardly any response to varying K (P) fertiliser treatments, whereas others were highly responsive. This resulted in large variations in yields among treatments for some of the soils. In both conventional and organic cropping systems representative of their type in Sweden in terms of management practices, negative field K balances of on average 20-70 kg ha^{-1} yr^{-1} were observed over an 18-year period, indicating reliance on a soil K delivery. This was confirmed by accompanying long-term declines in both available (K_{ex}) and reserve (K_{HCl}) soil K. The trend was also reflected in crop K concentrations in the corresponding cropping systems.

The long time-series available from both the cropping system trials and soil fertility experiments were also very valuable in the studies on K release and weathering, as these are slow soil processes in temperate and boreal climatic regions. Even though weathering under field conditions can be detected within a short time frame of a few years, its quantitative importance would be far more difficult to determine without long-term data. By analysing both crop and soil it was possible to assess the potential K delivery capacity of the soil and to address the sustainability of the current systems with respect to continued K supply. In the cropping system trials, K release rates were estimated at 35-60 kg ha^{-1} yr^{-1} in the two (sandy) loams and at 7-8 kg ha^{-1} yr^{-1} in the (loamy) sand. In the soil fertility experiments where K release and fixation were studied, K weathering rates were 40-65 kg ha^{-1} yr^{-1}

in (silty) clays and (sandy) loams in the plots that were non-K fertilised. The coarse-textured soil (loamy sand), on the other hand, had a weathering rate of 8 kg ha^{-1}, which is clearly insufficient for an agricultural system with little or no external input of K. It is noteworthy that the $_{corr}$HCl-extractable soil pools would have to be completely replenished within 30-100 years in the cropping system experiments and between 40 and 300 years in the soil fertility experiments to compensate for the net K output from the systems at the field scale. Hence, even in a fairly short-term perspective, the sustainability of current management practices in the cropping system experiment is highly questionable in terms of K supply. In the soil fertility experiments, on the other hand, the wide span in K delivery capacity and size of the K reserve pool clearly demonstrate that one of the soils would be able to sustain present crop uptake without the application of any K fertilisers, whereas for the others an external input of K would be necessary to make full use of the yield potential of the sites.

7 Recommendations and Future Perspectives

The practical application of the investigations presented in this thesis should be to increase the ability to evaluate the potential long-term K supply of agricultural soils that represent a wide range of parent materials. The results clearly show that the soils investigated vary significantly in their estimated K release rates and that this is due to the mineralogical composition of the soil as well as to the site specific field K balance. It was demonstrated that K_{HCl} represents a dynamic pool that responds rapidly to changes in the field K balance and that this dynamic K primarily originates from clay minerals/phyllosilicates. Hence, this study provides information that has direct practical application that could be used within the agricultural advisory service. As regards K_{HCl}, I suggest that this variable should be analysed with a high frequency on request by farmers, since this fraction of reserve K proved to be much more sensitive to management practices than previously thought. K_{HCl} should ideally be monitored on the same regular basis as K_{ex}, *i.e.* every 10 years, to capture significant changes in K_{HCl} such as those observed at some of the sites in this study within a fairly short time frame (<20 years). Furthermore, to enable monitoring of the non-exchangeable fraction of K_{HCl}, which is the part that reflects the size of the long-term available K reserve, K_{ex} (*i.e.* K-AL) should be subtracted from the K_{HCl} value ($={}_{corr}K_{HCl}$) before the data are interpreted. This is especially important in soils where the ratio between K_{ex} and K_{HCl} is high (>0.05), as any trends in ${}_{corr}K_{HCl}$ may be hidden by the K_{ex} values. A significant decrease in ${}_{corr}K_{HCl}$ implies that long-term K supply from the soil cannot be sustained and that the present management system would need to be revised.

As regards K fertiliser recommendations, the results indicate that ley crops benefit from small but frequent doses of K fertiliser (mineral fertiliser and/or manure). Ideally K fertiliser should be applied after each cut. A large root uptake of K by grass species early in the season may otherwise result in considerable variations in crop K concentration between individual cuts.

This thesis also highlights areas needing further investigation to generate results that are more widely applicable to agricultural areas with similar climate, soils and land use. Although the soils selected in the present study cover a wide range of parent materials, i.e. soil texture and mineralogy, and represent sites with different yield capacity, analyses of a larger number of systematically selected soil profiles would be required to obtain regional representativeness. A pilot study in line with this suggested approach was carried out in this thesis for Scottish grassland soils (Paper V), and hence the results from that study could be used as a starting point for future work in Sweden. The first step would be to complement the eight soil profiles described in this thesis (located in the provinces of Skåne, Östergötland and Uppland), with a number of soil profiles representing each of the eight agricultural production areas in Sweden. By using a statistical approach, the comprehensive dataset from the Swedish Environmental Monitoring of Agricultural Soils and Crops could be used to identify representative soil profiles. Quantitative mineralogical analysis and K_{HCl} determination should be carried out on these soils in order to extend the Swedish mineralogical data set presented in this thesis to cover a wider range of soils. By applying the mineralogical budgeting approach, the distribution of total-K into K-feldspar and phyllosilicates could subsequently be calculated. The relationship between K_{HCl} and phyllosilicate K (reserve K) (Paper I) could be adjusted for certain geographical regions/soil types. To have reliable models (relationships) for each region for the relationship between K_{HCl} and K in phyllosilicates, would provide information on how long-term the K_{HCl} pool is, *i.e.*, what capacity the soil has to refill the K_{HCl} pool. If K_{HCl} constitutes a large portion of K_{phyllo}, the soil (probably) has a limited capacity to replenish the K_{HCl} pool and *vice versa.* Hence, if used together with local and current K_{HCl} data, the regional models would give a good indication of the size, properties and dynamics of the K reserve and could be added to the 'Guidelines for Fertiliser Use and Liming' (SJV).

To optimise the use of information on reserve K in soil, it should be evaluated in relation to corresponding field K balance. At present, many farmers are taking an active part in the environmental task of monitoring and optimising N and P fertiliser use, by providing input data for N and P balance calculations. Potassium could easily be added to this scheme, which would help to prevent non-sustainable management of the soil K reserve. The information could serve as a basis for planning optimal use of different soils, *e.g.* in choice of crops, crop rotations and management practices. As shown in this thesis, ley crops are particularly likely to exhaust soil K reserves, and in particular low-input cropping systems appear to risk to suffer from K shortage due to insufficient fertiliser supply. However, certain soils have demonstrated a high inherent soil K delivery capacity, making these soils suitable for different types of agricultural production systems, while other soil types have shown to be more dependent on K input. In conclusion, modest or no use of K fertiliser places a significant demand on the K storage of the soil. Depending on soil mineralogy, this can either be acceptable or become very problematic. Therefore, the K delivering capacity ought to be considered in the management of agricultural soils.

One final philosophical note: it should be remembered that agriculture in its present shape has a relatively short history in relation to the time it has taken the soils in Northern Europe to develop and form as a result of soil forming processes. If this soil resource is to be well sustained for the future use of mankind, we must continue to improve our understanding of the pressures that we put on the soil and the consequences this might have for generations to come. Potassium delivery and cycling is a comparatively small but still important part of this picture.

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Thanks a lot Allan Lilly, Willie Towers and Colin Campbell for giving me access to and helping me use the impressive Scottish Soils Database and adjacent National Soils Archive. Your archive is a national treasure.

For highly appreciated statistical advice I want to acknowledge all the helpful staff at BioSS and especially Betty Duff and Jackie Potts.

The maps included in this thesis were produced by Mark Jones (Scotland) and Jan Eriksson (Sweden), for which I owe you my thanks. For help with soil analyses I want to thank Gunilla Lundberg, Gunilla Hallberg, Lise Gustafson and Kent Anderson as well as Allan Lundqvist for help with the ley herbage. Thank you, Lolita Almquist, for sorting out a lot of administrative issues.

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I want thank Ragnar Person at SLU and ITS at Macaulay for prompt technical support. Ragnar, your immediate response and help above and beyond the call of duty has been invaluable.

Although I spent most of my PhD years away from the Department of Soil and Environment, I truly want to thank all my colleagues and friends at SLU Ultuna. To everyone involved in undergraduate education, I am grateful to you for having given me the foundation and the inspiration to carry out this PhD. Thank you.

Last but not the least; I thank my family for your unconditional love and support. You are always there by my side and help out when needed.

Till min älskade make och vän, Ignacio, till Arvid, vår son;
Tack för att ni finns. Les amo.

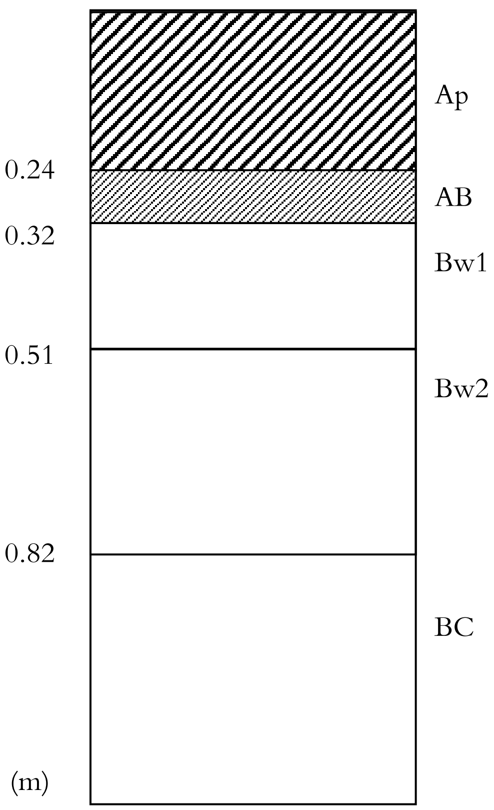
Supplementary data

Content

Soil profile descriptions

For the Swedish soils, soil profile description was carried out according to Guidelines for soil description (FAO 1990) and soil classification according to WRB (FAO 2001) and to Soil Taxonomy (Soil Survey Staff 2003). For the Scottish soils, soil profile descriptions were collated from the Scottish Soils Database and soil classification was done according to WRB (IUSS Working Group WRB 2007). Photos of the Swedish profiles are found on page 10.

Bollerup: Orthoeutric Cambisol / Dystric Eutrudept



Ap, 0-0.24 m. Clear wavy boundary; (10 YR 3/4) moist. (10 YR 6/3) dry; loam; common subrounded weathered to strongly weathered fine gravel to stones (mica, granite, schist): weak to moderate medium granular; slightly hard, friable, slightly sticky, very plastic; very few fine and medium channels, low porosity; few very fine and fine roots; non-calcareous

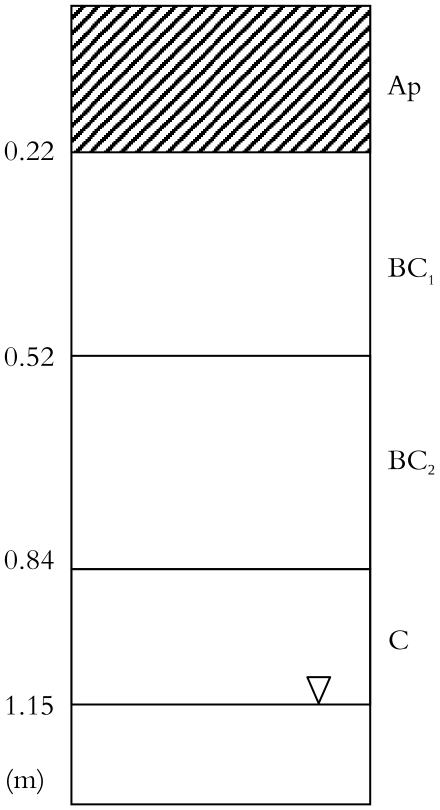
AB, 0.24-0.32 m. Abrupt smooth boundary; (10 YR 4/4) moist and (10 YR 5/4) dry; loam; common subrounded weathered to strongly weathered fine gravel to stones (mica, granite, schist); moderate fine to coarse subangular and angular blocky; slightly hard, firm, slightly sticky, very plastic; very few fine and medium channels, low porosity; very few very fine and fine roots; non-calcareous

Bw1, 0.32-0.51 m. Gradual irregular boundary; (10 YR 5/4-5/6) moist (10 YR 6/4) dry; loam; very few fine distinct mottles, diffuse boundary (10YR 5/8) wet; common subrounded weathered to strongly weathered fine gravel to stones (mica, granite, schist); moderate coarse and very coarse angular and subangular blocky; slightly hard, friable to firm, sticky, very plastic; few medium channels, low porosity; very few very fine and fine roots; non-calcareous

Bw2, 0.51-0.82 m. Clear wavy boundary; (10 Y/R 4/6) moist and (10 YR 6/4) dry; loam; very few fine distinct mottles, diffuse boundary (7.5YR 5/8) wet; common subrounded weathered to strongly weathered fine gravel to stones (mica, granite, schist); moderate coarse and very coarse angular and subangular blocky; slightly hard to hard, friable, sticky, very plastic; few medium channels, low porosity; very few very fine roots; non-calcareous

BC, 0.82-1.20 m. (10 YR 4/6) moist; few fine distinct mottles, sharp boundary (5YR 5/8) wet; loam; common subrounded and flat weathered to strongly weathered fine gravel to stones (mica, granite, schist); moderate coarse and very coarse angular and subangular blocky; hard to very hard, friable, sticky, very plastic; very few medium channels, very low porosity; no roots; non-calcareous

Önnestad: Hypereutric Regosol / Typic Udorthent



Ap, 0-0.22 m. Abrupt irregular boundary (20-35 cm); (10 YR 2/3) moist. (10 YR 4/3) dry; sandy loam; very few subrounded slightly weathered stones: weak to moderate coarse subangular blocky; soft, very friable, slightly sticky, slightly plastic; very few to few very fine to medium channels, low porosity; few very fine to medium roots; common biological features; non-calcareous

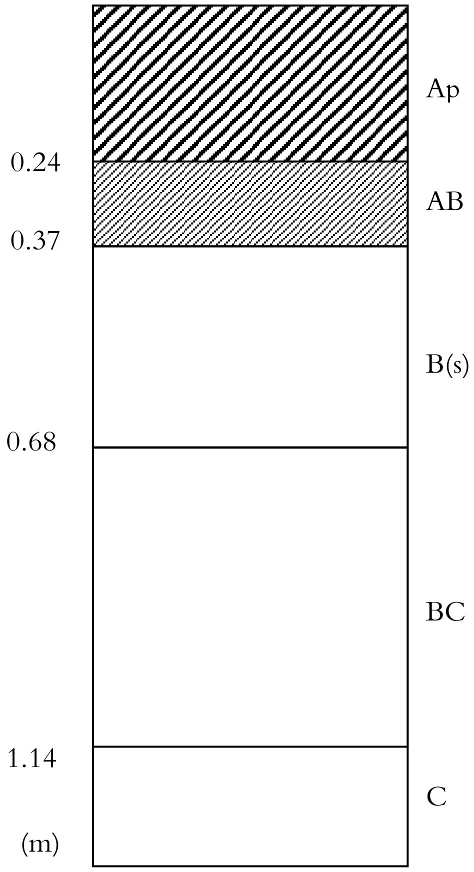
BC$_1$, 0.22-0.52 m. Diffuse smooth boundary; (5 Y 6/3) moist and (5 Y 7/3) dry; common medium distinct diffuse mottles (10 YR 7/8); sandy loam; very few subangular slightly weathered stones; weak coarse angular and subangular blocky; soft very friable slightly sticky not plastic; medium very few channels, very low porosity; very few fine roots; few biological features; non-calcareous (0.22-45 cm) strongly calcareous (0.45-0.52 m)

BC$_2$, 0.52-0.84 m. Abrupt wavy boundary; (5 Y 6/3) moist (5Y 7/2) dry; few medium distinct diffuse mottles (10 YR 6/8) wet (7,5 YR 6/8) dry; sandy loam; weak coarse angular and subangular blocky; soft very friable slightly sticky not plastic; medium very few channels, very low porosity; very few fine roots; few biological features; strongly calcareous

C, 0.84 < m. (2.5 Y 5/3) moist; very few fine distinct diffuse mottles (10 YR 6/8) wet, sandy loam; weak coarse angular blocky; soft very friable slightly sticky not plastic; medium very few channels, very low porosity; very few fine roots; strongly calcareous

∇= Ground water table

Östra Lungby: Orthidystric Regosol /Typic Udorthent



Ap, 0-0.24 m. Clear wavy boundary (0.12-0.26 m); (10 YR 2/3) moist. 10 YR 4/4 dry; loam; common subrounded slightly weathered medium and coarse gravel (granite, gneiss): moderate coarse subangular blocky; soft, very friable, sticky, non plastic; very few fine channels; few very fine and fine roots; few biological features; non-calcareous

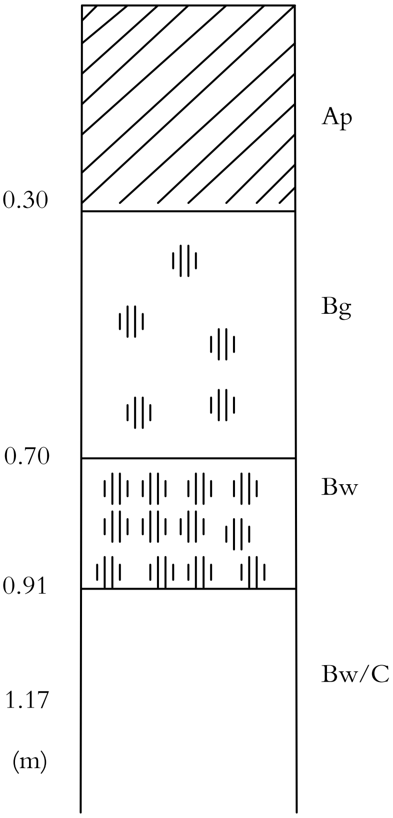
AB, 0.24-0.37 m. Gradual wavy boundary; (7.5 YR 4/6) moist and (10 YR 5/6) dry; sandy loam; many subrounded slightly weathered medium and coarse gravel (granite, gneiss); very weak medium granular; soft, very friable, non sticky, non plastic; very few medium and coarse channels; very few very fine and fine roots; few biological features; non-calcareous

B(s), 0.37-0.68 m. Gradual irregular boundary; (7.5 YR 5/8) moist (7.5 YR 5/8) dry; loamy sand; common subrounded slightly weathered medium and coarse gravel (granite, gneiss); single grain; loose, loose, non sticky, non plastic; very few very fine and fine roots; non-calcareous

BC, 0.68-1.14 m. Gradual wavy boundary; (10 Y/R 5/6) moist and (7.5 YR 6/4) dry; loamy sand; few subrounded slightly weathered medium and coarse gravel (granite, gneiss); single grain; loose, loose, non sticky, non plastic; non-calcareous

C, 1.14+ m. (7.5 YR 5/4) moist and (5 YR 7/2) dry; loamy sand; few subrounded slightly weathered medium and coarse gravel (granite, gneiss); single grain; loose, loose, non sticky, non plastic; non-calcareous

Fjärdingslöv: Haplic Phaeozem / Oxyaquic Hapludoll



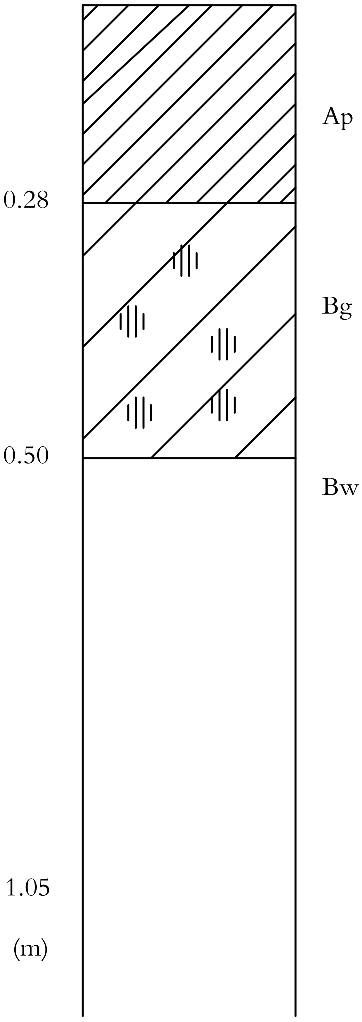
Ap, 0 - 0.30 m. Clear wavy boundary; brownish black (2.5 Y 3/3) moist and (10 YR 4/3) dry; sandy loam; very few, fine and medium subrounded gravel (flint), fresh or slightly weathered; weak to moderate medium and coarse subangular blocky; slightly sticky, slightly plastic, hard dry, friable moist; very few very fine and fine roots; few to common earthworm channels; slightly to moderately calcareous.

Bg, 0.30 – 0.70 m. Gradual wavy boundary; olive yellow (5 Y 6/3) moist; common medium distinct diffuse yellowish brown (10 YR 5/8) mottles; sandy loam; very few coarse angular gravel (flint), fresh or slightly weathered; weak to moderate medium granular; slightly sticky, non to slightly plastic, slightly hard dry, very friable to friable moist; no voids; very few very fine and fine roots; no biological features; strongly calcareous.

Bw, 0.70 – 0.91 m. Clear wavy boundary; yellowish brown (10 YR 5/8) moist; sandy loam; many subrounded stones (flint, granite), fresh to strongly weathered; weak medium granular; slightly sticky, non-plastic, loose dry, very friable moist; no voids; no roots; no biological features; strongly calcareous.

Bw/C, 0.91 – 1.17+ m. Olive brown (2.5 Y 4/6) moist; sandy loam; many subrounded stones (flint, granite), fresh to strongly weathered; weak medium granular; slightly sticky, slightly plastic, (loose dry, very friable moist); no voids; no roots; no biological features; strongly calcareous.

Ekebo: Haplic Phaeozem / Oxyaquic Hapludoll



Ap, 0 - 0.28 m. Abrupt smooth boundary; brownish black (10 YR 2/3) moist and dull yellowish brown (10 YR 5/3) dry; loam; few coarse subrounded to rounded gravel (flint, granite), fresh or slightly weathered; weak very coarse subangular blocky; sticky, slightly plastic, slightly hard dry, friable moist; few fine and medium roots; common earthworm channels; non-calcareous.

Bg, 0.28 – 0.50 m. Clear irregular boundary; brown (10 YR 6/4) moist and brown (10 YR 6/4) dry; abundant coarse distinct clear bright brown (7.5 YR 5/8) mottles; loam; many subrounded stones and boulders (granite), fresh or weathered; moderate very coarse subangular blocky; very sticky, slightly plastic, slightly hard dry, friable moist; very few fine roots; common earthworm channels; non-calcareous.

Bw, 0.50 – 1.05+ m. Reddish brown (5 YR 4/6) moist or bright brown (7.5 YR 5/8) moist; abundant medium distinct diffuse bright brown (7.5 YR 5/8) mottles and common fine (channel formed) distinct clear dull yellow orange (10 YR 7/3) mottles; sandy loam; common subrounded coarse gravel and stones (granite), fresh to strongly weathered; very weak medium granular; non-sticky, very plastic, slightly hard dry, firm moist; no voids; no roots; few earthworm channels and few charcoal (approx 0.90 m of depth); non-calcareous.

Högåsa: Arenic Umbrisol / Humic Dystrocryept

Brief general description of the soil

Fine sand deposit with a low clay content (generally <5%). A heterogeneous horizon of a more clayey matrix containing coarse sand, some gravel and (partially strongly weathered) stones found in the lower subsoil (C1 horizon). Conspicuous mottling in middle subsoil (C/B horizon). Root development mainly restricted to the Ap horizon (90% of the roots in top 30 cm).

Soil horizon description

Ap, 0–34 cm, abrupt smooth boundary; dark brown (10YR 3/4) moist, dull yellowish brown (10YR 5/3) dry; sandy loam; single grain structure; soft dry, very friable moist, non-sticky and non plastic wet; few medium channels.

Bw, 34–65 cm, gradual wavy boundary; yellowish brown (10YR 5/8) moist, dull yellowish orange (10YR 7/4) dry, a few old root channels of same colour as Ap; loamy sand; very few to few rounded fresh granite stones, one boulder in pit; single grain structure; soft dry, very friable moist, non-sticky and non-plastic wet; very few fine channels.

C/Bw, 65–96 cm, abrupt broken boundary; dull yellowish orange (10YR 6/4) moist, dull yellowish orange (10YR 7/3) dry; abundant prominent mottles of colour similar to Bw horizon, containing numerous very fine black soft accumulations; loamy sand; few rounded and subrounded fresh granite stones and boulders; single grain structure; soft dry, very friable moist, non-sticky and non-plastic wet; very few medium channels; few irregular reddish brown soft segregations and soft nodules.

C1, 96–117 cm, clear wavy boundary; reddish brown (5YR 4/8) moist, dull orange (5YR 6/4) dry; texture on average sandy loam but highly variable with few approx 5 cm big clods of 40% clay or more; common subrounded fresh to strongly weathered granite stones and strongly weathered black micaceous stones; weak medium subangular blocky; sticky and plastic wet; few medium and many very fine to fine channels.

C2, 117 cm+; colour as C/Bw; few subrounded to strongly weathered granite stones and strongly weathered black micaceous stones; single grain structure; soft dry, very friable moist, non-sticky and slightly plastic wet; very few fine channels.

Vreta Kloster: Haplic Phaeozem / Oxyaquic Hapludoll

Brief general description of the soil

Very heavy clay with a rather compact topsoil. Although no open cracks were observable in the *subsoil* (B horizons), the structure appeared rather well developed here, with 30% of the roots below the ploughed layer; root channels and shiny pedfaces were observed even in the 2Bw horizon. Clay warves were observed in the latter horizon, indicating a glacial origin of at least this part of the profile.

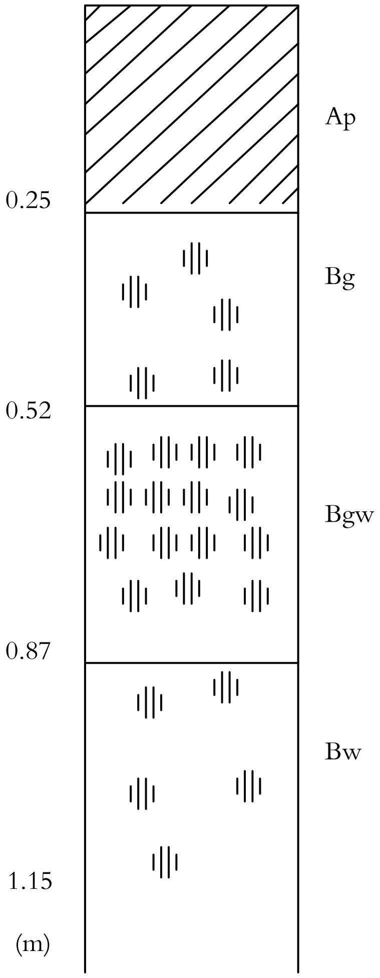
Soil horizon description

Ap, 0–33 cm, clear smooth boundary; grayish brown (7.5YR 4/2) moist, grayish brown (7.5YR 6/2) dry; clay; very few rounded fresh granite stones; moderate fine and medium blocky; hard dry, firm moist, slightly sticky and very plastick wet; common fine and medium channels.

Bw, 33–67 cm, gradual boundary; brown (7.5YR 4/4) moist; clay; very few rounded fresh granite stones; strong very fine angular blocky; firm moist, slightly sticky to sticky and very plastic wet; many very fine, very few fine and common medium channels; no carbonates; no reducing conditions (by potassium ferricyanate).

2Bw, 67 to >120 cm; ped interiors dull brown (7.5YR 5/4), faces brownish gray (7.5YR6/1), moist; clay; very few rounded fresh granite stones; strong medium to coarse prismatic falling apart along warves to medium platy; firm moist, slightly sticky and very plastic wet; many very fine and very few fine channels; distinct clay cutans on vertical and horizontal ped faces; no carbonates; no reducing conditions.

Kungsängen: Gleyic Cambisol / Typic Haplaquept

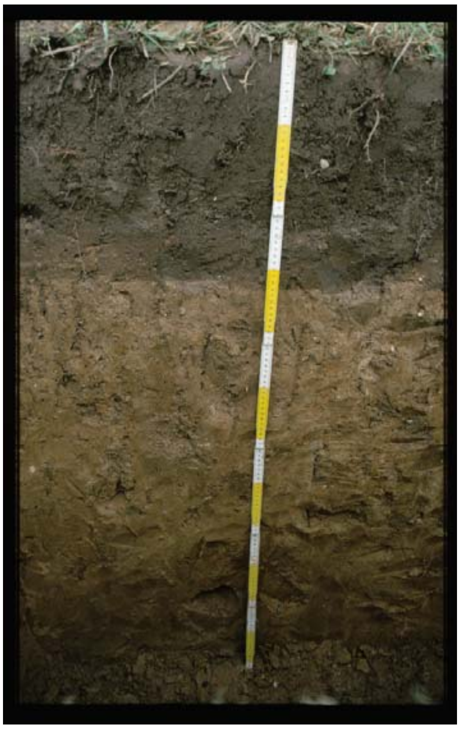


Ap, 0 - 0.25 m. Clear wavy boundary; brownish black (2.5 Y 3/3) moist and greyish yellow (2.5 Y 6/2) dry; silty clay; no rock fragments; strong, coarse angular and subangular blocky; hard dry, very firm moist, sticky, plastic; very low, very few fine channels; very few very fine and fine roots; few to common earthworm channels; no calcareous.

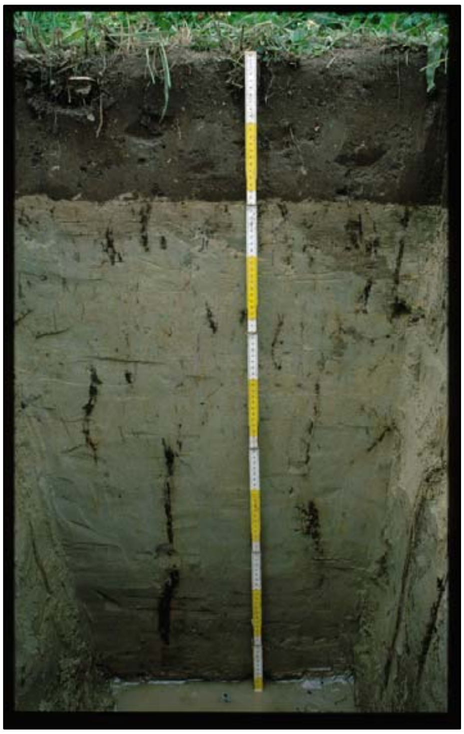
Bg, 0.25 – 0.52 m. Gradual irregular boundary; greyish olive (5 Y 4/2) moist and light grey (5 Y 7/2) dry; common fine prominent sharp orange (7.5 YR 6/8) mottles; silty clay; no rock fragments; strong coarse subangular blocky; hard dry, very firm moist, sticky, very plastic; very low, very few fine channels; very few very fine and fine roots; no biological features; no calcareous.

Bgw, 0.52 – 0.87 m. Clear wavy boundary; grey (10 Y 4/1) moist and light grey (10 Y 7/1) dry; abundant fine prominent sharp bright brown (7.5 YR 5/6) mottles; silty clay; no rock fragments; moderate fine and medium subangular blocky; hard dry, firm moist, sticky, plastic; very low, very few fine channels; no roots; no biological features; no calcareous.

Bw, 0.87 – 1.15+ m. olive grey (10 Y 4/2) moist and light grey (10 Y 7/1) dry; common fine to medium distinct clear yellowish brown (10 YR 5/6) mottles; silty clay; no rock fragments; strong very coarse angular blocky; (strong dry), firm moist, sticky, very plastic; very low, very few fine channels; no roots; no biological features; no calcareous.



Bollerup



Önnestad

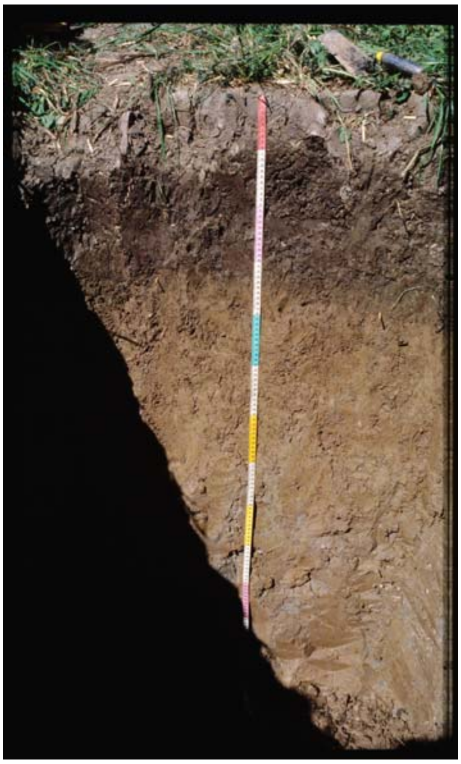
Östra Ljungby

Fjärdingslöv

Photo: Y. Andrist Rangel

Ekebo

Högåsa



Vreta Kloster

Kungsängen

Photo: Y. Andrist Rangel (Eke, Kun) and S. Andersson (Hög, Vre)

Strichen, freely drained: Fragic Mollic Dystric Cambisol

Profile name: MIDDLETON
Grid reference: NO243561
Soil series: Strichen

Ap: 0-23 cm; dark yellowish brown, 10YR 3/4 loam; no mottles; weak fine subangular blocky structure; moist; friable; common very fine fibrous primary and few fine fibrous secondary roots; few medium subangular primary and few large subangular secondary undifferentiated schist stones; clear smooth boundary.

Bs: 23-40 cm; yellowish brown, 10YR 5/8; fine sandy loam; no mottles; weak medium subangular blocky structure; moist; friable; few fine fibrous primary roots; common small subangular undifferentiated schist stones; clear irregular boundary.

Bx: 40-61 cm; yellowish brown, 10YR 5/6; fine sandy loam; no mottles; weak medium platy structure; moist; very firm; no roots; common small subangular undifferentiated schist stones; clear irregular boundary.

C: 61-100 cm; yellowish brown, 10YR 5/6; fine sandy loam; no mottles; very weak medium platy structure tending to massive structure; moist; firm; no roots; many large angular undifferentiated schist primary and few very large angular secondary stones; gradual irregular boundary.

R: 100+ cm; no mottles; no roots; undifferentiated schist.

Strichen, poorly drained: Epigleyic Mollic Eutric Stagnosol

Profile name: AUCKLUNKART
Grid reference: NJ350500
Soil series: Anniegathel

Ap: 0-32 cm; very dark grey, 5 Y 3/1; fine loam; common fine distinct clear strong brown (7.5YR 5/6) mottles; moderate coarse angular blocky structure tending to moderate fine angular blocky structure; moist; slightly sticky; firm; common fine fibrous roots; common small subrounded undifferentiated schist primary and few large subrounded undifferentiated gneiss secondary stones; clear smooth boundary.

Bg: 32-48 cm; brown, 7.5YR 5/2 sandy clay loam; many medium distinct clear strong brown (7.5YR 5/6) mottles; massive structure tending to moderate medium angular blocky structure; moist; slightly sticky; few fine fibrous roots; common small subrounded primary and few medium subrounded secondary undifferentiated schist stones; gradual wavy boundary.

Cg: 48-85 cm; dark brown, 7.5YR 4/4 clay loam; common fine distinct clear strong brown (7.5YR 5/6) mottles; massive structure tending to moderate very coarse prismatic structure; moist; plastic, sticky; firm; no roots; common small subrounded undifferentiated schist stones and few medium subrounded undifferentiated schist stones.

Arkaig, freely drained: Dystric Mollic Cambisol

Profile name: GLENBORRODALE
Grid reference: NM587629
Soil series: Aberscross

Ap: 0-14 cm; dark brown, 7.5YR 3/4; fine sandy loam; no mottles; moderate fine subangular blocky structure; moist; friable; abundant fine fibrous roots; common large angular undifferentiated gneiss primary and common large subangular undifferentiated gneiss secondary stones; gradual smooth boundary.

Bs: 14-40 cm; dark yellowish brown, 10YR 4/4; sandy loam; no mottles; moderate coarse subangular blocky structure; moist; friable; many fine fibrous roots; many large subangular undifferentiated gneiss stones; clear smooth boundary.

Bh: 40-56 cm; dark yellowish brown, 10YR 3/4; sandy loam; no mottles; weak medium platy structure; moist; friable; common fine fibrous roots; common large subangular undifferentiated gneiss stones; sharp smooth boundary.

C: 56-100 cm; light yellowish brown, 10YR 6/4; sand; no mottles; weak medium platy structure; moist; firm; few fine fibrous roots; many large subangular undifferentiated gneiss stones.

Countesswells freely drained: Umbric Podzol

Profile name: LOCHUISGE
Grid reference: NM791557
Soil series: Countesswells

Ap: 0-20 cm; very dark greyish brown, 10YR 3/2; coarse loamy sand; no mottles; moderate very fine subangular blocky structure; moist; friable; many very fine fibrous roots; common small subangular granite stones; sharp smooth boundary.

E: 20-31 cm; dark reddish brown, 5YR 3/4; coarse sand; no mottles; moderate very fine subangular blocky structure; moist; friable; common very fine fibrous roots; common small subangular granite stones; sharp wavy boundary.

Bs: 31-98 cm; yellowish red, 5YR 4/6; coarse loamy sand; no mottles; weak very fine subangular blocky structure; moist; friable; few very fine fibrous roots; very abundant very large subangular granite stones; sharp wavy boundary.

BC: 98-120 cm; yellowish brown, 10YR 5/8; coarse sand; no mottles; strong coarse platy structure; moist; friable; no roots; very abundant very large subangular granite stones.

Thurso, freely drained: Fragic Leptic Dystric Cambisol

Profile name: HILL OF SHEBSTER 2
Grid reference: ND014642
Soil series: Bilbster

Ap: 0-30 cm; dark grey brown, 10YR 4/2; sandy loam; no mottles; strong fine subangular blocky structure; moist; firm; many roots; few platy; sharp boundary.

Bx: 30-50 cm; yellowish brown, 10YR 5/4 loam; no mottles; moderate medium angular blocky structure; moist; very firm; strongly indurated; few roots; many small platy primary and common large platy secondary stones; sharp boundary.

CR: 50-85 cm; shattered, hard flaggy sandstones with some very dark brown (10YR 3/2) loamy interstitial material; many roots.

Thurso, poorly drained: Epigleyic Mollic Eutric Stagnosol

Profile name: QUOYBRAE
Grid reference: ND2670058110
Soil series: Thurso

Apg: 0-30 cm; dark brown, 10YR 3/3; sandy silt loam; common fine prominent clear dark brown (7.5YR 4/4) mottles; strong medium subangular blocky structure tending to strong fine subangular blocky structure; very moist; friable; common very fine fibrous primary and few fine fibrous secondary roots; few small subangular stones; clear smooth boundary.

ABg: 30-37 cm; dark brown, 10YR 3/3; sandy loam; few very fine distinct sharp strong brown (7.5YR 4/6) mottles; weak coarse platy structure tending to weak medium subangular blocky structure; moist; friable; few very fine fibrous primary roots; few medium subangular primary and few small subangular secondary stones; clear smooth boundary.

Bg: 37-68 cm; dark yellowish brown, 10YR 4/4; sandy clay loam; many medium prominent clear dark yellowish brown (10YR 4/6) mottles; weak very coarse subangular blocky structure tending to weak very coarse platy structure; moist; firm; no roots; common large subangular primary and few small subangular secondary stones; clear smooth boundary.

Cg: 68-90 cm; brown, 10YR 5/3; sandy loam; many medium prominent clear strong brown (7.5YR 5/8) mottles; massive structure; very moist; firm; no roots; common medium subangular primary and few small subangular secondary stones.

Ettrick, freely drained: Mollic Dystric Cambisol

Profile name: SPOTTES HALL
Grid reference: NX802664
Soil series: Linhope

Ap: 0-20 cm; dark brown, 10YR 3/3; loam; no mottles; moderate fine subangular blocky structure; moist; friable; many very fine fibrous roots; common medium subrounded stones; sharp smooth boundary.

B: 20-33 cm; strong brown, 7.5YR 4/6; loam; no mottles; weak medium subangular blocky structure; very moist; friable; common fine fibrous roots; common small subrounded primary and few medium subangular secondary stones; clear wavy boundary.

C1: 33-66 cm; dark brown, 7.5YR 4/4; sandy loam; no mottles; massive structure; very moist; firm; few very fine fibrous roots; abundant large angular stones; gradual wavy boundary.

C2: 66-95 cm; dark brown, 7.5YR 4/4; sandy loam; no mottles; massive structure; wet; non-plastic, slightly sticky; no roots; very abundant large angular stones.

Ettrick, poorly drained: Mollic Eutric Gleysol

Profile name: MIDTOWN
Grid reference: NX859766
Soil series: Littleshalloch

Ap: 0-46 cm; very dark greyish brown,10YR 3/2; fine sandy loam; no mottles; moderate fine subangular blocky structure; moist; friable; many very fine fibrous primary and secondary roots; many medium subrounded primary and secondary stones; clear wavy boundary.

Bg: 46-73 cm; pale brown, 10YR 6/3; loamy sand; no mottles; massive structure; moist; friable; few very fine fibrous primary and secondary roots; common medium subrounded primary and common small subrounded secondary stones; clear irregular boundary.

BCg: 73-110 cm; brown, 10YR 5/3; sandy loam; many medium faint diffuse yellowish brown (10YR 5/6) mottles; massive structure; moist; firm; no roots; many medium subrounded primary and common small subrounded secondary stones; gradual wavy boundary.

C: 110-130 cm; brown, 7.5YR 5/4; sandy loam; common medium faint clear strong brown (7.5YR 5/6) mottles; massive structure; moist; firm; no roots; many medium subrounded primary and common small subrounded secondary stones; gradual wavy boundary.

Foudland, freely drained: Haplic Dystric Cambisol

Profile name: GLENBUCHAT
Grid reference: NJ341195
Soil series: Foudland

Ap: 0-23 cm; dark brown, 10YR 3/3; sandy silt loam; no mottles; moderate medium subangular blocky structure tending to moderate medium granular structure; slightly moist; friable; common very fine fibrous primary and few fine fibrous secondary roots; few medium subrounded primary and few small subangular secondary stones; clear wavy boundary.

Bw: 23-52 cm; yellowish brown, 10YR 5/6; fine sandy loam; no mottles; weak medium subangular blocky structure; slightly moist; very friable; few very fine fibrous roots; common small angular primary and few medium angular secondary stones; gradual smooth boundary.

C: 52-104 cm; yellowish brown, 10YR 5/4; loamy sand; no mottles; very weak coarse subangular blocky structure; slightly moist; loose; no roots; many medium angular primary and common small subangular secondary stones; sharp smooth boundary.

2C: 104-150 cm; yellowish brown, 10YR 5/6; loamy sand; no mottles; very weak coarse platy structure tending to single grain structure; slightly moist; loose; no roots; abundant large angular primary and many small angular secondary undifferentiated schist stones.

Foudland, poorly drained: Gleyic Mollic Hypereutric Stagnosol

Profile name: CLACHAN
Grid reference: NS254824
Soil series: Fisherford

Ap: 0-26 cm; dark greyish brown, 10YR 4/2; fine sandy loam; no mottles; very weak coarse subangular blocky structure; very moist; friable; many fine fibrous roots; few small subangular phyllite stones; clear smooth boundary.

Bg: 26-45 cm; olive, 5 Y 5/3; fine sandy loam; common medium distinct clear strong brown (7.5YR 5/6) mottles; massive structure; moist; friable; few fine fibrous roots; common small subangular phyllite primary and few medium subangular quartz-schist secondary stones; clear smooth boundary.

BCg: 45-120 cm; olive, 5 Y 5/4; fine sandy loam; common medium distinct clear strong brown (7.5YR 5/6) mottles; massive structure; moist; friable; no roots; common small subangular phyllite primary and few medium subangular quartz-schist secondary stones.

Sourhope, freely drained: Mollic Leptic Eutric Cambisol

Profile name: DENOON
Grid reference: NO341431
Soil series: Sourhope

Ap: 0-28 cm; dark brown, 10YR 3/3; loam; no mottles; moderate medium granular structure; moist; friable; abundant very fine fibrous roots; few small subangular andesite stones; clear irregular boundary.

B: 28-75 cm; dark yellowish brown, 10YR 4/6; loamy sand; no mottles; weak coarse subangular blocky structure; moist; friable; common very fine fibrous roots; stones; diffuse wavy boundary.

CR: 75-170 cm; dark yellowish brown, 10YR 4/6; loamy sand; no mottles; massive structure; moist; firm; few very fine fibrous roots; no stones.

Darleith, freely drained: Dystric Mollic Cambisol

Profile name: CLITH
Grid reference: NM491857
Soil series: Darleith

Ap: 0-16 cm; dark grey, 7.5YR 4/3; humose loam; no mottles; moderate fine subangular blocky structure; moist; friable; many fine fibrous roots; few medium subangular basalt stones; gradual smooth boundary.

B: 16-31 cm; dark grey, 7.5YR 4/3; loam; no mottles; moderate fine subangular blocky structure; moist; friable; many fine fibrous roots; few medium subangular basalt stones; clear smooth boundary.

BC: 31-38 cm; dark brown, 7.5YR 4/4; sandy loam; common very fine prominent sharp strong brown (7.5YR 5/8) mottles; moderate fine subangular blocky structure; moist;friable; common fine fibrous roots; no stones; sharp smooth boundary.

C: 38-60 cm; dark brown, 7.5YR 4/4; sandy loam; common very fine prominent sharp strong brown (7.5YR 5/8) mottles; moderate coarse platy structure; moist; friable; common fine fibrous roots; no stones.

Mineral phases and their assumed elemental composition as used for the normative calculations in Paper I and Paper V

Usage	Mineral phase	Elemental composition
Paper I	Quartz	SiO_2
	Calcite	$CaCO_3$
	Plagioclase	$Na_{0.8}Ca_{0.2}Al_{1.2}Si_{2.8}O_8$
	K-feldspar	$K_{0.8}Na_{0.2}AlSi_3O_8$
	Illitic dioctahedral clay[a]	$K_{0.75}Al_{1.75}Fe^{(II)}_{0.25}Al_{0.5}Si_{3.5}O_{10}(OH)_2$
	Non-illitic dioctahedral clay[b]	$Ca_{0.12}K_{0.23}(Si_{3.61}Al_{0.39})(Al_{1.55}Fe^{(III)}_{0.26}Mg_{0.23})O_{10}(HO)_2$
	Trioctahedral clay (chlorite)	$Fe(II)_{2.3}Mg_{2.3}Si_{2.6}Al_{2.8}O_{10}(OH)_8$
	Amphibole	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Paper V	Quartz	SiO_2
	Albite	$NaAlSiO_8$
	Oligoclase	$Na_{0.8}Ca_{0.2}Al_{1.2}Si_{2.8}O_8$
	Andesine	$Na_{0.6}Ca_{0.4}Al_{1.4}Si_{2.6}O_8$
	Labradorite	$Na_{0.4}Ca_{0.6}Al_{1.6}Si_{2.4}O_8$
	K-feldspar	$KAlSi_3O_8$
	Sanidine	$K_{0.75}Na_{0.25}AlSi_3O_8$
	Calcite	$CaCO_3$
	Amphibole	$Ca_2Mg_5Si_8O_{22}(OH)_2$
	Pyroxene	$Ca_{0.9}Na_{0.1}Mg_{0.9}Fe^{II}_{0.2}Al_{0.4}Ti_{0.1}Si_{1.9}O_6$
	Muscovite	$KAl_2AlSi_3O_{10}(OH)_2$
	Illitie[a]	$K_{0.75}Al_{1.75}Fe^{II}_{0.25}Al_{0.5}Si_{3.5}O_{10}(OH)_2$
	ML dioctahedral phyllosilicates[b]	$Ca_{0.12}K_{0.23}(Si_{3.61}Al_{0.39})(Al_{1.55}Fe^{III}_{0.26}Mg_{0.23})O_{10}(HO)_2$
	Montmorillonite	$Na_{0.2}Ca_{0.1}Al_2Si_4O_{10}(OH)_2(H_2O)_{10}$
	Nontronite	$Na_{0.3}Fe^{III}_2Si_3AlO_{10}(OH)_2\cdot 4(H_2O)$
	Kaolinte	$Al_2Si_2O_5(OH)_4$
	Chlorite	$Mg_{2.3}Fe^{II}_{2.3}Si_{2.6}Al_{2.8}O_{10}(OH)_8$
	Biotite	$KMg_{2.5}Fe^{II}_{0.5}AlSi_3O_{10}(OH)_2$
	Saponite	$Ca_{0.1}Na_{0.1}Mg_{2.25}Fe^{II}_{0.75}Si_3AlO_{10}(OH)_2\cdot 4(H_2O)$
	Hematite	$Fe^{III}_2O_3$
	Goethite	$Fe^{III}O(OH)$
	Ilmenite	$Fe^{II}TiO_3$

[a] Srodon and Eberl (1984)
[b] Laird *et al.* (1991)

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