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Base cations in forest soils

A pilot project to evaluate different extraction methods

Jonas Olofsson

ABSTRACT

Base cations in forest soils – a pilot project to evaluate different extraction methods

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The acidification has been a known problem in Sweden for several decades. Sulphurous compounds, spread from the British Isles and the European continent led to a decrease in the pH-value of the rain that fell over Sweden. Since the acidification was discovered in the 1960s, active measures against the sulphurous deposition have been undertaken. The sulphurous deposition has decreased by 90 %, and the problem was for some time considered under control, until recently when a new era of the acidification may have started.

Due to the increased demand of renewable energy, and Sweden's potential to use biomass instead of fossil fuels, whole tree harvesting has been more utilized. Studies indicate that the forest soils are depleted in base cations in a faster rate when whole tree harvesting is performed compared to regular stem harvesting. Mass balance calculations and simulations indicate that an increased bio uptake of base cations due to whole tree harvesting leads to an increased biological acidification. However, although many studies agree that the impact of the whole tree harvest on the base cation supply of the soils is significant, long running Swedish experiments indicate that the difference between whole tree harvesting and regular stem harvesting diminishes over time. After a 40 year period, the difference in base cation supply between whole tree harvested soils and stem harvested soils are small. The reason for this could be different processes that reallocate base cations from different pools, which are not usually studied.

The aim has been to investigate and evaluate different chemical extraction methods (Aqua Regia, HCl, EDTA, $BaCl_2$, NH_4OAc and water) capability to extract the base cations calcium, potassium, magnesium and sodium from four different Swedish forest soils and what this means for our understanding of how much base cations a soil contains.

The extractions indicated that there is a statistical significant difference between the methods ability to extract base cations. Generally Aqua Regia was the most potent method, followed by HCl, EDTA, $BaCl_2$, NH_4OAc and water in decreasing order of effectiveness to extract the base cations. Linear correlations were found between EDTA, $BaCl_2$ and NH_4OAc. The internationally widely used method NH_4OAc was considered to be at risk of underestimating the amount of base cations in the soil.

Keywords: Acidification, whole tree harvest, stem harvest, forestry, base cations, extractions, Aqua Regia, $BaCl_2$, NH_4OAc, EDTA, comparison, calcium, magnesium, potassium, sodium.

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REFERAT

Baskatjoner i skogsmark – ett pilotprojekt för att utvärdera olika bestämningsmetoder

Jonas Olofsson

Försurningsproblematiken har länge varit ett känt problem i Sverige. Svavelhaltiga föroreningar som spreds från de brittiska öarna och den europeiska kontinenten ledde till att pH-värdet i regnet som föll över Sverige sjönk. Sedan upptäckten på 60-talet har aktiva åtgärder vidtagits mot utsläppen vilket har lett till en minskning av de försurande föroreningarna med 90 %. På grund av den stora utsläppsreduktionen som skett ansågs försurningsproblematiken vara under kontroll, tills nyligen då en ny etapp av försurningen kan ha påbörjats.

På grund av den ökande efterfrågan av förnyelsebar energi, i kombination med Sveriges stora skogstillgångar, har helträdsskörd av träd blivit alltmer nyttjad. Studier visar att markens baskatjonförråd utarmas i större utsträckning av helträdsskörd, då även grenar, rötter och toppar tas om hand jämfört med vanlig stamskörd då endast stammen tas med från skogen. Massbalanssimuleringar antyder att ett ökat bioupptag av baskatjoner på grund av helträdsskörd leder till en ökad biologisk försurning. Trots att många studier är överens om helträdsskördens inverkan på markens innehåll av baskatjoner visar långliggande försök i Sverige att skillnaderna mellan uttag av hela träd och stamved minskar med tiden. Efter en period på 40 år återstår endast små skillnader mellan avverkningsmetoderna. Orsakerna till varför mätningarna och massbalansberäkningarna och simuleringarna inte stämmer överens kan vara många, t.ex. att det finns processer som kan omfördela baskatjoner från de som vanligtvis studeras.

Syftet har varit att undersöka och utvärdera olika kemiska extraktionsmetoders (Aqua Regia, HCl, EDTA, $BaCl_2$, NH_4OAc och vatten) förmåga att extrahera baskatjonerna kalcium, kalium, magnesium och natrium från fyra olika skogsjordar i Sverige och vad resultaten betyder för vår uppfattning av mängden baskatjoner i marken.

Extraktionerna visade att en statistiskt signifikant skillnad fanns mellan metodernas förmåga att extrahera de olika baskatjonerna. Generellt var Aqua Regia den metod som extraherade den största mängden baskatjoner, HCl, EDTA, $BaCl_2$, NH_4OAc och vatten följde i fallande ordning efter förmåga att extrahera baskatjonerna. Linjära korrelationer mellan EDTA, $BaCl_2$ och NH_4OAc upptäcktes. Den internationellt ofta använda metodiken för att extrahera baskatjoner, NH_4OAc, ansågs riskera att underskatta mängden baskatjoner i marken.

Nyckelord: Försurning, baskatjoner, extraktioner, Aqua Regia, $BaCl_2$, NH_4OAc, EDTA, helträdsuttag, kalcium, magnesium, kalium, natrium.

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PREFACE

This master thesis is the finishing part of the Master of Science programme in Environmental and Water Engineering at Uppsala University (UU) and the Swedish University of Agricultural Sciences (SLU). The thesis corresponds to 30 ETCS. The extractions were performed at the research lab at SLU, Uppsala and the analysis of my samples was conducted at KTH, Stockholm. My supervisors were Professor Jon Petter Gustafsson at the department of soil and environment and Associate Professor Stefan Löfgren at the department of Aquatic Sciences and Assessment, both at SLU, Uppsala. Subject reviewer has been Associate Professor Erik Karltun at the department of soil and environment, SLU.

Firstly I would like to thank my supervisor Jon Petter Gustafsson for being a great support during the course of this project. You have always answered any questions I had, big or small, which I am very grateful for. I would also like to thank my supervisor Stefan Löfgren for his help, tips, ideas and encouragement during my work.

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Sedan försurningsproblematiken upptäcktes på 1960-talet har aktiva åtgärder t.ex. politiska beslut, vidtagits för att stoppa de orsakande utsläppen. Sedan dess har de försurande föroreningarna minskat med 90 % vilket ledde till att försurningsproblematiken ansågs vara under kontroll, tills nyligen då en ny era inom försurningen kan ha inletts.

På grund av den ökande efterfrågan att använda fossilfria bränslen, i kombination med Sveriges stora skogsrikedom, har helträdsuttag blivit alltmer vanligt. Helträdsuttag innebär att man inte bara tar tillvara på stammen från trädet utan också grenarna, rötterna och topparna (GROT). GROTet kan därmed användas som biobränsle. Problemet med att även ta bort det näringsrika GROTet är att dessa då inte stannar kvar i skogen, förmultnar och återgår till skogsmarken. Träd och växter tar upp näring i form av baskatjoner, vilket är ett samlingsnamn för grundämnena kalcium, magnesium, kalium och natrium. Studier visar att det finns en stor skillnad mellan mängden baskatjoner i marken vid vanlig stamavverkning jämfört med helträdsuttag.

Baskatjoner är dels essentiella näringsämnen till träd och växter, men kan även hjälpa till i att motstå försurning. Det är således viktigt att veta hur mycket baskatjoner det finns i marken och att ha en tillräckligt hög nivå av dessa joner. Trots att många studier visar att helträdsuttag minskar mängden baskatjoner i marken snabbare än vanlig stamavverkning så visar långlivade svenska försök att skillnaderna minskar över tid. Faktiska mätningar visar att efter ca 40 år är skillnaderna i mängden baskatjoner i marken mellan helträdsuttag och stamavverkning väldigt små. Orsaken till detta kan vara flera, bland annat att det kan finnas processer som kan förflytta baskatjoner från områden i marken som vanligtvis inte studeras. Studier visar bland annat att svampars rotnätverk eventuellt kan förse träd med baskatjoner, i utbyte mot att träden förser svamparnas rötter med kol, en slags symbios mellan växter.

Syftet med examensarbetet har varit att undersöka och utvärdera olika kemiska extraktionsmetoders (Aqua Regia, HCl, EDTA, $BaCl_2$, NH_4OAc och vatten) förmåga att extrahera näring i form av baskatjonerna kalcium, kalium, magnesium och natrium från fyra olika skogsjordar i Sverige. En extraktion är en vanlig kemisk separeringsmetod där ett ämne isoleras från en lösning eller blandning. Resultaten från examensarbetet ska även bidra till uppfattningen av mängden och lokaliseringen av baskatjoner i svenska skogsmarker.

De kemiska försöken visade att det fanns en skillnad i de olika metodernas förmåga att extrahera baskatjonerna. Det fanns även klara samband mellan metoderna, vilket kan vara bra att veta vid t.ex. jämförelse av olika metoder. Dessutom visades att en av de mest använda metoderna nationellt riskerar att underskatta mängden baskatjoner i marken.

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1 INTRODUCTION

The acidification has been a known problem in Sweden for several decades. As early as 1967, a professor at the Swedish University of Agriculture Sciences (SLU), Svante Odén published an article on the subject in the Swedish newspaper Dagens Nyheter (Odén, 1967). In the article Odén displayed evidence that the pH-value of the precipitation in Europe had declined below 4.7. He suggested that the acid rain would acidify Swedish soils and watercourses with potential damage to forests and living organisms as a result. The professor argued that the acified rain was due to the burning of sulphurous fossil fuels at the European continent and the British Islands. The sulphur compounds then converted into sulphuric acid when it reached the atmosphere.

Since then, active measures against the sulphuric deposition have been undertaken. The deposition of the pollutants has decreased by 90 % (Sverige & Naturvårdsverket, 2007). Due to the great reduction of sulphur deposition, the acidity problem was for some time considered under control, until recently, when warnings have been raised that a new stage of the acidification may have started.

Due to an increased demand of renewable energy and Sweden's potential to use biomass instead of fossil fuels, whole-tree harvesting (WTH) has been more utilized (Swedish Energy Agency, 2011). Many different studies has documented that WTH has an increased loss of base cations in the forest soil versus regular stem harvesting (Feller, 2005; Thiffault *et al.*, 2011; Zetterberg *et al.*, 2013) and several results from cation mass balance calculations indicate that WTH risks cation depletion in just one or two tree generations (Sverdrup & Rosen, 1998; Akselsson *et al.*, 2007). More advanced dynamic acidification models (Aherne *et al.*, 2012; McDonnell *et al.*, 2013) support the views that an increased biological uptake due to WTH results in an increased biological acidification. Despite the seemingly agreeable results, long running empirical studies do not coincide with the model results. The studies (Walmsley *et al.*, 2009; Brandtberg & Olsson, 2012; Zetterberg *et al.*, 2013) indicate that the differences between WTH and regular stem harvesting diminishes over time. There could be several reasons why the results do not coincide, but one important component might be that the calculations and simulations do not take different processes into consideration that reallocate base cations from different pools, which are not usually studied. It is also known that todays base cation determination methods differ in their results, but the magnitudes of the differences are less studied. Not considering different reallocating processes combined with the use of less effective determination methods could lead to an underestimation of input of base cations, which do not originate from i.e. weathering, in the long term. Consequently there is a risk of exaggerating the threat from the effects of base cations on the acidification of soil and surface water in connection with forest harvest. Hence, it is very important to be able to estimate these base-cation pools correctly, and explain what chemical and biological processes that redistribute them.

1.1 AIM AND OBJECTIVES

The aim is to investigate how different extraction methods differ and correlate in their capacity to extract the base cations sodium (Na), calcium (Ca), potassium (K) and magnesium (Mg) from four different Swedish soils and what this means for our understanding of how much plant available base cations a soil contains.

Further, the aim is also to acquire knowledge concerning the quantity of these cations where they are located, what affects their location and how the different soils differ.

Finally, the aim is to give a recommendation of which of the methods that is suitable as an alternative to today's standard method and which of the methods that estimate the base cation supply properly.

1.2 FORMULATION OF QUESTIONS

What fraction of the different base cations are the different methods able to extract?
What are the differences between the methods abilities to extract base cations?
How do the different extraction methods correlate?
How big part of the total content of base cations is exchangeable with the methods?
Which of the examined locations have the greatest amount of base cations?
How does the deposition of sulphur and sea salt impact the extraction results?
What processes may contribute to the relocation of base cations in the soil system?
Which of the examined extraction methods is most suitable for podzolic soils?

1.3 DELIMITATIONS

Different limitations have been taken. The only ions analysed has been potassium (K), sodium (Na), magnesium (Mg) and calcium (Ca). Other limitations are the extractions methods used and the locations that have been investigated which are limited to six and four different ones respectively. When investigating the correlations between the methods, the focus was mainly on only three methods: NH_4OAc, $BaCl_2$ and EDTA.

2 THEORY

2.1 ACIDIFICATION

The cause of acidification is that acids are either produced in the soil, or are added from an outside source. The inflow of acids from elsewhere usually originates from human activity, and this is referred to as anthropogenic acidification. Anthropogenic acidification can be caused by either sulphuric or nitrogen deposition. It's mainly the combustion of sulphuric fossil fuels that has contributed to the acidification in Sweden. When the fossil fuels formed from different sources, thousands of years ago, anaerobic decomposition used sulphur as the oxidant. At the combustion of the sulphuric fossil fuel, sulphuric acid is released from pyrite or iron sulphide. Acidifying processes within the soil itself are carbonic acid and organic acids. Both roots and soil living organisms produce carbon dioxide (CO_2). Some of the carbon dioxide dissolves into the soil water and creates carbonic acid, equation (1).

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^- \qquad (1)$$

Even though the carbonic acid has a relatively high acidity constant, pK_a, and is regarded as a weak acid, since lower pK_a-value implies a stronger acid, it still has a great quantitative importance. However, it is only an important acidifier if pH is greater than 5.5. At lower pH-values, the carbonic acid will appear in its non-dissociated form, which does not add any free protons.

The top layer of the soil is called litter, where dead organic material is decomposed, and different organic acids are produced, equation (2).

$$RCOOH \rightleftharpoons RCOO^{-} + H^{+} \tag{2}$$

The organic acids have lower pK_a-values than the carbonic acid and hence are regarded as stronger acids. The organic acids have the ability to acidify the soil to pH 3. Swedish podzols usually have low pH due to the great production of organic acids.

Cation uptake by plants is also an acidifying process. When a plant takes up a cation, a proton is emitted for every cation charge. The main cations are Ca^{2+}, K^{+}, Mg^{2+}, Na^{+} and NH_4^{+}. Uptake of Ca^{2+} results in the return of two protons, K^{+} results in the return of one proton. The uptake of anions results in a return of one or more negatively charged ions e.g. OH^{-}, depending on the charge of the anion. Even though these processes counteract each other, there is still a net acidification because the uptake of cations is often greater than the uptake of anions. This results in a production of acid in the soil, which is why there is a seasonal variation of the pH in the soil. In a natural forest the plant uptake of cations is not an acidifying process in the long run. When the biomass is not removed from the system, the produced acidity is neutralized when the plant is decomposed. However, when the biomass is removed from the system, as it is when there is forestry or farming, there will be a net soil acidification.

2.2 NEUTRALIZATION

There are also many different processes that may neutralize the protons produced during the acidifying processes. There is silicate, carbonate, aluminium and iron weathering, cation exchange, denitrification, adsorption and desorption of sulphate. The system of proton donating processes and their counter acts are complex. To be able to get some clarity in the proton cycle within a system Van Breemen *et al.* (1984) established proton budgets. As mentioned above, many different processes can neutralize the protons produced by the plant uptake of cations. The production and consumption of protons does not necessarily occur in the same sections of the ecosystem. In podzols, the production of protons usually takes place in the forest floor, while the consumption of protons occurs further down in the profile, in the mineral soil. Hence, it is important to have appropriately defined boundaries of the studied system. This is further proven when explaining acidification by using the ides of capacity and intensity (van Breemen *et al.*, 1983). The capacity of a soil, defined as a soils weatherable minerals and amount of cation exchange sites, depends on the quantity or size of the system, while the intensity, defined as pH and thermodynamic constants, is not. By including horizons beyond the rooting zone, the soil depth of the studied system will increase and the buffer capacity of the soil will rise. Depending on the interest of the study, different boundaries might be applicable. If the aim is to study soil acidification and the effects on forestry, the rooting zone could be a suitable system while if the interest is water quality, the system should be increased to include greater depths of the soil.

2.3 BASE CATIONS

The next four parts contains brief explanations of the different base cations, their different features and their importance as a nutrient for plant growth.

2.3.1 Calcium

Calcium (Ca) is the dominating plant nutrient among the cations. It contributes to give the plant strong cellular walls, aid in the cell-division and is responsible for the activation of different enzymes (Marschner & Marschner, 2012). Among the different cation plant nutrients, Ca^{2+} usually dominates in both the soil solution and the exchangeable fraction. In podzols, the exchangeable fraction generally decreases with depth. In the deeper parts of the soil, the amount of Ca is lower due to competition from Al^{3+} and H^{+} (Eriksson, 2011). Calcium in its mineral form is the dominating store of the nutrient. Its found in different minerals like feldspar and augite, but also as calcite in lime rich soils (Eriksson, 2011).

Exchangeable Ca^{2+} plays an important role in the chemical and physiological properties of a soil. Even though deficiency effects are rare, it is important to keep the amount of exchangeable Ca^{2+} at high levels. In some areas weathering cannot cover the shortage and fertilization must be performed in order to keep the base saturation at an unchanged level (Eriksson, 2011).

The Ca^{2+} ion has a small radius and a relatively high charge, giving it a high charge to radius ratio.

2.3.2 Magnesium

Magnesium (Mg) is an essential plant nutrient that is found in the chlorophyll molecule. It participates in different synthesis processes within the plant, for instance the protein synthesis and the pH regulation of the cells. Lack of Mg usually leads to reduced growth (Marschner & Marschner, 2012). Mg is abundant in most soils and make up 10-30% of the exchangeable cations (Eriksson, 2011). Mg is increased with increased clay content of a soil and with increased Fe content of rocks. The exchangeable Mg content of a soil is usually less than the Ca content, but the amount can be similar if the source material is rich in Mg or if the soil is located near a coastal area. The sea salt contains some Mg, which is deposed over land from the sea. The majority of Mg in a soil occurs as non-exchangeable form in different minerals such as hornblende, biotite and augite (Eriksson, 2011). A plants ability to retract Mg from the soil depends on the surrounding pH and Mg^{2+} and K^{+} ratio. Field studies have shown that the uptake of Mg is decreased if the ratio between K-AL (easy soluble K) and Mg-AL (easy soluble Mg) exceeds 1.5-2.5. K-AL and Mg-AL is considered as easy soluble and plant available potassium and magnesium and are determined by the extraction with ammonium-lactate acetate. If the amount of K in the soil is great, the diminishing uptake occurs at the lower end of the interval and if the K content is low, the reduction in uptake occurs at the upper end of the interval.

2.3.3 Potassium

Potassium (K) is the plant macronutrient that is responsible for the regulation of the osmotic potential of the cells. Lack of K leads to a decreased ability to regulate the osmotic potential, which leads to an inadequate capacity to withstand cold and aridness (Marschner & Marschner, 2012). The K in a soil exists solved in the soil solution, in exchangeable form, fixed form and in mineral form (Sparks *et al.*, 1996). This and the exchangeable K is directly available for the plants, while the fixed and mineral form is not. These forms of K can, however, become available to the plants from i.e. weathering. The difference between fixed K and mineral K is the bonds. In mineral bound K, the bonds are of crystal structures while fixed K is not. Fixed K is wedged between 2:1 layers in illite. To be able to extract the K^+ ions from the 2:1 layers, an ion with similar size, such as an ammonium ion (NH_4^+) or a hydronium ion (H_3O^+) have to be used as the extraction agent. The mineral form of K represent up to 99 % of the total K storage (Sparks & Huang, 1985; Eriksson, 2011). This implies that the weathering process plays a key role in making the K available to the plants. Chemical weathering convert K from non-available, mineral form, to available forms of K that the plants can take advantage of. The weathering rate depends heavily on the specific area of the soil particles. A soil that consists of fine particles has a higher weathering rate than a soil with coarse grains. The weathering rate can increase due to acid exudates from roots. The fixed K from 2:1 layers can become available when the K^+ concentration in the soil solution reaches a critical level.

2.3.4 Sodium

Sodium (Na) is the only base cation that is not an essential element for plant growth. The concentration of Na in the soil is, however, a main factor in the management of both sodic and saline soils. A soil with high salinity, which can be caused by high Na concentrations, reduces plant growth by damaging soil colloids, promote soil swelling and by tampering with the osmotic potential. These effects hinder aeration, percolation and root penetration in the soil (Sparks *et al.*, 1996).

2.3.5 Base cation migration

Ions may wander from one zone of the soil to another. In order to keep a constant charge balance, every journey of one cation includes an anion of the same charge. The negatively charged surfaces in the soil forces the minus charged anions, such as chloride and sulphate, to migrate causing base cations, such as calcium, to follow them to keep the charge balance neutral. The mobile anions are the ones that determine the ionic flow through the soil (Reuss & Johnson, 1986). Due to the decreased deposition of sulphur, the leaching of sulphate has decreased, causing the reduction in migration of cations through the soil (Lofgren *et al.*, 2009).

2.3.6 Sea salt deposition

Sea salt deposition over land is a major factor to take into consideration. Sea salt contains negatively charged chloride ions (Cl^-), which are deposed over land from the sea. Research (Franzen, 1990) shows that when waves break, small bubbles of air are created. These bubbles burst, tossing salt sea water into the air. The seawater is then transported over land by winds and later deposited. A gradient of chloride deposition from the coast to midland occurs, where the greatest deposition is at the coast, and the lowest is at the midland. As mentioned above, Cl^- moves through the soil profiles, forcing base cations to follow. Franzen (1990) discovered a relation between the concentration of chloride in the precipitation and the distance from the west coast of Sweden, as well as other relations including wind speeds and deposition rates.

2.4 CATION EXCHANGE CAPACITY

A soils capacity to electrostatically bind cations, its cation exchange capacity (CEC) is a measurement of the total amount of ions that adsorbs to the negatively charged soil particles. It consequently corresponds to the amount of negative charges on the particle surfaces of the soil (Carter & Gregorich, 2008). CEC is usually measured by the leaching of a soil with e.g. $BaCl_2$. The goal is to force the cations of the soil into solution, by replacing them with Ba^{2+}. The sum of the extracted cations charges is the CEC, assuming that the cations from solved salts are negligible. This assumption is acceptable in most Swedish soils, since these have been exposed to leaching (Eriksson, 2011). The magnitude of the CEC is pH dependent; therefore CEC is divided into two different types of measurements. The quantity of the variable negative charges increase with increased pH. At low pH the CEC is limited because some of the variable charges are undissociated. The CEC measured at an acidic soil is called the effective CEC. The CEC can also be measured at a neutral pH, called CEC_{pH7}. The CEC_{pH7} in an acidic soil is measured by titrating the soil with a strong base until the pH reaches neutral (7.00). CEC_{pH7} is then measured as mentioned earlier.

The concept base saturation is also a central concept. This is the ratio between the sum of the base cations and CEC. In other words it describes how big part of the total amount of cations in the inner solution (CEC) that is base cations. The other part of cations (100 %-base saturation) is made up of acidic cations. Lower CEC implies that the soil is acidified.

2.5 EXTRACTION METHODS

The general extraction method used is the method of addition. The method of addition is accomplished by the addition of high concentrations of a cation that is not considered in the analysis. The cation expels the exchangeable cations from the exchange complex into the extract solution. The soils exchangeable cations are retrieved in the extract solution, where the concentration of the different cations can be analysed. The different extraction agents used in the project have various functions, which are described more in depth in the following sections. Even though a standardized extraction agent for all types of soils would be preferred, it is not possible. This is due to the diversity in soil properties and environments. Some extraction agents are suitable to use on e.g. arid soils, while others might result in an inaccurate value if used on the same soil. The different methods are based on shaking experiments, where soil and reagents are shaken for different amounts of time. The shaking times used in each of the extraction methods were all regarded of enough length to reach the thermodynamic equilibrium.

2.5.1 Ammonium acetate

The extraction with 1 N ammonium acetate (NH_4OAc), buffered to pH 7, is a widely used method. The aim of the extraction is to saturate the exchange sites in the soil with ammonium ions (NH_4^+), forcing the base cations into the solution.

This extraction agent has some drawbacks, especially concerning highly weathered, acid, soils. The buffered solution raises the pH of the soil to 7, which causes the CEC of the soil to increase compared to the CEC of the soil at its natural pH (Sparks *et al.*, 1996). Still, the method is frequently used, not only on suitable samples such as neutral and alkaline soils, but also on weathered, acid soils with variable charges (Gillman & Hallman, 1988). All topsoils and subsoils examined contain organic material and/or clay mineral, which indicate that variable charges are present. The variable charges are dependent on pH, why a buffered extraction agent might not be the prime alternative when extracting base cations. How much of an impact the increased pH has on the results is depending on the difference in pH between the soil and the extraction agent (Sparks *et al.*, 1996).

2.5.2 Barium chloride

The extraction with 0.1 M Barium chloride ($BaCl_2$) is a common extraction method that can be found in a number of different varieties. The aim is to create an excess of barium ions (Ba^{2+}), which suppress the exchangeable ions of the soil and transfer them to the solution. Ba^{2+} is a strong electrolyte and has a strong ability to compete for exchange sites. Due to these abilities, combined with its unusual presence in the soil, makes it a widely used extraction agent. By not buffering the $BaCl_2$-solution, the ability to measure the exchangeable base cations and the soils true pH is possible. This is important if the pH of the buffered solution and the pH of the soil differ a lot.

2.5.3 EDTA

Ethylenediaminetetraaceticacid (EDTA) is a chelating agent used frequently to e.g. remediate contaminated areas, or to analyse the availability of trace metals in soils. Due to EDTAs potent chelating abilities, combined with its non-selective features it works as a great extractant for elements, with the catch that dissolution of different elements often occurs. The concentration (0.05 M) was chosen based on the works of Manouchehri *et al.*, (2006) where different concentrations of EDTA were compared concerning the amount of trace metals extracted. 0.05 M was considered sufficient on the extraction of e.g. Ca, Fe, Mg and Al. Some research (Kim *et al.*, 2003; Manouchehri *et al.*, 2006) discovered that in calcareous soils with higher pH (>6.5) Ca and Mg compete with Al and Fe for chelation with the EDTA. This is due to the increase in pH that an alkaline soil creates. In non-calcareous soils the changes of pH are not significant. In soils with low Ca content the extracted Ca will reabsorb to the solid phase, as the Al and Fe reactions with EDTA dominates due to their thermodynamic constants of stability (Manouchehri *et al.*, 2006).

2.5.4 Hydrochloric acid

The method used for the extraction of long-term potassium (K) reserves in Sweden is hydrochloric acid at 100ºC. There is no international standardized method to measure the long-term K (Andrist-Rangel *et al.*, 2013). The most typical extraction reagent is an acid, commonly hydrochloric acid (HCl) or nitric acid (HNO_3). Several studies (Ghorayshi & Lotse, 1986; Rupa *et al.*, 2001; Andrist-Rangel *et al.*, 2013) have shown that the K extracted with the acid methods has a correlation with the plant uptake. The research found that the K extracted from the soil with e.g. HCl (K_{HCl}) decreased when plants was grown. The main source of K in a soil are different K-bearing minerals (Simonsson *et al.*, 2009). Simonsson *et al.*, (2007) discovered that the long-term K pool is dynamic regarding the availability to plants. This finding suggests that the K_{HCl} is affected by both release and fixation of K. What type of minerals that contribute to the K_{HCl} was investigated by Andrist-Rangel *et al.*, (2013). The studies concluded that the extracted K from the HCl-extraction method almost solely was obtained from 2:1 clay minerals and the biggest contributors were clay and fine silt fractions with a size smaller than 20 µm. However, the study included an exception where a coarser fraction, sand, contained a significant amount of K. They also concluded that the mineralogy is more important than particle size when investigating the extraction of K with hot HCl. The clay, finer silt and sand all contain phyllosilicates, which are active in the fixation of K. The hot HCl extract K from these minerals, rather than others, which is a proof of the methods suitability for extracting K.

2.5.5 Water

The extractions with water represent the least amount of extractable base cations in the soil. De-ionized water is used as the extraction agent to ensure that there are no unwanted ions present that will affect the extraction. The base cations extracted with solely de-ionized water is regarded as available to plants.

2.5.6 Aqua Regia

A certified lab performed the extraction with an international standardized method called ISO 11466. The method uses aqua regia, an acid mixture that consists of one part nitric acid and three parts hydrochloric acid. Aqua regia is often used in different analytic procedures but is most known for its ability to dissolve gold. Due to this capability, it is frequently used in the refining of pure gold. It has a strong oxidising effect, which is why it is used when analysing i.e. a soil´s base cation content. However, the method of digesting soil with Aqua regia cannot be regarded to give the total content of base cations in the soil. This is because the dissolution of all components of the soil is not necessarily complete (Andersen & Kisser, 2004). Although the organic matrix is dissolved, some parts of silicate matrices might not be, which leaves base cations in a non-soluble form. The Aqua regia method is often described to give the "pseudo-total concentration" of elements in the soil.

2.5.7 Sequential extraction

The idea behind the sequential extraction is to compare the different extraction methods in an easy way. The order of the extractions are set from the least aggressive method to the most aggressive one, with water being first, ammonium acetate second, EDTA third and extraction with hot HCl being the last. Since the EDTA has been buffered with NaOH, the Na content cannot be analysed in the EDTA or HCl extractions, since Na contamination will occur. As base cations are extracted from each method, only the long-term K will be left in the soil samples when the extraction with hot HCl is the only one left. The aim with the sequential extraction is to get a clear picture of which cations the different methods extract and what cations are left in the soil after each extraction.

2.5.8 Comparisons between different extraction methods

Comparisons between different cation extraction methods has been investigated in several different studies (i.e. Golden *et al.*, 1942; Pratt & Holowaychuk, 1954; Barrows & Drosdoff, 1958; Vanbladel *et al.*, 1975; Borge, 1997; Luer & Bohmer, 2000; Karltun, 2001; Holden *et al.*, 2012). The issue with comparing the different methods with each other is that the results of the extractions depend heavily on soil characteristics. A method that might extract a lot of base cations from one soil, might extract a lot less from a different one with i.e. different pH, organic- or clay content. To be able to get a fair comparison between the different methods, similar soils have to be used in the extractions. In presentation by Karltun (2001) at the Forest Soil Expert Panel Meeting, results of a comparison between a method with ammonium acetate buffered to pH 7 and a barium chloride method was presented. The soil samples in the study were divided into samples from organic horizons and mineral horizons. The results indicated that barium was more efficient in extracting bivalent cations from the organic horizons while the results from the mineral soils indicated that barium extracted calcium better, but not magnesium. Likewise, a Norwegian study performed by Borge (1997) suggested that the ammonium in buffered (pH 7) ammonium acetate does not extract multivalent base cations effectively, especially in the horizons with organic material (O and E).

2.6 BASE CATION SUPPLY

The following paragraphs contain a short description of the processes that supply base cations in the soil system.

2.6.1 Physical weathering

The physical, or mechanical weathering is a process where different types of rocks convert into dissolved deposits without its mineral structure being altered. The physical weathering results in an increase in the specific surface area, which enables the chemical weathering to become more effective. Physical weathering in Podzols is driven mainly by frost, vegetation, flowing water, and wind. All these factors break rock into smaller particles.

2.6.2 Chemical weathering

When the physical weathering has increased the specific surface area of the parent material, the chemical weathering becomes more effective. The minerals undergo chemical transformations, where they are dissolved into ions. Some of the weathering products deposits as secondary minerals, while other more easily dissolved minerals end up in the soil solution as solved salts. Chemical weathering in Podzols is driven mainly by the composition of the minerals, the specific surface area, the temperature, the water content of the soil and pH. In the Swedish climate the chemical weathering has a lower efficiency during the winter when the temperature is low.

2.6.3 Biological weathering

The role of processes that reallocate nutrients from inaccessible stores in the soil to the roots of the trees is a somewhat debated subject. One process that has gotten a lot of attention in later years is the biological weathering, especially the role of mycorrhizal mycelia. The mycorrhiza is well developed within the mineral soils horizons of the boreal forests (Finlay *et al.*, 2009). It acts as a channel, which transports organic metabolites, protons and other substances from the trees photosynthesis to the mineral surfaces in the mineral soil. This results in a dissolution of the minerals, which becomes mobile. The mycorrhizal mycelia then transports mobilised nutrients and ions to the tree (Finlay *et al.*, 2009). The importance of the biological weathering within the researchers community is not in agreement. Some studies (Sverdrup, 2009) states that the biological weathering is only a small part of the total weathering, while other studies (Hinsinger *et al.*, 2006; Finlay *et al.*, 2009) claims that the biological weathering, and the mycorrhizal role of it, may contribute a significant portion of the total weathering.

Whether the ectomycorrhizal can respond to a tree´s increasing nutrient demand has been investigated by Rosenstock (2009). He states that there are few experiments that investigates the relation between weathering activity and nutrient demand, but claims that there are indirect evidence that an increase in Mg, K and P demand increases the weathering activity of ectomycorrhizal fungi.

A study performed by Jongmans *et al.* (1997) discovered several tiny (3-10 µm) tunnels in minerals in the E-profile of different podzols around Europe. These pores had been created by rock-eating mycorrhizal fungi, which had exuded strong organic acids from their hyphal tips, which weathered the minerals. Jongmans *et al.* (1997) argued that the rock-eating fungi could translocate nutrients from inaccessible micropores directly to the trees. This nutrient gateway implies that the nutrients do not necessarily pass through the soil solution, where other organisms can take advantage of it, but instead go directly to the host of the mycorrhizal fungi.

The acidification results in a lower amount of base cations in the soil. This leads to a lower ratio of calcium ions to aluminium ions (Ca^{2+}/Al^{3+}), which is though to have a deteriorating effect on the roots (Jongmans *et al.*, 1997). Jongmans *et al.* (1997) continues by arguing that trees can receive Ca^{2+} and Mg^{2+} ions from the inside of minerals, and that the Al^{3+} therefore might be irrelevant to the root uptake of Ca^{2+}.

Mahmood *et al.* (1999) investigated how whole tree harvesting (WTH) affected the ectomycorrhizal colonies at Tönnersjöheden experimental forest. They showed that the humus layer was thinned due to the WTH, which according to several studies is important for not only ectomycorrhizal root growth, but also other parts of the forestry. The thinner humus layer lead to both lower quality and amount of ectomycorrhizal roots, which could be significant to tree growth, however, it did not affect the ectomycorrhizal composition. Another finding indicated that a lower Ca^{2+}/Al^{3+} could lead to a lower ectomycorrhizal production. The WTH could consequently lead to lower amounts of nutrients available, but also less efficiency in the capacity of uptake of the remaining nutrients, such as base cations.

2.6.4 Deposition

The deposition of base cations is an important factor when looking at the mass balance of nutrients in a forest (Ferm *et al.*, 2013). The deposition of base cations involves several different processes. Some of the base cations are deposed as precipitation (wet deposition), some as gases and particles (dry deposition) and some as precipitation, which is runoff from the tree crowns (crown drops) (Ferm *et al.*, 2013). These different depositions combined compose the total deposition. The emissions of base cations can come from different sources, both natural and anthropogenic ones. Sodium and magnesium can be derived from the sea salt deposition, while most of the potassium and calcium is from anthropogenic sources (Torseth *et al.*, 1999; Ferm *et al.*, 2000). The combustion of coal, wood and during different industrial processes contribute to the emission of particles containing base cations. Due to the decreasing combustion of e.g. coal, the emission of base cations have decreased (Ferm *et al.*, 2013).

2.7 FACTORS LEADING TO BASE CATION LOSSES

The following paragraph contains information about the different factors and processes that decrease the amount of base cations in the soil.

2.7.1 Tree harvest

In a natural environment, where no forestry is performed, nutrients such as base cations that have been utilized by the trees are returned to the soil when the trees die and decompose. In a forest that is harvested, at least parts of the trees are removed from the area with the result that nutrients are being removed from the ecosystem.

What method to use when investigating the nutrient status of trees has been debated (Cape *et al.*, 1990). One way to eliminate effects on the nutrient concentration from ageing processes and growth dilution is to calculate nutrient ratios in foliage, i.e. base cations/nitrogen (N). Different ratios between base cations and N can be derived for normal and optimal growth (Mellert & Goettlein, 2012).

Olsson *et al.*, (2000) investigated the whole tree harvesting (WTH) effects on base cation concentrations in needles and discovered that the concentration of Ca and Mg in needles were lower after WTH 16 years after felling when comparing WTH and conventional harvesting. However, the differences between WTH and conventional harvesting (CH) had disappeared 6 years later. A similar study by Thiffault *et al.*,

(2011) found lower foliar Ca and Mg concentrations after WTH compared to CH, with the biggest difference in soils with the lowest concentrations of nutrients in the soil. However, there are findings (Saarsalmi *et al*., 2010; Wall & Hytonen, 2011) that found no significant difference in the concentration in needles and growth from trees growing on soils where WTH had been performed compared to soils where CH had been conducted. Wall & Hytonen (2011) on the other hand, discovered that the trees growing on the soil that had been conventionally harvested became taller than the trees growing on the WTH soil. There was, however, no difference in total stem volume between the different locations. A remark to this study is that the WTH performed prior to the plantation of the trees examined in this research did not include needles. The needles were left on site. Wall & Hytonen (2011) also discovered that the amount of exchangeable Ca were lower in the WTH soils. It did not, however, affect the growth of the trees and the amount of Ca in their needles.

Other research (Olsson, 2011; Zetterberg *et al*., 2013) have concluded that WTH does not give lasting changes in the soil concentration, but rather temporary variations that diminishes over time. Later research by Zetterberg *et al*., (2016) performed at three different locations in Sweden suggests that the Ca^{2+} pools are depleted after harvest, independent of type of treatment (WTH or conventional harvesting). The results showed that the soil Ca^{2+} pools converged over time between WTH and conventional harvesting. However, the WTH Ca^{2+} pools were lower 38 years after the treatment. A model simulation in the same research could not predict the diminishing differences between CH and WTH, which led to the conclusion to be cautious when simulating the changes after CH and WTH.

2.7.2 Soil erosion

Soil erosion of a soil covered with vegetation is limited. The examined locations have a vegetation cover that keeps the soil erosion to a minimum; subsequently the transfer of base cations out of the system is limited. Soil erosion occurs when energy from rain and wind affect the soil to such a degree that it is being moved. Another important source of soil erosion occurs during the tree harvest. A common practice during harvesting is the use of tree felling machines. Researchers from USA (Pimentel, 2006) has investigated the soil erosion of crop land and claims forest soils need at least 60 % of its soil covered by vegetation to withstand severe soil erosion.

2.7.3 Leaching

Leaching occurs when base cations, which are solved in soil water, are removed from the soil system to the ground water and further to nearby surface water due to rain, flooding or snowmelt. Until recently, leaching has been a bigger source of removal of base cations than tree uptake, but research by Belyazid *et al.* (2006) showed modelled results that the uptake has increased and surpassed the leaching removal, indicating that tree harvesting and WTH in particular will have a more important role than leaching in the future. The proposed reason for the decline of leaching is the increased N deposition, which increases tree growth and consequently base cation uptake.

2.8 PODZOLS

The Swedish Podzol is a common soil on the northern hemispheres humid, tempered and cold zones. The Podzol is the most common soil in Sweden, covering almost 50 % of the country's surface, depending on what type of classification that is being used. It is mainly found in coniferous forests.

The soil consists of five different horizons, O, A, E, B and C. The O horizon is mainly composed of varyingly decomposed organic materials such as dead plants. The E horizon is a heavily weathered section of the soil. It has a pale, ash like, colour that has given the spodosol its name ("spodos" from Greek translates to "ash"). The E horizon is poor in nutrients and colloids. In some of the southern parts of Sweden, the E horizon is not distinguishable. The soil has been mixed into a horizon with humus and mineral soil called an A horizon. The A horizon is created by either farmers that has cultivated the land, or by ground worms and other soil organisms. The A horizons do not emerge in the northern half of Sweden.

The O, E and A horizons are called leaching horizons. They transcends into the beneficiation horizons, B and C, which are found further down in the soil profile. The B horizon, also called the spodic horizon lacks organic matter and humus. The B horizon always receives some Fe and Al from the E horizon through illuviation. The B horizon has a characteristic rusty brown colour due to high concentrations of ferryhydrite and goethite. In the upper parts of the B horizons, the highest concentrations of Fe and Al in its secondary form are usually found. In these parts of the soil profile, the humus content is higher than the E horizon and the underlying horizons. The C horizon is almost unaffected by the soil forming processes such as podzolization. This horizon has not been altered sufficiently by the podsolization to become a B horizon.

A process called podzolization creates the Podzols. This is a relatively fast process; most of the podzols have been created within the last 10,000 years. There is a relationship between climate, vegetation and the rate of the podzolization. At the northern parts of Sweden, where the temperature is considerably colder, the podzolization is slower. During the podzolization process organic material and different solubles such as Fe and Al are leached from the A- and E horizons and enriched in the B horizon.

A study (van Breemen *et al*., 2000) suggests that mycorrhizal fungi is involved in the podzolization process. The investigation showed that mycorrhizal fungi perforated many different minerals in the E horizon of podzols, but only a few if any in the B horizon. This indicates that plants, which utilize mycorrhizal fungi, might have a role in the podzolization process.

3 SITES

This chapter contains information on the different locations where the soil samples were collected, their soil type, deposition rates and yearly precipitation. In Figure 1 the location of the sites are marked.

3.1 ASA

Asa is located in the province of Småland, 140 km east of the west coast of Sweden. The location has been used as a research station and experimental forest since 1988. Phenology, variation on tree growth and the climate are all studied at Asa. The site is located 165 m above sea level in the Boreonemoral zone. The soil mainly consists of till with glaciofluvial deposits and peat. The location is situated above the highest ancient coastline. The soil is classified as a Spodosol, with Haplic podzol being the most common type of spodosol.

Asa is located in the Boreonemoral zone and has an annual mean temperature of 5.5 ºC. The annual precipitation is 688 mm on average.

Due to its relatively close location to the Atlantic sea, the impact of sea salt deposition from precipitation is significant. During strong western winds the chloride concentration in the rain can reach levels of 1 mg/L, see Figure 2. A summary of the site-specific characteristics can be found in Table1.

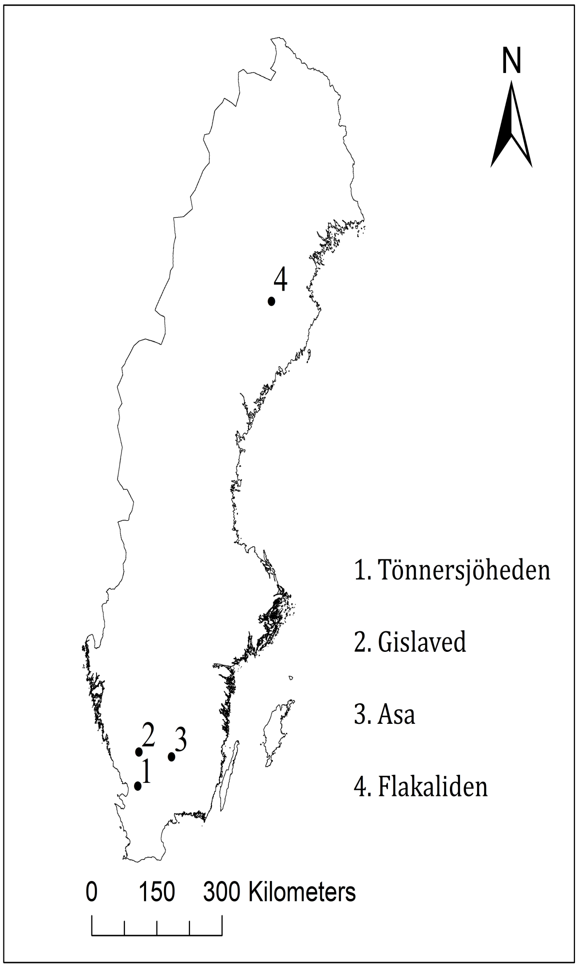

Figure 1. Map over Sweden, displaying the location of the examined sites. © Lantmäteriet i2012/921.

The different soils from Asa has been named:
AO = O-profile
AA = A-profile (0-10 cm depth)
AB = B-profile (30-40 cm depth)
AB/C = B-profile (50-60 cm depth)

3.2 FLAKALIDEN

Flakaliden is located in the Västerbotten province, 70 km west of the Gulf of Bothnia. The location is used for a forest research project, which started in 1986. The trees in the research area were felled in 1963, after which a new plantation of Norway spruce was performed. The area is located 310 m above sea level, above the highest coastline. The soil consists of un-surged material, mainly a very rocky iron podzolic and sandy till. The rock type of origin is gneiss.

During the long-running experiments performed at Flakaliden, two different nutrition treatments have been used. In the first treatment, the Norway spruce was treated with a nutrition solution, while the second treatment consists of adding nutrients in the form of solid fertilizers. Control sites where no fertilizers have been added also exist.

Flakaliden has a cold climate. During the long winter period, the days are short and cold and during the summer period the days are long and balmy. The soil freezes during the winter and thaw in May. The vegetation period is 135 days per year with a mean temperature of 10.5 ºC. The average temperature over the whole year is 2.0 ºC. Half of the precipitation at Flakaliden falls as snow. This corresponds to 300 mm of rain when the spring flood occurs. The mean amount of rain that falls during the vegetation period is 270 mm, which usually exceeds the evaporation. This means that the trees usually have a good supply of water.

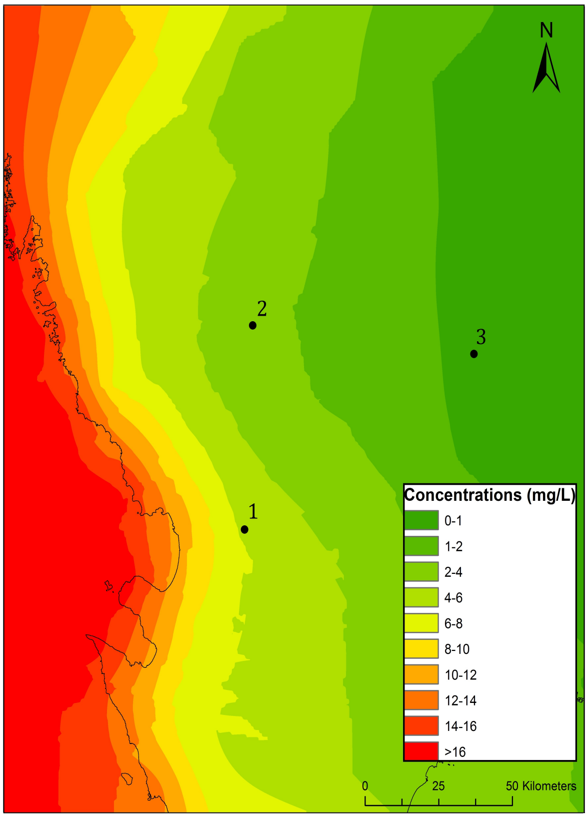

Figure 2. Indicate the possible chloride concentrations in the precipitation at 1. Tönnersjöheden, 2. Gislaved and 3. Asa when there are strong western winds. The map is based on the work of Franzén (1990). © Lantmäteriet i2012/921.

Flakaliden is located far away from the Atlantic sea (400 km). Due to its location, the effect from sea salt in the rainfall is considered to be negligible. A summary of the site-specific characteristics can be found in Table 1.

The different soils from Flakaliden has been named:

FO = O-profile
FE = E-profile (0-10 cm)
FB1 = B-profile (20-30 cm)
FB2/C = B-profile (50-60 cm)

3.3 GISLAVED

Gislaved is located in southern Sweden in the province of Småland, 85 km from the west coast of Sweden. The soil type is fine-grained moraine with great thickness, classified as a podzol (iron podzol). Due to the proximity to the west coast, the impact from sea salt deposition is relatively high. During high western winds the chloride concentration in the rain can reach levels of 4 mg/L, see Figure 2.

Gislaved is located 217 m above sea level in the Boreonemoral zone, above the highest ancient coastline. The site has an annual mean temperature of 6.0 ºC and the annual precipitation is 750 mm. The tree distribution at the site is 90 % fir (*Picea abies*) and 10 % pine (*Pinus sylvestris*). The trees are 50-55 years old and the stand has been thinned 6 months prior to the sampling. No residues from the thinning (i.e. GROT) were present in the vicinity of the sampling location. A summary of the site-specific characteristics can be found in Table 1.

The different soils from Gislaved has been named:

GO = O-profile
GE = E-profile (0-3 cm)
GB = B-profile (3-8 cm)
GB/C = B-profile (8-17 cm)

3.4 TÖNNERSJÖHEDEN

Tönnersjöheden is located in the southwest of Sweden in the Halland province, 20 km from the west coast of Sweden. The location has been used as a research forest since 1923, managed by the Swedish University of Agricultural Sciences (SLU). The area is located 50-65 m above sea level. The well-drained soil in Tönnersjöheden is till, glaciofluvial material and surged sand and peat and the soil type is an Arenosol.

Tönnersjöheden is located in nemo-boreal zone. It has a mean annual temperature of 6.7 °C and an annual precipitation of 1064 mm.
Due to Tönnersjöhedens location close to the Atlantic sea, the amount of sea salt deposition is relatively great. An estimated concentration of up to 4-6 mg/L chloride can occur in the precipitation at Tönnersjöheden, when there is strong western winds (Franzen, 1990). A summary of the site-specific characteristics can be found in Table 1.

The different soils from Tönnersjöheden has been named:

TO = O-profile
TA = A-profile (0-10 cm)
TB = B-profile (10-20 cm)
TBC = B-profile (40-50 cm)

Table 1. Summary of site-specific characteristics.

	Asa	Flakaliden	Gislaved	Tönnersjöheden
Altitude (m.a.s.l.)	165	310	217	60
Mean annual precipitation (mm)	688	570	750	1064
Mean Annual temperature (°C)	5.5	2.0	6.0	6.7
Growing season (days)	190	135	200	211
Nitrogen deposition (kg $ha^{-1}yr^{-1}$)	8.8	1.0	6.2	5.5
Sulphur deposition (kg $ha^{-1}yr^{-1}$)	4.5	2.0	5.5	5.1
Chloride deposition (kg $ha^{-1}yr^{-1}$)	0.3	0	0.5	1.1
Soil	Podzol	Podzol	Podzol	Podzol

Table 2. The pH-value and total organic content of each soil.

Tönnersjöheden	pH H_2O	pH $CaCl_2$	Tot-C%
TO	3.74	2.80	N/A
TA	3.82	3.30	N/A
TB	4.39	4.16	N/A
TBC	4.67	4.33	N/A
Asa	pH H_2O	pH $CaCl_2$	Tot-C%
AO	3.92	3.27	N/A
AA	4.20	3.67	9.17
AB	4.67	4.41	1.93
AB/C	4.83	4.59	0.80
Flakaliden	pH H_2O	pH $CaCl_2$	Tot-C%
FO	4.09	3.43	N/A
FE	4.13	3.44	2.88
FB1	4.89	4.47	4.11
FB2/C	5.02	4.89	0.59
Gislaved	pH H_2O	pH $CaCl_2$	Tot-C%
GO	3.78	2.79	46.10
GE	4.09	3.14	1.46
GB	4.01	3.35	1.88
GB/C	4.79	4.23	1.46

Table 3. The mineralogy of the different soils.

Soil	Quartz	K-feldspar	Plagio-clase	Amphi-bole	Epi-dote	Di-mica	Di-Verm	Allo-phane	Ferri-hydrite
AO	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
AA	45.6	15.2	23.5	2.2	3.0	2.5	2.0	1.6	1.9
AB	43.4	15.5	25.3	2.5	3.0	3.2	1.8	0.8	1.8
AB/C	41.5	15.4	27.7	2.4	3.0	3.2	1.8	0.8	1.8
FO	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
FE	54.9	15.3	22.4	1.6	1.8	1.2	1.0	0.0	0.1
FB1	38.5	13.5	23.2	4.4	2.3	3.8	0.0	8.1	3.6
FB2/C	40.0	13.7	26.7	4.3	2.5	5.2	0.0	1.0	0.9
GO	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
GE	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
GB	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
GBC	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

4 METHODS

This chapter contains information on how the different soil samples were collected and how the extractions and modelling was performed.

4.1 SOIL SAMPLING

The general soil sampling methodology is a hand dug hole of approximately 0.5 m^2 area and 1 m depth. The samples from the humus layer (O horizons) were collected with a special corer device ("humus holesaw"). The samples from the A/E and upper B where collected with a steel cylinder that was rotated into the soil. The lower B samples were collected by hand with a small shovel from within the test hole.

4.2 EXTRACTION METHODS

This Section describes how the different extraction methods were conducted, how much soil and extraction fluid was used and for how long the different methods were shaken. A summary of the extractions is found in Table 4.

Table 4. A summary of the extractions with water, NH_4OAc, $BaCl_2$, EDTA and HCl

Extraction reagent	Amount of organic soil (g)	Amount of mineral soil (g)	Volume of extraction agent added to organic soil (ml)	Volume of extraction agent added to mineral soil (ml)	Shaking time (h) (Boiling time for HCl)
Water	10.00	10.00	100	25	16
NH_4OAc	2.00	15.00	100	100	1.5
$BaCl_2$	1.00	10.00	50x2	50x2	1x2
EDTA	2.00	10.00	100	100	16
HCl	2.00	2.00	50	50	2

4.2.1 Ammonium acetate

The extraction followed the instructions of the Swedish habitat mapping (SK), written by Erik Karltun (1996).

Two (2.00) grams of the organic soil and 15.00 grams of the mineral soil were added to a shaking bottle. One hundred (100) ml of 1N NH_4OAc (pH: 7.0) were added to the bottle and the put on a shaking table for 1.5 h. After the shaking procedure the bottle were centrifuged for 10 minutes at 2500 rpm. The supernatant was then filtrated through an ash free Munktell OOH filtration paper into a 20 ml scintillation vial and stored in a cooler until analysis with ICP.

4.2.2 Barium chloride

One (1.00) grams of the organic soil and 10 grams of the mineral soil were added to a shaking bottle. 50 ml of 0.1 M $BaCl_2$ were added to the bottle and put on a shaking table for 1 h. After the shaking procedure the bottle was centrifuged for 10 minutes at 2500 rpm. The supernatant was then filtrated through an ash free Munktell OOH filtration paper into a 250 ml E-flask. Another 50 ml of 0.1 M $BaCl_2$ were then added to the same soil and put on the shaking table for another 1 h. After the second shaking procedure the bottle was centrifuged for 10 minutes at 2500 rpm and the supernatant was then filtrated into the same E-flask. The two extraction solutions were mixed and then transferred to a 20 ml scintillation vial and stored in a cooler until analysis with ICP.

4.2.3 EDTA

Two (2.00) grams of the organic soil and 10.00 grams of the mineral soil were added to a shaking bottle. 100 ml of 0.05 M EDTA were added to the bottle and put on a shaking table for 16 h. After the shaking procedure the bottle was centrifuged for 10 minutes at 2500 rpm. The supernatant was then filtrated through an ash free Munktell OOH filtration paper into a 20 ml scintillation vial and stored in a cooler until analysis with ICP.

4.2.4 Hydrochloric acid

Two (2.00) grams of the organic soil and 2.00 grams of the mineral soil were added to a glass bottle. 50 ml of 2.00 M HCl was added to the bottle after which the bottle was sealed with a glass pear and thoroughly stirred by swinging the bottle. The bottle was then placed in a boiling water bath, with the extraction fluid in the bottle and the surrounding water levelled. The boiling lasted for two hours with the bottle being stirred every 30 minutes. After the boiling procedure the bottle was cooled to room temperature. The extraction fluid was then filtrated through an ash free Munktell OOH filtration paper into a volumetric flask. The solution was then diluted eight times with deionized water and then transferred to a scintillation vial and stored in a cooler until analysis with ICP.

4.2.5 Water

10.00 grams of the organic soil and 10.00 grams of the mineral soil were added to a shaking bottle. 100 ml of water were added to the organic soil and 25 ml of water were added to the mineral soil and put on a shaking table for 16 h. After the shaking procedure the bottle was centrifuged for 10 minutes at 2500 rpm. The supernatant was then filtrated through an ash free Munktell OOH filtration paper into a 20 ml scintillation vial and stored in a cooler until analysis with ICP.

4.2.6 Aqua regia

The Aqua regia extraction was performed at Eurofins, a certified lab. The extraction was performed with the ISO standard method ISO 11466.

4.2.7 Sequential

The sequential extraction was performed on the soil from Tönnersjöheden. It used the extractions with water, NH_4OAc, EDTA and finally HCl. The extractions were performed as described above. The extraction fluid was removed after each extraction, and the new one was added to the soil sample. After each extraction, the sample were centrifuged and the supernatant was filtered through an ash free Munktell OOH filtration paper into a 20 ml scintillation vial and stored in a cooler until analysis.

4.3 STATISTICAL ANALYSES

To able to confirm if the different extractions methods have a statistically significant difference or not, different statistical analysis can be performed on the data from the extractions. The different analyses are described below.

4.3.1 T-test

The t-test is a tool that analyse if there is a difference between different groups by conducting a hypothesis test. In this case if there are any differences between the methods ability to extract base cations. The investigated groups were divided into organic soils and mineral soils. Prior to conducting the analysis, the data from the extractions were subtracted from each other, resulting in a normal distributed data set. The differences between the methods were then compared to zero, with the null hypothesis that the difference between two methods does not differ from zero. The t-test was performed with the data-analysis add-in in Microsoft Excel.

4.4 LINEAR REGRESSION

The linear regression is a tool used to investigate the linear correlation between to variables e.g. the amount of base cations extracted by two different extraction methods. The linear regressions were performed using the Microsoft Excel data-analysis add-in Linear Regression. The application of linear regression has many benefits. If e.g. the linear fit between two different extraction methods is well, data from one method can easily be recalculated into the result of the other method. This can be very helpful when comparing data from one extraction method to another. It is also convenient when exchanging from one method to a new one. If there is a linear correlation between the methods, old data can be recalculated without the need to redo the extractions with the new method. This is beneficial with the increasing demand on harmonization from e.g. the European Union and when comparing e.g. the base cation content in soils.

5 RESULTS

In this Section all of the results from the base cation extractions and other results such as statistical analysis will be presented. The basis for the graphs is found in table form in the appendix.

5.1 EXTRACTIONS

The results from the different extraction methods used on the different soils of the different locations are presented in the graphs below. The results are divided into four figures, each displaying the results for each base cation examined. The Y-axis of the graphs is logarithmic in order to display low and high values in the same graph. Figure 3 displays extractable calcium in the different horizons at each location and all of the extraction methods. Similarly Figure 4 displays the results for extractable potassium, Figure 5 displays extractable magnesium and Figure 6 displays extractable sodium. Information about the different horizons and their naming, which is displayed under the x-axis in the graphs, can be found in Section 3.

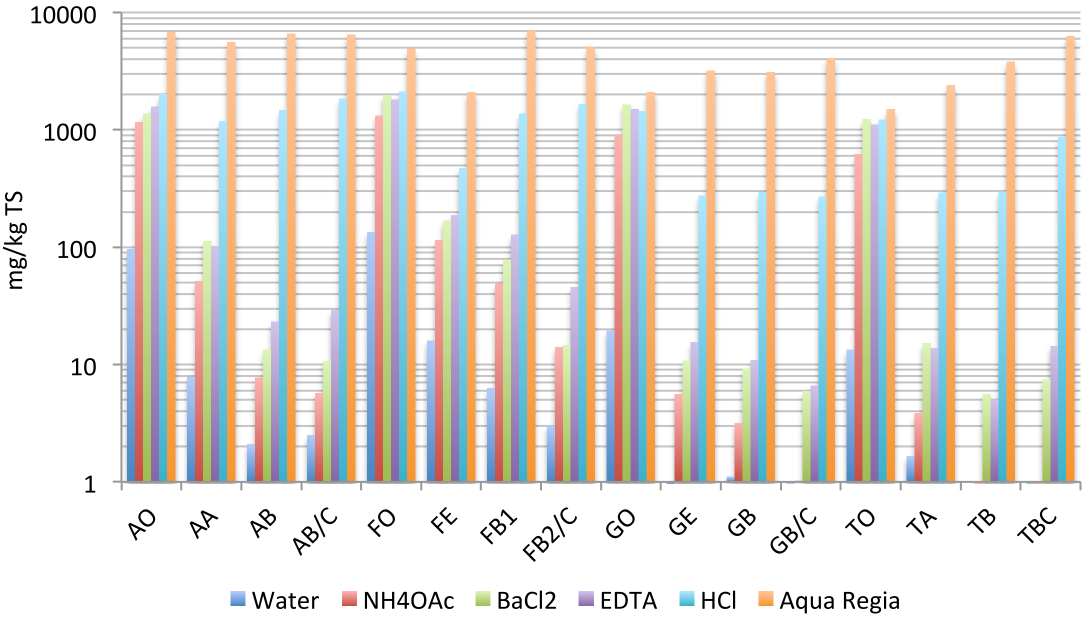

Figure 3. The extraction of calcium at the different locations with the different extraction methods.

In the extraction of Ca (Figure 3) some trends are visible. Water extracts least Ca, generally NH_4OAc, $BaCl_2$ EDTA, HCl and Aqua regia follow in increasing order of extraction effectiveness. Another visible trend is that all extraction methods except Aqua regia extracts the largest amount of Ca in the organic horizons (AO, FO, GO and TO). Also, the differences between the methods in the organic soils are less than in the mineral soils. Both HCl and Aqua regia is able to extract a considerable amount of Ca in the mineral soils and the organic soils while the other methods has a far less tendency to extract Ca in the mineral soils. The pseudo total amount of Ca, extracted with Aqua regia displays that the amount of Ca increases with depth.

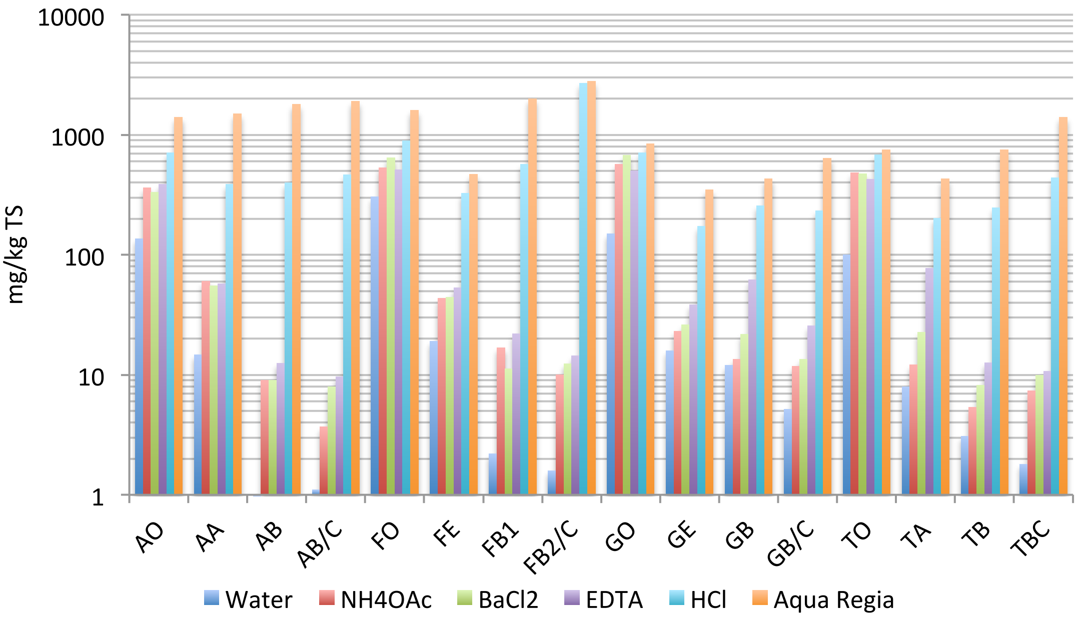

Figure 4. The extraction of potassium at the different locations with the different extraction methods.

The extractions of K (Figure 4) shows similar results as the Ca extractions, that Aqua regia is the method that extracts most K, generally followed by HCl, EDTA, $BaCl_2$, NH_4OAc and water. However, in the organic horizons, $BaCl_2$ is generally extracting more K than EDTA. Other observations are greater differences between the methods in the mineral soils compared to the organic soils and a general trend that the pseudo total amount of K increases with depth.

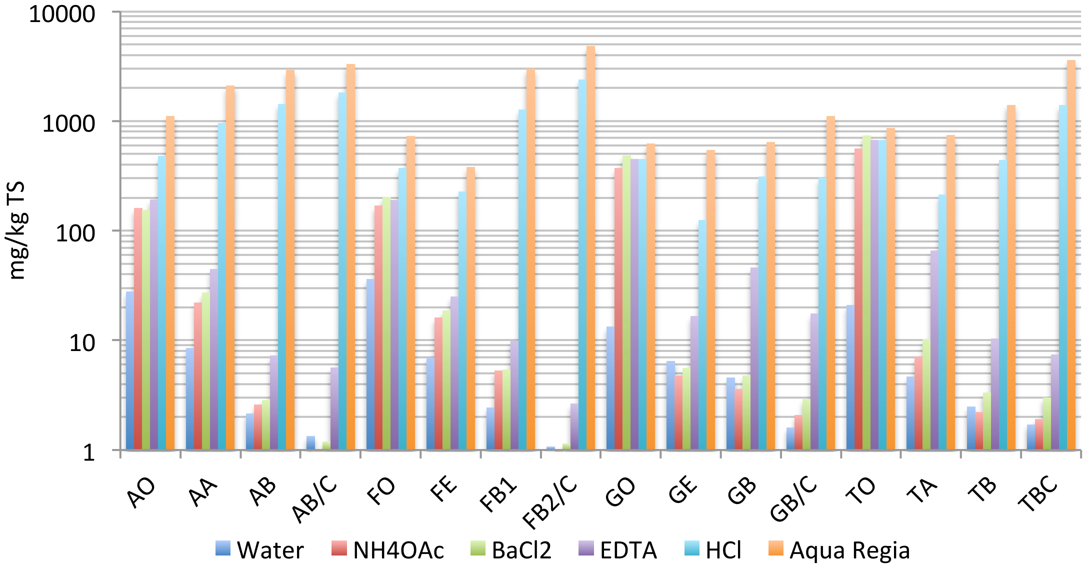

Figure 5. The extraction of magnesium at the different locations with the different extraction methods.

The extractions of Mg (Figure 5) reveal that Aqua regia extracts most Mg in all of the different soils, generally HCl, EDTA, $BaCl_2$, NH_4OAc and water follow in decreasing order of effectiveness. In the organic soils, $BaCl_2$ is the better extractant compared to EDTA in three of the four examined soils. The pseudo total amount of Mg, extracted with Aqua regia presents that the amount of Mg increases with depth, while the opposite is true for the other methods.

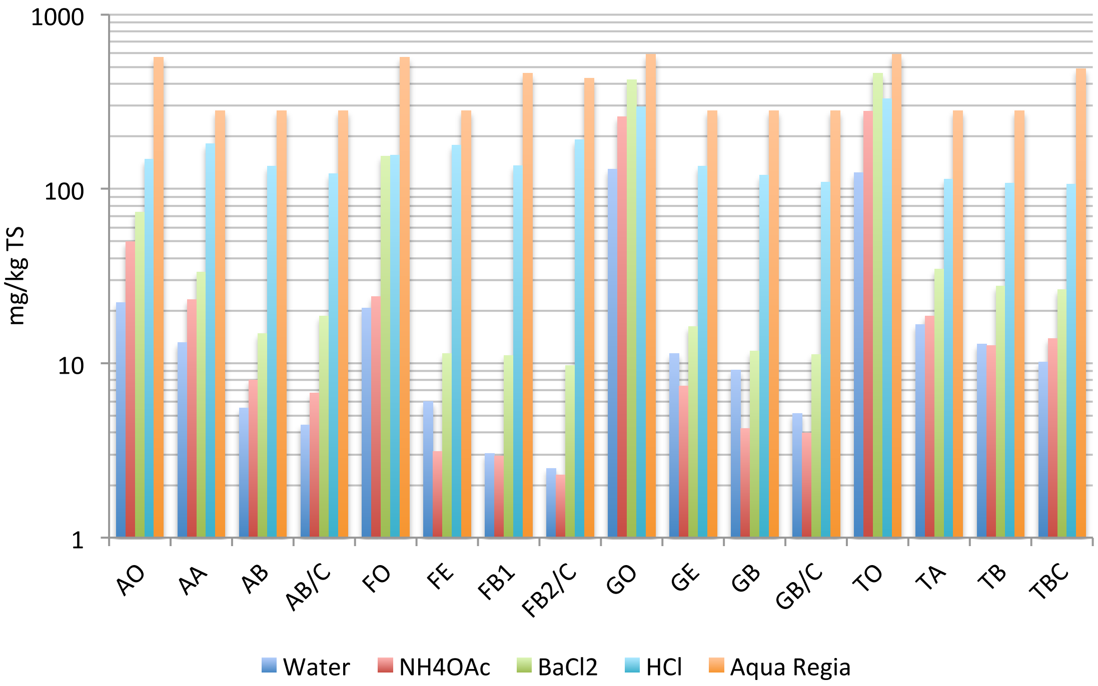

Figure 6. The extraction of sodium at the different locations with the different extraction methods.

The extractions of Na (Figure 6) display that Aqua regia extracts the greatest amount of sodium generally followed by HCl, $BaCl_2$, NH_4OAc and water in decreasing order of effectiveness. However, in the organic soils, $BaCl_2$ is able to extract more Na than HCl at three out of the four examined soils. Another observation is that the pseudo total amount of Na, extracted by Aqua regia, is significantly lower compared to the other base cations. At some of the mineral soils (FE, FB1, FB2/C, GE, GB, GB/C and TB) the extractions with water is able to extract more Na than NH_4OAc.

Figure 7 displays the sequential analysis. The columns represent the amount of base cations extracted at each horizon at Tönnersjöheden. Each section of the stacked column represents the amount of base cation each method extracted and the combined column represents the total amount that was extracted with all the different extraction methods. The first method used (water) is shown in the bottom of the column and the last (HCl) is shown at the top. To get a comparison of the amount of base cations the sequential analysis extracts, each column is compared to the extraction method that extracted the most base cations from the horizon. Which of the single methods that is compared to the sequential analysis is written after the horizon name on the x-axis.

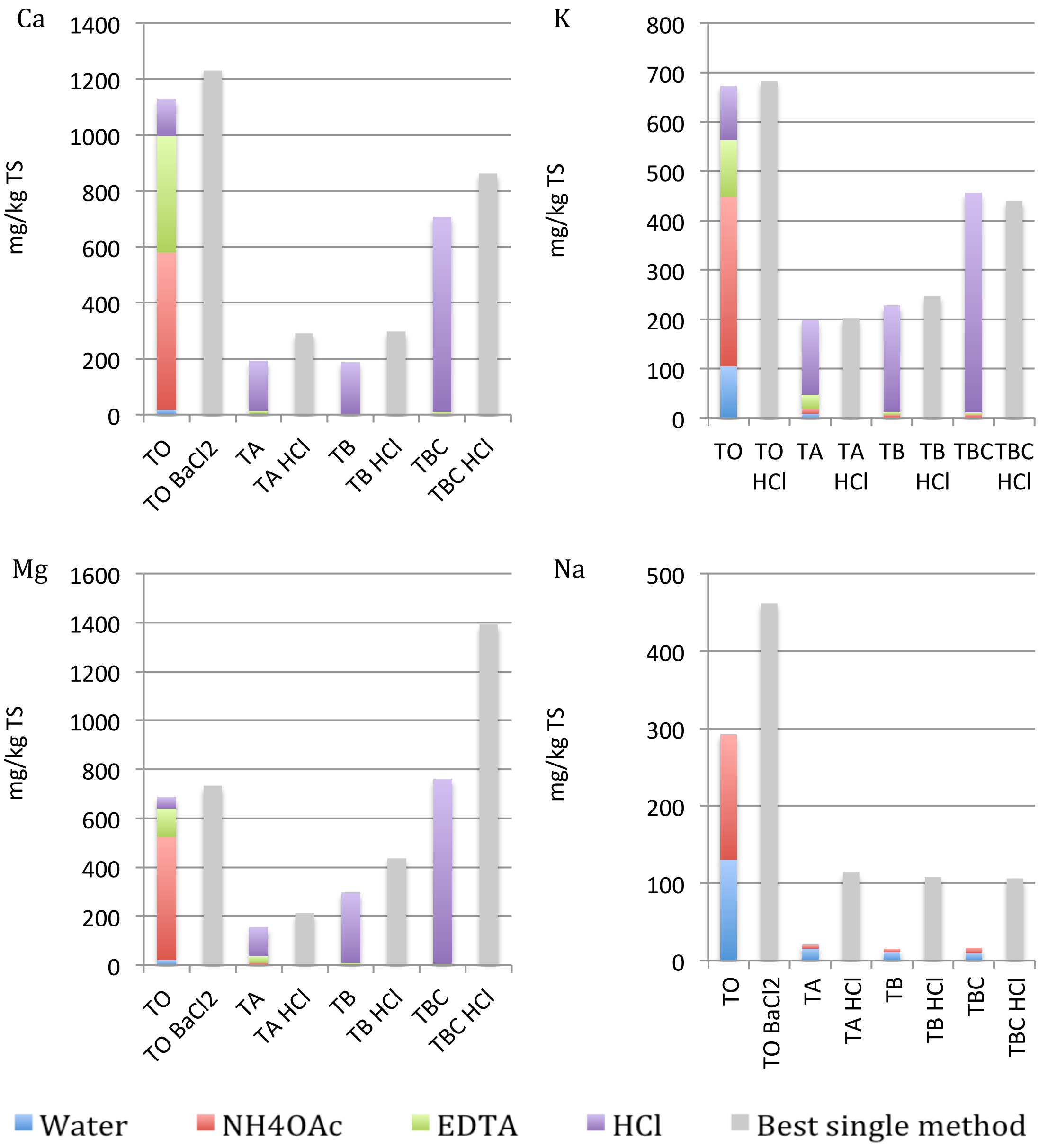

Figure 7. The extractions of the different base cations performed with the sequential analysis compared to the single most effective method of each horizon at Tönnersjöheden.

The sequential analysis (Figure 7) reveals that the different methods used were able to extract some base cations, mainly from the organic soil. In the mineral soils it was principally the last extraction method used in the analysis, HCl that was able to extract a considerable amount of the different base cations. The more base cations the earlier methods in the analysis are able to extract, the less the latter ones are able to. Throughout the best single method is able to extract more base cations than the sequential analysis is.

5.1.1 Percentage extracted of pseudo total amount

In this Section, graphs that display the different extraction methods ability to extract Ca, K and Mg compared to the pseudo total content in the different soils and horizons is presented. This is more or less equivalent with how much each method is able to extract, in percentage terms. The results are presented in Figure 8 and Figure 9.

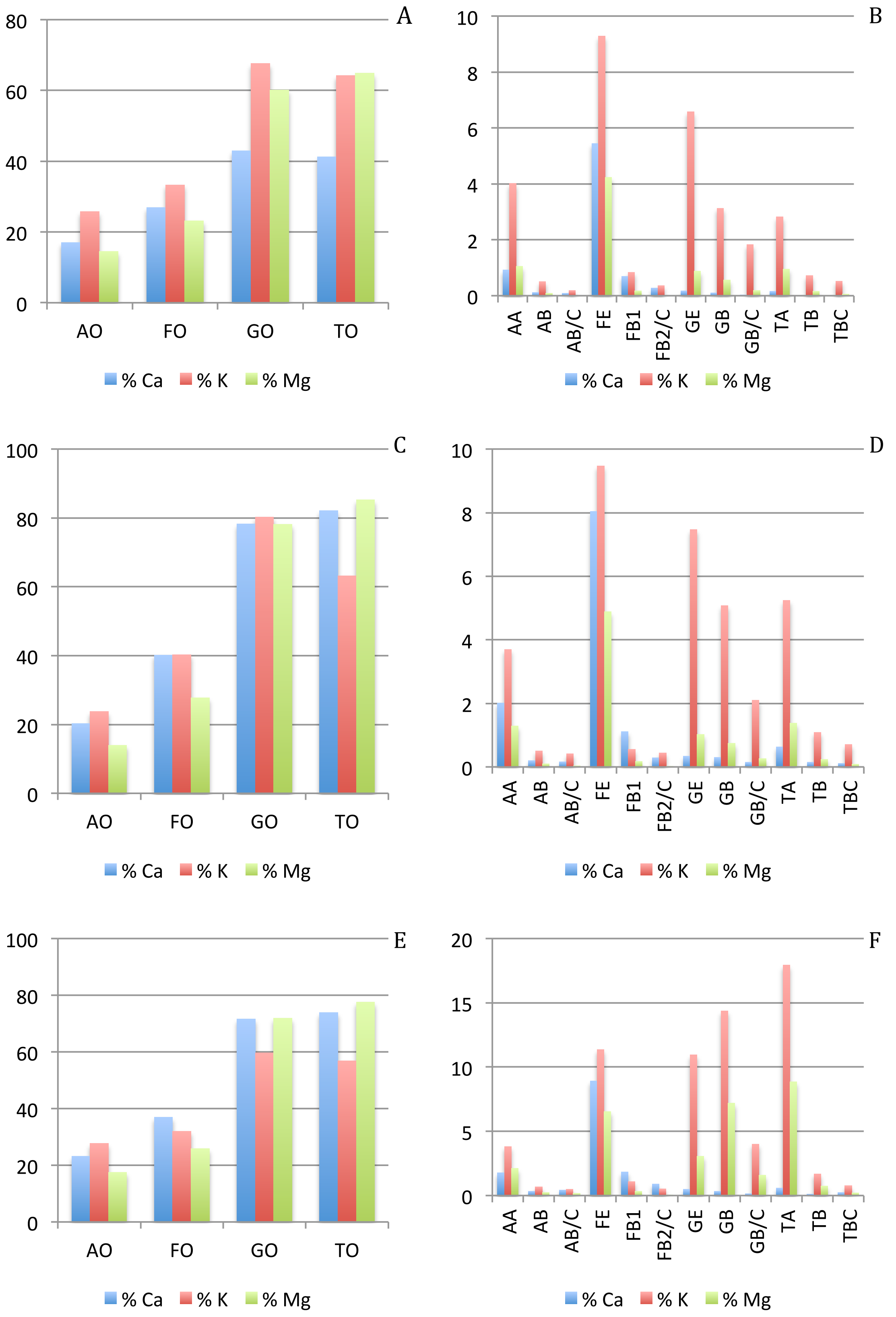

Figure 8. The percental extractions from the different extraction methods. A and B are NH_4OAc, C and D are $BaCl_2$, E and F are EDTA. Each method is divided into organic soils and mineral soils, which can be noted on the x-axis.

The percentage extracted of each base cation compared to the pseudo total amount by NH_4OAc, $BaCl_2$ and EDTA (Figure 8) shows that the greatest parts are extracted in the organic soils. Every method also shows an increasing trend of the percentage extracted from Asa, Flakaliden, Gislaved and Tönnersjöheden in the organic soils. The extraction of K by NH_4OAc stands out in the mineral soils, generally in the A- and E horizons (AA, FE, GE and TA) but also the upper part of the B horizon at Gislaved (GB) indicates higher amounts of K extracted. These trends seem to be true not only for NH_4OAc, but $BaCl_2$ and EDTA also demonstrates similar trends. Generally, NH_4OAc, $BaCl_2$ and EDTA extract very low percentages of Ca. It is only in the E horizon from Flakaliden (FE) that more than 2 % of the total pseudo amount of Ca is extracted.

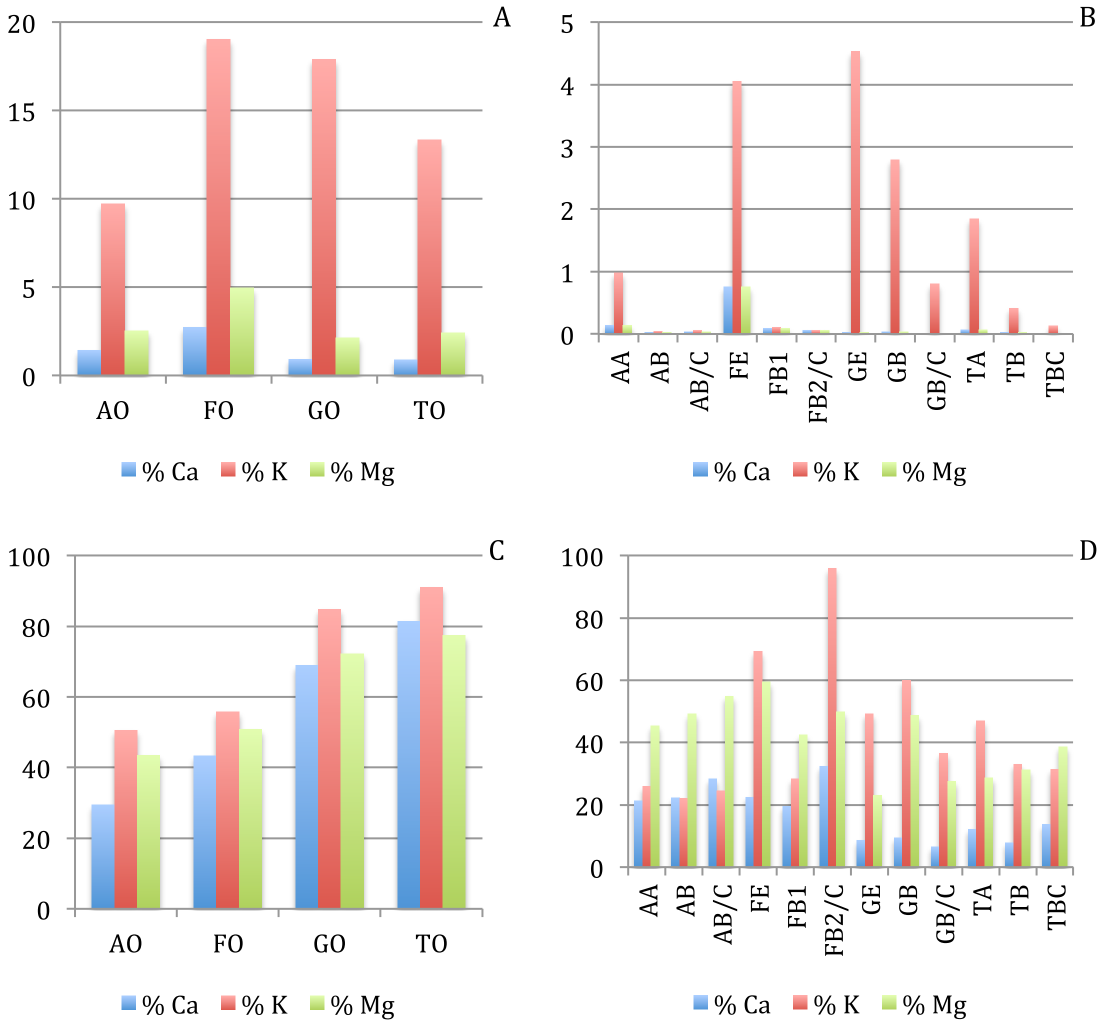

Figure 9. The percental extractions from water (A and B) and HCl (C and D). Each method is divided into organic soils and mineral soils, which can be noted on the x-axis.

In the percentage extracted of the pseudo total amount, performed with HCl and water (Figure 9) the results for water demonstrated that it is mainly K that water is able to extract, both in the organic and mineral soils. The percentage of Ca and Mg by water is very low, not even reaching one percent in mineral soils and under five percent in the organic soils.

Similarly as for NH_4OAc, $BaCl_2$ and EDTA, HCl shows an increasing trend in the percentage extracted from Asa, Flakaliden, Gislaved and Tönnersjöhedens organic soils. Generally in the organic soils, the largest percental extractions are of K, than Mg and lastly Ca. In the mineral soils the trends are different, but it is still K and Mg that is generally the most extracted, percentage wise.

5.2 COMPARISON BETWEEN METHODS

This chapter contains information about the similarities and differences between the different extraction methods. Various statistical analyses have been conducted on the large quantity of data received from the extraction methods. The results from these statistical analyses and comparisons between the methods are found in the coming sections.

5.2.1 T-test

The results from the t-test are divided into organic and mineral soils as well as for the different base cations examined. This was done to investigate if the extraction methods had any differences in extracting Ca, K, Mg and Na from the different type of soils. The results are presented in Table 5. “Yes” means that there is a statistical significant difference between the methods, and “No” means that there is not statistical a significant difference between the methods. In Table 5 the results from the t-test analysis on the organic soils are presented and in Table 6 the corresponding results for the mineral soils are presented.

Table 5. A summary of the t-test analysis for the organic soils. Yes means there is a statistical significant difference between the methods ability to extract the certain base cation and No means there is not a statistical significant difference. The tests were performed with a 95 % confidence interval.

Calcium	NH_4OAc	$BaCl_2$	EDTA	HCl	Water
NH_4OAc	-	Yes	Yes	Yes	Yes
$BaCl_2$	Yes	-	No	No	Yes
EDTA	Yes	No	-	No	Yes
HCl	Yes	No	No	-	Yes
Water	Yes	Yes	Yes	Yes	-
Potassium	NH_4OAc	$BaCl_2$	EDTA	HCl	Water
NH_4OAc	-	No	No	Yes	Yes
$BaCl_2$	No	-	No	No	Yes
EDTA	No	No	-	Yes	Yes
HCl	Yes	No	Yes	-	Yes
Water	Yes	Yes	Yes	Yes	-
Magnesium	NH_4OAc	$BaCl_2$	EDTA	HCl	Water
NH_4OAc	-	No	No	Yes	No
$BaCl_2$	No	-	No	No	No
EDTA	No	No	-	No	No
HCl	Yes	No	No	-	Yes
Water	No	No	No	Yes	-
Sodium	NH_4OAc	$BaCl_2$	EDTA	HCl	Water
NH_4OAc	-	Yes	N/A	Yes	No
$BaCl_2$	Yes	-	N/A	No	No
EDTA	N/A	N/A	-	N/A	N/A
HCl	Yes	No	N/A	-	Yes
Water	No	No	N/A	Yes	-

Table 6. A summary of the t-test analysis for the mineral soils. Yes means there is a significant statistical difference between the methods ability to extract the certain base cation and No means there is not a statistical significant difference. The tests were performed with a 95 % confidence interval.

Calcium	NH_4OAc	$BaCl_2$	EDTA	HCl	Water
NH_4OAc	-	Yes	Yes	Yes	No
$BaCl_2$	Yes	-	No	Yes	Yes
EDTA	Yes	No	-	Yes	Yes
HCl	Yes	Yes	Yes	-	Yes
Water	No	Yes	Yes	Yes	-
Potassium	NH_4OAc	$BaCl_2$	EDTA	HCl	Water
NH_4OAc	-	No	Yes	Yes	Yes
$BaCl_2$	No	-	Yes	Yes	Yes
EDTA	Yes	Yes	-	Yes	Yes
HCl	Yes	Yes	Yes	-	Yes
Water	Yes	Yes	Yes	Yes	-
Magnesium	NH_4OAc	$BaCl_2$	EDTA	HCl	Water
NH_4OAc	-	Yes	Yes	Yes	No
$BaCl_2$	Yes	-	Yes	Yes	No
EDTA	Yes	Yes	-	Yes	Yes
HCl	Yes	Yes	Yes	-	Yes
Water	No	No	Yes	Yes	-
Sodium	NH_4OAc	$BaCl_2$	EDTA	HCl	Water
NH_4OAc	-	Yes	N/A	Yes	Yes
$BaCl_2$	Yes	-	N/A	Yes	Yes
EDTA	N/A	N/A	-	N/A	-
HCl	Yes	Yes	N/A	-	Yes
Water	Yes	Yes	N/A	Yes	-

5.2.2 Linear regressions

The linear regressions have been divided into several sections. The soils have been separated into organic soils and mineral soils and to get a comparison between the methods ability to extract certain base cations, the linear regressions has also been divided into Ca, K, Mg and Na. The extraction methods that have been investigated with the linear regression are NH_4OAc, $BaCl_2$ and EDTA. The reason for comparing these methods to each other, and to not include the methods with water and HCl are several. The method with $BaCl_2$ is a common method that has been used for a long time in Sweden, while NH_4OAc has been widely used internationally. To compare these two methods with the more untested EDTA could give an indication to which tend to extract more base cations and if the correlations are good enough to recalculate data extracted with one method to fit the extractions with a different one.

The general linear regressions, where no consideration to individual base cations has been taken is presented in Figure 10.

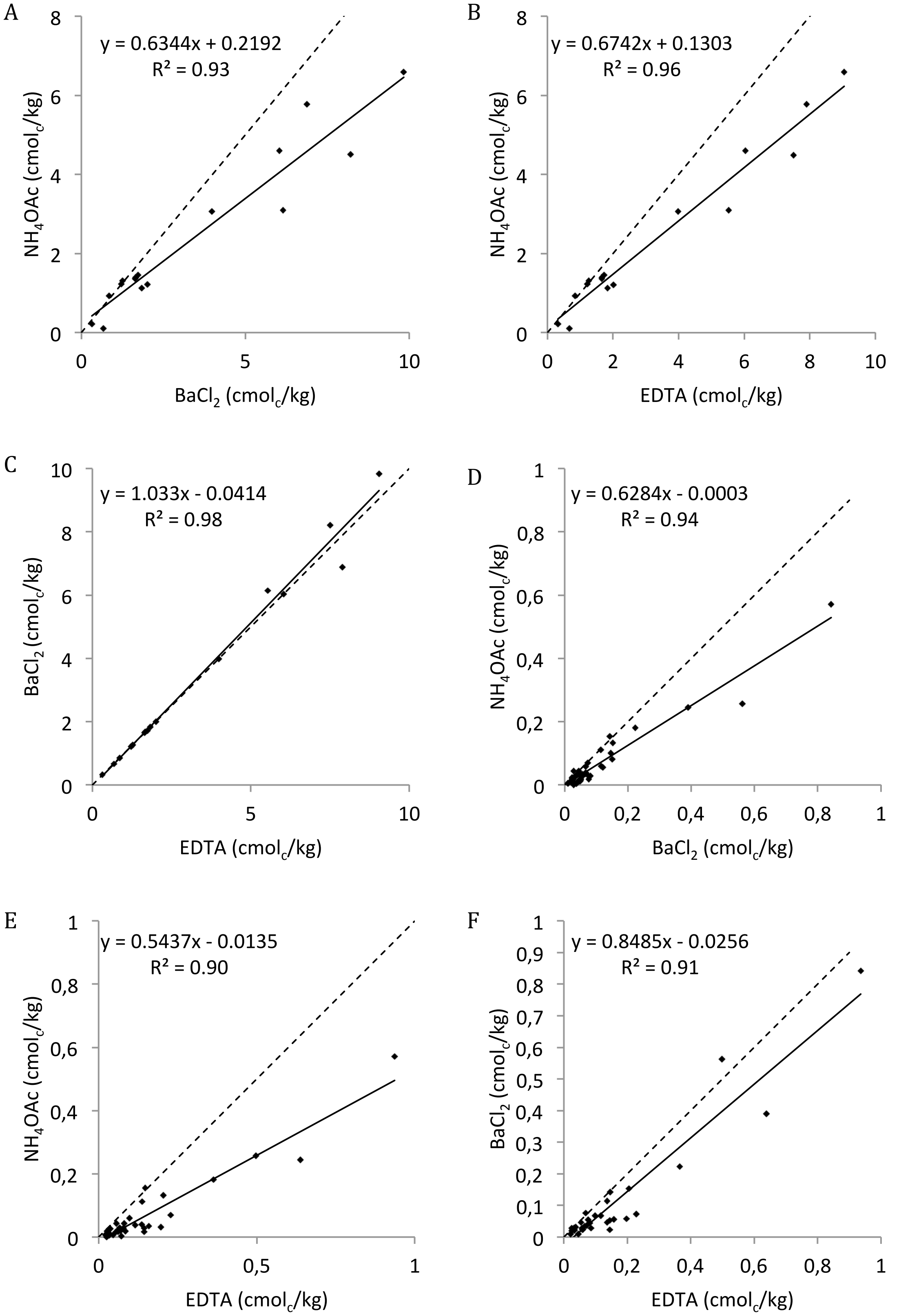

Figure 10. The linear regressions for all base cations divided into organic soils (A, B and C) and mineral soils (D, E and F). A describes the linear correlation between NH_4OAc and $BaCl_2$ in the organic soils, B the linear correlation between NH_4OAc and EDTA in the organic soils and C the linear correlation between $BaCl_2$ and EDTA in the organic soils. D, E and F describes the linear correlations in the mineral soil accordingly. The dotted line represents the 1:1 relationship between the methods.

The analysis with linear regression where no consideration to the different base cations has been taken (Figure 10) shows that the differences between the methods (observations of the slope of the curves) is greater at the mineral soils than in the organic soils. When comparing NH_4OAc vs. $BaCl_2$ in the organic soils, the slope of the curve is 0.6344 compared to 0.6284 for the mineral soils. The curve demonstrates that the trends are that NH_4OAc extracts 63.44 % of what $BaCl_2$ does in the organic soils and 62.84 % in the mineral soils. By doing a similar observation, EDTA and $BaCl_2$ are equivalent in their ability to extract base cations in the organic soils, and they are both better than NH_4OAc. Both EDTA and $BaCl_2$ are better than NH_4OAc in the mineral soils, and EDTA is better than $BaCl_2$, according to the linear regression. All of the regressions performed have an R^2-value above 0.90, which can be considered as a good fit, and that a linear trend is present among the methods.

5.2.2.1 Calcium

In Figure 11 the linear correlation between the methods ability to extract Ca is presented.

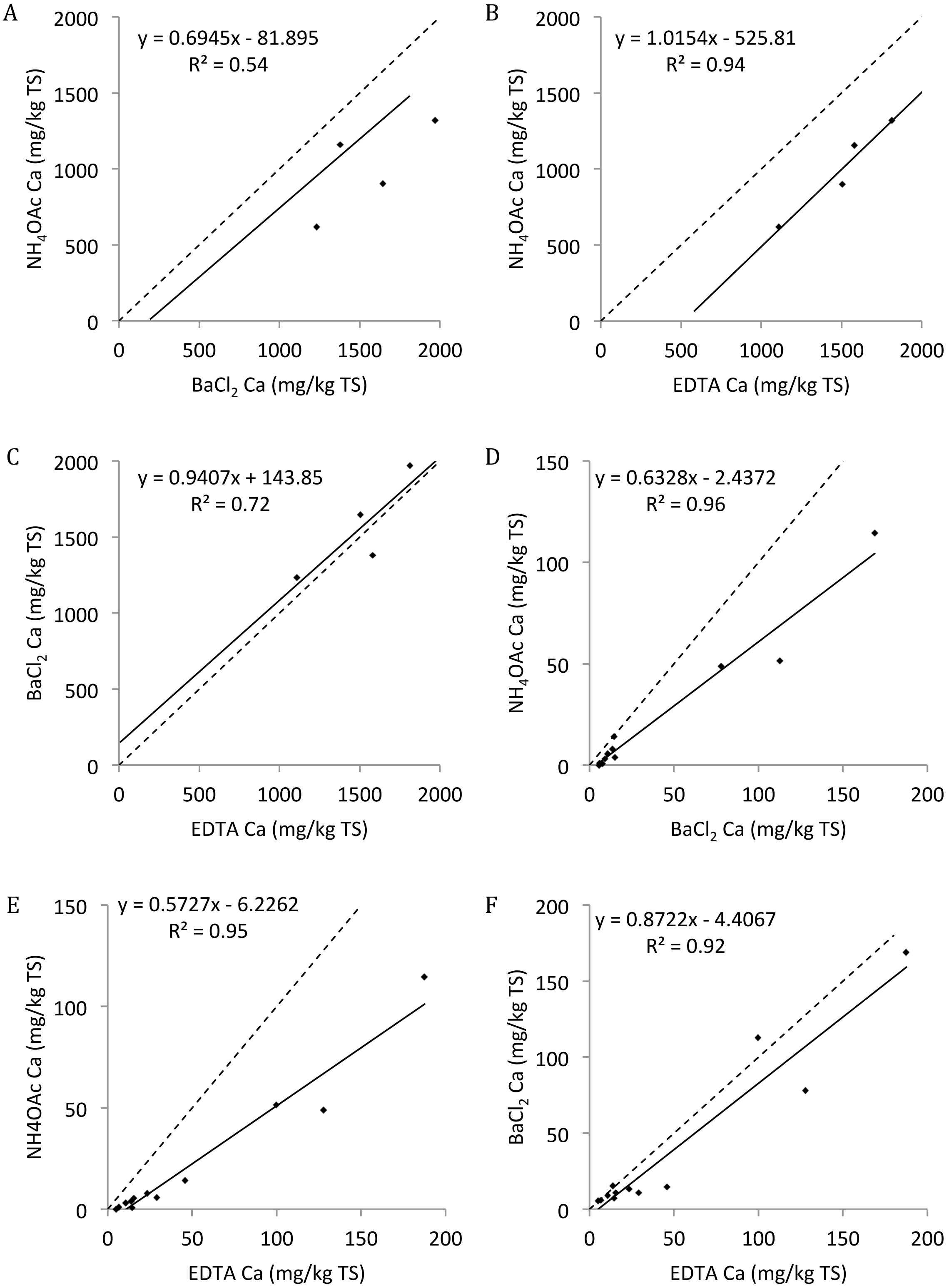

Figure 11. The linear correlations between the methods ability to extract Ca from the organic horizons (A, B and C) and from the mineral horizons (D, E and F). The dotted line represents the 1:1 ratio between the methods.

The linear regressions performed on the data from the Ca extractions (Figure 11) displays similar trends as the result for the general extractions. EDTA, $BaCl_2$ and

NH_4OAc is the order of decreasing effectiveness in extracting Ca. Due to the few data points in the regressions in the organic soils, the sturdiness decreases a lot. With a R^2-value at 0.54, the comparison between NH_4OAc and $BaCl_2$ in the organic soils indicate that there is no linear trend. However, since all of the data points are located below the dotted 1:1 ratio line, the result indicates that $BaCl_2$ is extracting more Ca than NH_4OAc. The results also displays that there are linear trends between the methods ability to extract Ca, but the available data from the organic soils makes it hard to interpret the results from the linear regressions in the organic soils.

5.2.2.2 Potassium

In Figure 12 the linear correlation between the methods ability to extract K is presented.

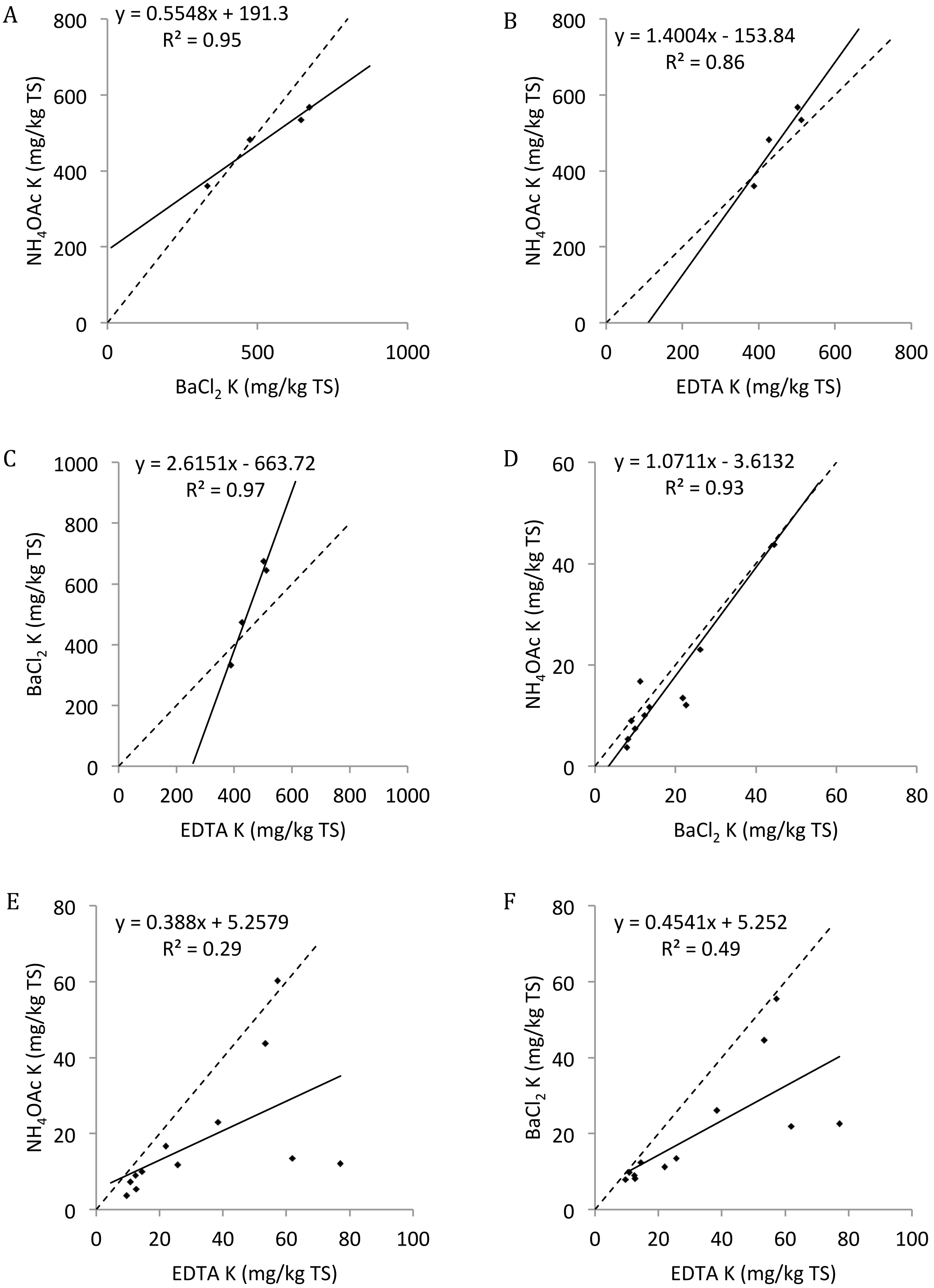

Figure 12. The linear correlations between the methods ability to extract K from the organic soils (A, B, and C) and from the mineral soils (D, E and F). The dotted line represents the 1:1 ratio between the methods.

The linear regressions performed on the data from the extractions of K shows that there are linear trends between the methods in the organic soils. However, when comparing

NH_4OAc and $BaCl_2$ to EDTA in the mineral soils, the R^2-value is 0.29 and 0.49, respectively. These values indicate that there is no linear trend between these methods. The regressions demonstrate that NH_4OAc and $BaCl_2$ are equal in their ability to extract K in the mineral soil, while the regressions in the organic soils are very sensitive, due to the few data points. Even though there seem to be no linear trend in the soils between NH_4OAc vs. EDTA and $BaCl_2$ vs. EDTA, when comparing the data available to the dotted 1:1 ratio line, it is evident that EDTA extracts more K than both $BaCl_2$ and NH_4OAc in the mineral soil.

5.2.2.3 Magnesium

In Figure 13 the linear correlations between the methods ability to extract Mg is presented.

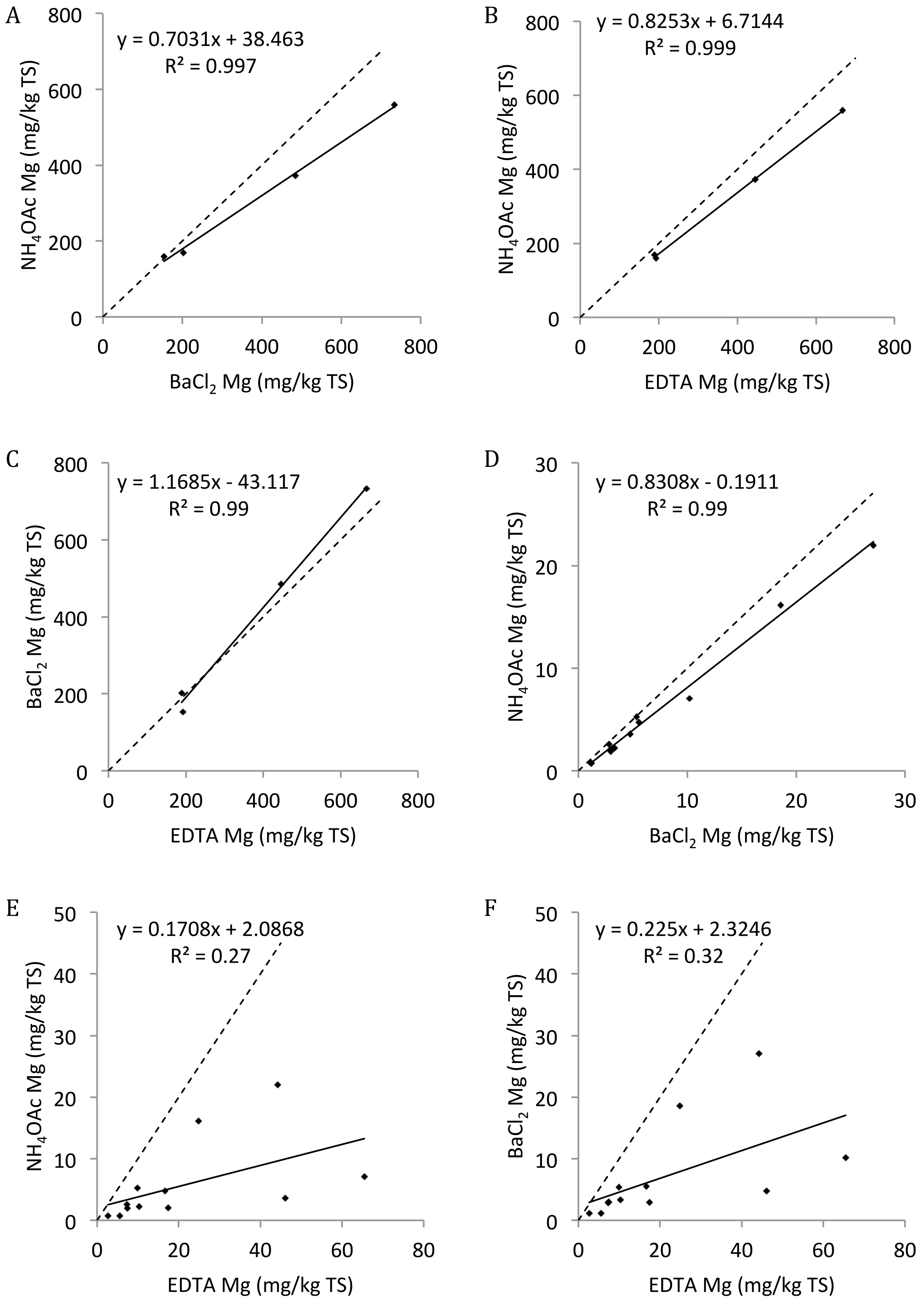

Figure 13. The linear correlations between the methods ability to extract Mg from the organic soils (A, B and C) and from the mineral soils (D, E and F). The dotted line represents the 1:1 ratio between the methods.

The linear regressions performed on the data from the Mg extractions (Figure 13) displays linear trends between the methods ability to extract Mg in the organic soils. In the mineral soils, however, the result is different. A linear trend between NH_4OAc and $BaCl_2$ is present with an R^2-value of 0.99. The linear trends between NH_4OAc vs. EDTA and $BaCl_2$ vs. EDTA show that there is no linear trend.

5.2.2.4 Sodium

In Figure 14 the linear correlations between the methods ability to extract Na is presented.

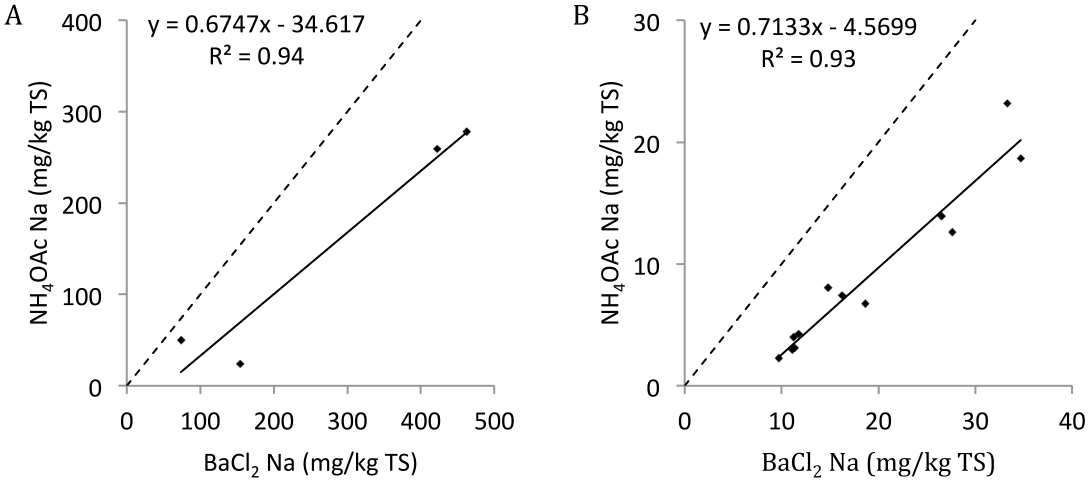

Figure 14. The linear correlations between the methods ability to extract Na from the organic soils (A) and the mineral soils (B). The dotted line represents the 1:1 ratio between the methods.

The linear regression analysis on the data from the Na extractions displays a linear trend between NH_4OAc and $BaCl_2$ in the organic and mineral soil (Figure 14). It also displays that $BaCl_2$ is better at extracting Na than NH_4OAc.

6 DISCUSSION

The results from the different extraction methods, the statistical analyses and their connection to various site-specific parameters are discussed in the sub chapters below. Different arguments to why the results turned out the way they did will also be put forward.

6.1 EXTRACTIONS

The different extraction methods follow some similar trends. The most obvious is that water extracts the least amount of every base cation; HCl the second largest amount of every base cation and aqua regia extracts the largest amount of every base cation. The other methods (NH_4OAc, $BaCl_2$ and EDTA) take turns in which of them is the most successful extractor, depending on which base cation and what soil that is examined.

The difference between the methods is most pronounced in the mineral soils, where HCl is the dominating extractor of all the different base cations. Generally EDTA, $BaCl_2$, NH_4OAc and water follows in decreasing order of effectiveness. When comparing the amount of base cations extracted with the total carbon content of the soil, the trend is the more C, the more base cations is extracted by all the different methods except HCl and Aqua Regia. By this simple comparison a conclusion that the base cations extracted by NH_4OAc, $BaCl_2$, EDTA and water are mainly bound to the organic matter in the soil. However, the organic soils contain in the order of 30 times more total carbon, yet NH_4OAc, $BaCl_2$, EDTA and water does not extract 30 times more base cations from the organic soils compared to the mineral soils. Other factors that contribute to the large differences between the organic soils and the mineral soils are pH and the mineralogy of each soil (Eriksson, 2011).

The organic horizon samples have a lower pH compared to the underlying horizons. Since the organic soils contain more total carbon, and therefore more variable charges (Eriksson, 2011), the pH plays a more important role in the organic soils compared to the mineral soils. When the soil has a lower pH, the variable surface charges of the organic material is less negatively charged than at a higher pH. More negative charged surface contributes to the bonding of positively charged base cations. A soil with large quantities of organic matter, and a relatively high pH should result in the extraction of larger amounts of base cations, especially the divalent base cations Ca^{2+} and Mg^{2+} which bond stronger to the organic matter than the monovalent, K^+ and Na^+ (Sparks *et al.*, 1996).

A trend evident at every location is an increase of the pseudo total amount of most base cations with depth. When looking at the pseudo total amount of base cations, extracted with Aqua Regia, the lowest horizons seem to contain the largest amount of base cations. This can be explained by weathering, or the lack of it. The top-most horizons are subject to greater weathering, which produce more base cations from the parent material, which are either leached or taken up by vegetation (Eriksson, 2011).

As mentioned earlier, Aqua Regia, HCl, EDTA, $BaCl_2$, NH_4OAc and water is the general trend in decreasing order of extraction effectiveness throughout all extractions. However, there are some exceptions. In the extraction of K, $BaCl_2$ are almost identical, and often an inferior extractor, compared to NH_4OAc, which does not occur in the extractions of the other base cations. The capacity of the NH_4^+ ion as an adequate extractor of K^+ has been studied thoroughly in different articles (Pratt & Holowaychuk, 1954; Borge, 1997; Luer & Bohmer, 2000). Other phenomenon that occurs in the extraction of K is that water is able to extract a considerable amount of K. The reason for this disparity is the weak bond K has to organic matter (Eriksson, 2011). The extraction of K with water in the mineral soil can be regarded to have a direct correlation with the organic material in the soil, since it is a too weak extraction agent to be able to extract K that is bound to minerals. The weak bond between K and organic matter can also explain why NH_4OAc is able to extract as much K as $BaCl_2$. The NH_4^+-ion has a very similar ion radius as K (Eriksson, 2011) which also contributes to why NH_4OAc is able to extract some fixed K. The extraction of K by NH_4OAc and $BaCl_2$ is mainly from the organic matter. The K that is bound between e.g. 2:1 clay minerals is probably difficult for the different methods, except HCl (Andrist-Rangel *et al.*, 2013) and Aqua Regia (Andersen & Kisser, 2004), to force into solution. Since the ratio between the amount of extraction agent and organic matter in the mineral soils increase, even a weaker method such as water and NH_4OAc is able to extract a considerable amount. Another reason why NH_4OAc often is better at extracting K than $BaCl_2$ might be some kind of anion effect. The acetate ion may contribute in the extraction of K at a larger extent than the Cl^- ion.

The reason why EDTA generally extracts more base cations than water, NH_4OAc and $BaCl_2$, even in the mineral soils where there is low amounts of organic matter is due to its chelating abilities. The EDTA is better at extracting base cations from the organic matter and even when there are low amounts of organic matter present in the mineral soils, it is not negligible. Another reason might depend on the weathering effect of EDTA. EDTA might be able to weather low-grade minerals with high weatherability, and thereby releasing base cations. Direct comparisons between all of these methods does not exist in the literature, however, studies on the comparisons between some of the methods (Pratt & Holowaychuk, 1954; Barrows & Drosdoff, 1958; Vanbladel *et al.*, 1975; Faulkner *et al.*, 2001; Karltun, 2001) and studies on the individual methods e.g. Manouchehri *et al.*, (2006) corresponds with the results obtained in this study.

The sequential analysis was made to illustrate the difference between the methods and to investigate whether a chain of extractions would extract more base cations than a single method. In Figure 7, the different extractions with the sequential analysis are presented. The general trend is that HCl is extracting the vast majority of the base cations in the mineral soil while water, NH_4OAc and EDTA is able to extract a considerable amount of the different base cations in the O horizon (TO). The general result from the sequential analysis is that a single method actually extracts more base cations than a chain of methods. The reason for this is probably due to the buffered extraction agents NH_4OAc and EDTA. Since the analysis is performed on the same soil by all the methods, some residues from every extraction agent in the chain are inevitable. Both NH_4OAc and EDTA are buffered to alkaline pH, which make the soil alkaline. This probably affects the effectiveness of the HCl extraction, which is utilizes the acid properties to extract the base cation (Andrist-Rangel *et al.*, 2013). Another interesting observation is that the EDTA always is able to extract more base cations after the extraction of NH_4OAc is done. This indicates that the EDTA is able to target both the same kind of base cations as NH_4OAc and also different ones, which the NH_4OAc is not able to extract. In the organic soils, the last extraction method, HCl, is able to extract additional base cations. This also indicates that NH_4OAc, EDTA and HCl target both the same base cations and also that HCl is able to target some base cations that NH_4OAc and EDTA is not able to extract. These base cations are probably bound to minerals, which the HCl is able to dissolve.

In the sequential analysis of Mg in the organic soil (TO), HCl is almost not able to extract any additional Mg. This indicates that EDTA probably is an equally good extraction agent as HCl when it comes to extracting Mg in the organic soil. This is supported in Tönnersjöhedens (TO) and Gislaveds (GO) O horizon but not in Asas (AO) or Flakalidens (FO) as seen in Figure 5. This might be explained by the pH of the different soils. GO and TO has lower pH than AO and FO, which implies that a lower amount of Mg is bound to the variable charges. It might be easier to extract the majority of the Mg^{2+} ions if there are fewer available to extract. This would also indicate that most of the Mg extracted is bound to organic material. This, in turn, indicates that HCl is not able to extract hardly any Mg from its mineral form.

6.1.1 Percentage extracted of pseudo total amount

The percentage extracted with the different methods indicates some interesting trends. Among the organic soils the extractions made in Asa yield the least amount of base cations, seen as a percentage of the pseudo total amount. Flakaliden, Gislaved and finally Tönnersjöheden follow in an increasing order of percental amount of extracted base cations.

In the mineral soils, potassium is generally the base cation that is extracted to the largest extent, percental wise. All of the methods demonstrate similar results with greater percental extractions in the A/E horizons and lower percental extractions in the deeper B horizons. Especially the water extraction stands out in its ability to extract potassium. Even though it extracts a low percental amount of K, compared to the other base cations (Ca and Mg) it extracts multiple more. The reason for waters seemingly great ability to extract K, even from the mineral soils has an explanation. K has a very weak bond to organic matter. The K that is extracted by water can be assumed to have its origin in the organic matter. This is probably also true for the K extracted by the other methods, and the reason for their more successful (both in absolute and percental) extraction is due to their suppressing and chelating abilities, which are far greater than the waters.

Perhaps the most interesting percental results are the ones from the HCl extractions. The general trends in the organic soils are that the Ca is the least extracted base cation; K is the most extracted while Mg places in between the other two ions, seen as extracted part of the pseudo total content. The HCl method is usually used to examine the K content of a soil by releasing fixed K from e.g. 2:1 clay minerals (Andrist-Rangel *et al.*, 2013). However, in the organic soils most of the base cations can be expected to be held by the electrostatic surface charges of the organic material. Since the divalent base cations (Ca^{2+} and Mg^{2+}) have a higher charge than the monovalent base cations (K^+ and Na^+), they bind stronger to the surface of the organic material such as humus. K has a very weak bond to organic material; this could be one reason to why K is the most extracted ion while Ca and Mg are the less extracted ones, percental to the pseudo total content. In the mineral soils the trends are a bit different. In Asa, the highest percental extraction is Mg, in Gislaved it is K and in Flakaliden and Tönnersjöheden it is divided fairly equally between K and Mg. A general trend for all of the locations however, is that Ca is always the least extracted base cation, percental wise. The reason for this is because the mineral Ca is by far the most common (Eriksson, 2011). This, together with a small radius and high charge, giving it a high charge to radius ratio makes it the least cation extracted, percental wise.

6.2 COMPARISON BETWEEN METHODS

This chapter discuss the results from the comparison of the different methods. The discussion is mainly focused on the t-test and the linear regression analyses.

6.2.1 T-test

The general results from the t-test indicate that there is a bigger difference between the extraction methods ability to extract base cations in the mineral soil, Table 6, versus the organic soils, Table 5. The only statistical significant differences in the organic soils are between the extractions with water and the rest of the extraction methods. The result is not surprising since all of the methods, except the water method, are extracting substantial amounts of base cations from the organic matter. What might be more surprising is that HCl does not exhibit a statistical significant difference in the organic soil. The results from the HCl extractions in the organic horizons generally demonstrates larger amount of extracted base cations, however, the logarithmic values does not indicate a large enough variance between the different methods to obtain a statistical significant difference. One explanation is that the analysis is performed on the soils from all the different locations. Even though some soils, such as the organic soil from Tönnersjöheden indicate substantial differences between the ability to extract e.g. Ca between HCl and NH_4OAc, other soils, such as the organic soils in Gislaved has a less of a difference in the ability to extract Ca between NH_4OAc and HCl. The analysis is also performed on a few data, which affects the result of the t-test.

The differences between the methods in the mineral soil are more pronounced. HCl has a statistical significant difference between itself and all of the other methods, regardless of which of the base cations it extracts. The same is true when investigating the difference between the water method and the rest of the methods, with one exception. When comparing the difference in the ability to extract Ca between NH_4OAc and water, the result is no statistical significant difference. This might not be as odd as it looks. When looking closer on Figure 7, the results from the extractions in the mineral soils indicate that NH_4OAc and water extract low amounts of Ca. Even though NH_4OAc extracts more Ca percentage wise in every mineral soil examined, the differences in absolute extracted Ca are not great enough to be defined as a statistical significant difference.

6.2.2 Linear regressions

The results from the linear regressions where no consideration to the different base cations have been taken are presented in Figure 10. The comparison between the methods has been limited to NH_4OAc, $BaCl_2$ and EDTA. The reason for not including Aqua regia, HCl and water in the comparison is that they are regarded as "end members", while Aqua regia delivers the pseudo total content. Both NH_4OAc and $BaCl_2$ have been used for several years, while EDTA is a more rarely used method that turned out to have similar results as NH_4OAc and $BaCl_2$.

In the organic soils, the coefficient of multiple determination (R^2) is between 0.93-0.98, which can be considered as a reasonable fit. Some conclusion can therefore be drawn from these linear regressions. In the comparison between NH_4OAc and $BaCl_2$ the slope of the curve is 0.63. This implies that the trend between the methods is that NH_4OAc extracts 63 % of what the $BaCl_2$ does. A comparison between the data points and the dotted line (1:1 ratio line) indicates that almost all points are located beneath it, which signifies that $BaCl_2$ extracts more base cations than NH_4OAc. When comparing the ability of NH_4OAc and EDTA to extract base cations in the organic soils, a similar trend as NH_4OAc vs. $BaCl_2$ can be seen. The slope of the trend line is 0.67, which implies that NH_4OAc extracts 67 % of what the EDTA does. A comparison between the 1:1 ratio line and the data points reveals that the EDTA extracts more base cations at almost every point. Since the NH_4OAc vs. $BaCl_2$ and NH_4OAc vs. EDTA had similar results, it is expected that the comparison between the $BaCl_2$ and EDTA also has an excellent fit, R^2=0.98. The slope of the line is 1.03, which indicates that the two methods are very similar in their ability to extract base cations from the organic soils. Although there are few values from the organic soils, the linear regressions give an indication that the EDTA and $BaCl_2$ are equal in their ability to extract base cations from the organic soils, and that they are both superior methods compared to NH_4OAc.

When comparing NH_4OAc, $BaCl_2$ and EDTA in the mineral soil, Figure 10, the data is a bit more scattered, with a lower R^2 as a result. However, the R^2 is still above 0.9 for all of the comparisons, which indicates that there is a clear linear correlation between the methods. When comparing NH_4OAc and $BaCl_2$ the slope and 1:1 ratio line indicates that $BaCl_2$ is better at extracting base cations and that NH_4OAc extracts, similar to the extractions in the organic soil, 63 % of what the $BaCl_2$ does. When comparing NH_4OAc and EDTA, the trend indicates that EDTA extracts almost double the amount of what the NH_4OAc does. The last general comparison in the mineral soil is between $BaCl_2$ and EDTA. The results from the regression displays EDTA as a more potent extraction agent. The slope of the trend line predicts that $BaCl_2$ extracts 85 % of what the EDTA extracts.

As a summary, the trend indicates that EDTA and $BaCl_2$ are equal in their ability to extract base cations in the organic soils, and that they are both extracting roughly 55 % more than NH_4OAc. In the mineral soil, the trend indicates that EDTA extracts 18 % more than $BaCl_2$, which in turn extracts almost 60 % more than NH_4OAc.

6.2.2.1 Calcium

The linear regressions between the methods ability to extract Ca from the organic soils provides a bad fit with a R^2 between 0.54-0.94. From graph A, B and C in Figure 11, the trends are presented. The comparison between NH_4OAc gets a R^2 of 0.54, which is considered to not be a reasonable value. However, some information is attainable from the graph. When comparing the data with the 1:1 ratio line, it is obvious that all of the points are located beneath it, indicating that $BaCl_2$ is extracting more Ca than NH_4OAc in every O horizon. The comparison between NH_4OAc and EDTA has a R^2 of 0.94, indicating a good linear fit between the methods. The trend of the data indicates that EDTA extracts roughly 500 mg/kg TS more than the NH_4OAc at every point. The comparison between $BaCl_2$ and EDTA also has a fairly low R^2, 0.74. From the slope of the graph and with a comparison between the data and the 1:1 ratio line, a conclusion that the methods are equal in their ability to extract Ca in the organic soils can be drawn.

The regressions between the methods ability to extract Ca from the mineral soils contain more data and has a better fit, R^2 between 0.92-0.96. Similar to the earlier discussions, comparisons between the methods indicate that $BaCl_2$ is better than NH_4OAc and EDTA is better than $BaCl_2$ to extract Ca.

6.2.2.2 Potassium

The linear regressions, presented in Figure 12, display some interesting trends. The regressions performed on the data from the organic soils have a reasonable R^2, between 0.86-0.97. However, since the regression is constructed with few data, the slope of the trend line is very sensitive. Since the sensitivity of the trend line is very high, a comparison between the data points and the 1:1 ratio line might be a better investigation. The data points are roughly scattered around the 1:1 ratio line, wherefore a conservative comparison is that the methods are equal in their ability to extract potassium from the organic soils. This result is confirmed by the results from the t-test in Table 5.

The comparisons between the NH_4OAc and $BaCl_2$ can be regarded to have a very similar ability to extract potassium in the mineral soil. The comparison between NH_4OAc vs. EDTA and $BaCl_2$ vs. EDTA has a very low R^2. This might be due to two outliers in the EDTA data. If these data points were removed, the linear trend would increase dramatically and would result in a less difference between the methods.

6.2.2.3 Magnesium

The comparison between the different methods ability to extract Mg follow a different trend as for the other base cations. In the organic soils, Figure 13, $BaCl_2$ has the highest capability to extract Mg, EDTA the second best and NH_4OAc has the least ability. As for the other comparisons in the organic soils, there is few data. This is probably one of the reasons, the variance in the data being another, why the t-test declares that there is no statistical significant difference between the methods. However, when comparing the data points in each graph for the organic soils with the 1:1 ratio line, it is obvious that EDTA and $BaCl_2$ extracts more Mg than NH_4OAc, while the difference between $BaCl_2$ and EDTA is ambiguous.

In the mineral soil the trends are more distinguished. In agreement with the t-test, the linear regression displays small differences between NH_4OAc and $BaCl_2$. However, when looking at the comparisons between NH_4OAc vs. EDTA and $BaCl_2$ vs. EDTA, the differences is evident. In both cases, the EDTA extracts more Mg in the mineral soil.

6.2.2.4 Sodium

The comparison between the methods ability to extract sodium is only performed on NH_4OAc and $BaCl_2$. The reason for not including EDTA in the comparison is because the EDTA solution was buffered with NaOH, which yields contamination of Na in the extraction.

When comparing NH_4OAc and $BaCl_2$ in the organic soil, the trend is that $BaCl_2$ extracts more Na, which the t-test also confirms. When examining the data closer, it is evident that the extraction data has a large variance, which smoothens out the difference between the methods.

The difference in the methods ability to extract Na in the mineral soil is supported by both the t-test and the linear regression. The linear trend indicates that $BaCl_2$ extracts almost 50 % more Na than NH_4OAc in the mineral soils.

In a comparison between NH_4OAc and $BaCl_2$ performed by Karltun (2001), regressions conducted with Partial Least Square (PLS) regressions displays similar results as the ones obtained in this thesis. Karltun argued that the methods do have linear correlations in their abilities to extract base cations, although $BaCl_2$ seems to be the better extractor of bivalent cations in both the organic material and the mineral soils. The exception found was that $BaCl_2$ is not more effective in its ability to extract Mg in the mineral soil, which this study however concluded that it is, both through the t-test and the linear regressions.

Some finishing general discussion

Depending on which of the methods used, the estimation of the base cation stores differ. To get a proper estimation of the available supply, it is important to choose a method that is able to extract as much of the exchangeable base cations as possible, otherwise there is a risk of underestimating the stores. The total stores of base cations are significantly larger than both the plant available and exchangeable supply and, especially in the mineral soil. The availability of base cations from the total stores is determined by how fast different weathering processes affect the minerals of the soil rather than the actual size of the total store. Since the weathering of minerals in the soil is a very slow process, it is even more crucial to get a precise estimation of the plant available store.

A critical question is whether the plant available base cations will be depleted, in other words if the weathering and deposition is able to contribute enough base cations to the system in such a rate that the losses from tree uptake, leaching and soil erosion is balanced with the increase. The starting point of this mass balance is the knowledge of what is already available.

7 CONCLUSIONS

- Aqua Regia, HCl, EDTA, $BaCl_2$, NH_4OAc and water is the general order of decreasing ability to extract base cations from both the organic soils and mineral soils.

- EDTA, $BaCl_2$, NH_4OAc and water extracts the largest amount of base cations from the organic horizons. The amount of extracted base cations by these methods decreases with depth and carbon content of the soil.

- The statistical analysis with t-test displays that the differences between the examined methods ability to extract base cations are greater in the soils from the mineral horizons than in the soils from the organic horizons.

- There are linear correlations between EDTA, $BaCl_2$ and NH_4OAc, which indicates that EDTA and $BaCl_2$ are equivalent and both better than NH_4OAc at extracting base cations in the soils from the organic horizons. In the soil from the mineral horizons the trends illustrate that the order of decreasing effectiveness is EDTA, $BaCl_2$ and NH_4OAc.

- The use of NH_4OAc and $BaCl_2$ as extraction methods in podzolic mineral soils may underestimate the supply of base cations in the soil.

- The most effective extraction method for the determination of exchangeable base cations in the examined soils is EDTA.

8 IMPLICATIONS

The current standardized methods ($BaCl_2$ and NH_4OAc) may underestimate the amount of base cations in primarily the mineral soils. In the soil from the organic horizons, the different methods extract similar amounts of base cations. Depending on several reasons such as cost, time efficiency, labour required and environmental reasons one could argue for or against which of the examined extraction methods are most suitable to use when examining the nutritional status of soil. The results derived from this master thesis could be the basis for further full scale projects or decisions concerning which method is most suitable to use when creating a better picture of both short and long term available base cations in our Swedish woodlands. There are still many questions regarding the availability of base cations left unanswered, but these results can hopefully aid future research.

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APPENDIX

Below is the data from all of the extractions at all locations.

NH4OAc	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
AO	1157.08	360.97	159.74	49.96
AA	51.50	60.30	21.99	23.16
AB	7.73	9.00	2.59	8.03
AB/C	5.70	3.68	0.76	6.74
FO	1319.42	533.56	169.39	24.11
FE	114.53	43.69	16.12	3.12
FB1	48.96	16.74	5.29	2.93
FB2/C	14.06	10.02	0.74	2.29
GO	901.46	568.31	372.85	259.11
GE	5.58	23.05	4.75	7.41
GB	3.17	13.47	3.57	4.24
GB/C	1.03	11.74	2.07	3.99
TO	618.97	481.74	558.55	278.44
TA	3.86	12.15	7.08	18.68
TB	0.08	5.39	2.22	12.62
TBC	0.83	7.38	1.91	13.91

BaCl2	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
AO	1379.53	332.34	153.66	73.56
AA	112.66	55.54	27.09	33.28
AB	13.42	9.03	2.84	14.82
AB/C	10.68	7.95	1.19	18.62
FO	1970.76	645.26	202.47	154.10
FE	168.83	44.52	18.56	11.39
FB1	77.97	11.23	5.37	11.10
FB2/C	14.65	12.37	1.15	9.70
GO	1644.85	673.99	484.85	422.20
GE	10.78	26.13	5.54	16.27
GB	9.20	21.83	4.75	11.76
GB/C	5.95	13.47	2.91	11.26
TO	1232.08	474.04	733.11	461.95
TA	15.21	22.56	10.20	34.68
TB	5.60	8.18	3.32	27.65
TBC	7.42	9.89	3.00	26.50

EDTA	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
AO	1582.10	387.60	192.29	
AA	99.76	57.25	44.28	
AB	23.26	12.50	7.24	
AB/C	28.92	9.59	5.61	
FO	1813.22	512.04	189.15	
FE	187.59	53.43	24.90	
FB1	127.81	22.05	9.95	
FB2/C	45.78	14.42	2.63	
GO	1503.39	501.94	446.03	
GE	15.45	38.37	16.59	
GB	10.87	61.86	46.08	
GB/C	6.61	25.71	17.46	
TO	1109.20	426.43	667.29	
TA	13.82	77.11	65.46	
TB	5.01	12.65	10.29	
TBC	14.39	10.72	7.40	

H2O	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
AO	96.07	135.92	27.83	22.25
AA	7.83	14.68	8.49	13.15
AB	2.10	0.79	2.15	5.53
AB/C	2.51	1.10	1.34	4.43
FO	133.68	304.73	36.16	20.79
FE	15.92	19.07	6.96	6.04
FB1	6.28	2.19	2.44	3.04
FB2/C	3.02	1.59	1.07	2.50
GO	19.52	150.39	13.27	129.65
GE	0.96	15.87	6.48	11.35
GB	1.11	12.01	4.58	9.15
GB/C	0.45	5.15	1.60	5.15
TO	13.35	99.98	20.79	123.87
TA	1.65	7.96	4.66	16.70
TB	1.02	3.09	2.48	12.87
TBC	0.87	1.81	1.70	10.17

HCL	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
AO	2007.23	707.85	478.20	147.81
AA	1190.64	388.62	953.20	181.26
AB	1472.13	397.81	1427.01	134.84
AB/C	1839.99	465.83	1811.32	122.05
FO	2124.18	892.95	371.44	155.66
FE	472.42	325.75	225.98	178.54
FB1	1370.17	567.31	1273.56	136.29
FB2/C	1650.86	2684.43	2391.48	191.58
GO	1446.84	712.45	448.07	296.47
GE	274.19	172.47	124.22	135.34
GB	293.79	257.81	311.68	119.72
GB/C	269.50	234.19	302.68	109.16
TO	1220.23	682.83	665.46	330.08
TA	290.89	202.11	212.01	114.02
TB	296.99	248.13	437.19	107.95
TBC	862.37	440.05	1392.68	106.40

Aqua regia	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
AO	6800	1400	1100	<570
AA	5600	1500	2100	<280
AB	6600	1800	2900	<280
AB/C	6500	1900	3300	<280
FO	4900	1600	730	<570
FE	2100	470	380	<280
FB1	7000	2000	3000	460
FB2/C	5100	2800	4800	430
GO	2100	840	620	<590
GE	3200	350	540	<280
GB	3100	430	640	<280
GB/C	4100	640	1100	<280
TO	1500	750	860	<590
TA	2400	430	740	<280
TB	3800	750	1400	<280
TBC	6300	1400	3600	490

Sequential analysis				
H2O	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
TO_SEK	17.72	105.05	21.54	130.79
TA_SEK	1.89	8.72	4.72	15.43
TB_SEK	0.99	2.50	2.30	11.05
TBC_SEK	0.82	1.84	1.51	9.98
NH4OAc	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
TO_SEK	562.97	343.22	504.29	161.30
TA_SEK	4.23	10.70	5.10	5.09
TB_SEK	0.65	4.97	0.97	4.12
TBC_SEK	0.89	5.95	0.69	6.50
EDTA	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
TO_SEK	417.38	54.93	115.79	
TA_SEK	7.22	33.44	28.04	
TB_SEK	2.76	7.23	5.70	
TBC_SEK	9.25	5.21	3.84	
HCl	Ca (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)
TO_SEK	130.22	108.68	45.68	
TA_SEK	179.28	150.70	116.13	
TB_SEK	182.98	214.87	287.49	
TBC_SEK	696.23	444.51	754.01	