From minerals to trees: Reducing uncertainty in estimating weathering rates for sustainable forest growth

Sophie-Charlotte Casetou-Gustafson
Faculty of Forest Sciences
Department of Ecology
Uppsala

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Cover: Forest soil pit at Flakaliden.
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Abstract

Sustainable forest growth is fundamentally dependent on long-term supply of nutrients from mineral dissolution. Over the past century, losses of base cations (Ca, K, Mg, Na) from forest soils have been accelerated through increased forest production and anthropogenic acidification. Substantial uncertainties about the accuracy in weathering rate estimates has hampered designation of appropriate levels for maintaining sustainable forest production. The aim of this thesis was to improve the accuracy of estimates by using better mineralogical data inputs to a frequently applied weathering estimation model (PROFILE) and by comparing weathering rates derived from three different methods that differ conceptually, based on harmonised input data and boundary conditions. A new site-specific approach for calculating indirect quantitative soil mineralogy with the "Analysis to Mineralogy" ('A2M') model was developed, by direct determination of the mineralogical input data to A2M. Overall, A2M-derived quantitative mineralogy reproduced the main pattern of "reference" mineral contents (measured directly by X-ray powder diffraction (XRPD)). An exception to this was observed for major K-bearing minerals in the regional quantitative A2M mineralogy. Regardless of these observed discrepancies, PROFILE weathering estimates were uncertain irrespective of the type of mineralogical input data that was used. For Ca and Mg, uncertainties arose from lack of knowledge about presence or absence of specific minerals characterised by high dissolution rates (*i.e.* apatite, amphibole, pyroxene, calcite and illite). For K and Na, uncertainties related to use of inaccurate dissolution rate coefficients for dioctahedral mica and plagioclase. Overall, the PROFILE model and the depletion method were shown to estimate present-day and long-term weathering rates of Ca and Mg with reasonable accuracy. Comparisons of weathering rates in a base cation budget showed that trees take up base cations from forest soils, at least when growing intensively, probably from sources other than weathering.

Keywords: Weathering, Soil minerals, Base cations, Sustainable forest growth.

Author's address: Sophie-Charlotte Casetou-Gustafson, SLU, Department of Ecology, P.O. Box 7044, 750 07 Uppsala, Sweden

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Sammanfattning

Ett hållbart skogsbruk är beroende av att näringsämnen som förs bort i skördad biomassa och genom utlakning kompenseras genom vittring av mineral och bidrag från andra källor. Under det senast seklet har ökad skogsproduktion och antropogen försurning resulterat i ökade förluster av baskatjoner (Ca, K, Mg, Na) från skogsmarken. Det har funnits en osäkerhet om tillförlitligheten i skattningar av vittringshastigheten i svensk skogsmark som har resulterat i svårigheter att fastställa nivåer för långsiktigt hållbara skördeuttag och skogsproduktion. Syftet med denna avhandling var att öka tillförlitligheten i skattningar av vittringshastigheter i skogsmark genom att förbättra tillförlitligheten hos mineralogiska data som vanligen används i modeller (PROFILE), och genom att jämföra tre konceptuellt olika metoder för att bestämma vittringshastighet under enhetliga förutsättningar vad gäller data och fysiska avgränsningar. En ny plats-specifik metod för att beräkna kvantitativ mineralogi indirekt med beräkningsprogrammet “Analysis to Mineralogy” (‘A2M’) utvecklades genom jämförelser med direkta mätningar av mineralogi (X-ray power diffraction, XRPD) som användes som referens. A2M reproducerade den huvudsakliga kvantitativa mineralogiska sammansättningen, med undantag för beräkningar av viktiga K-haltiga mineral när de bestämdes med antagande om regional mineralogi. När den "regionala mineralogin" användes reproducerade inte A2M förekomsten av K-haltiga mineral korrekt. När mineralogiska data från A2M och XRPD användes i PROFILE resulterade de i olika vittringshastigheter som inte tydligt motsvarade skillnaderna i mineralogi. Osäkerheter i bestämning av vittringshastigheten hos Ca och Mg var orsakad av osäkerhet kring förekomsten av lättvittrade Ca- och Mg-haltiga mineral (apatit, amfibol, pyroxen, kalcit och illit). För K och Na var osäkerheten om vittringshastigheter kopplade till troligen felaktiga koefficienter för upplösning av dioctahedral mica (glimmer) och plagioklas. En generell slutsats var att PROFILE, och beräkningar av historisk vittring från massförlust av baskatjoner med Zr som referens, var för sig resulterade i rimligt säkra skattningar av dagens respektive den långsiktiga vittringen av baskatjoner. Baskatjonbudgetar för två olika bestånd med ung granskog visade att marken var den dominerande källan till trädens upptag av baskatjoner, där vittringen bidrog till en mindre del.

Nyckelord: Vittring, Mineraler, Baskatjoner, Hållbart skogsbruk

Författarens adress: Sophie-Charlotte Castetou-Gustafson, SLU, Instutitionen för ekologi, Box 7044, 750 07 Uppsala.

Dedication

To my family!

“I’m not a mineralogist, but I like stones. I’m not a limnologist or chemist, but I like water. I’m not a biologist, but I like trees. I’m an ecologist.”

Third semester teacher at Greifswald university, name unknown.

Contents

List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Casetou-Gustafson, S.,* Hillier, S., Axselsson, C., Simonsson, M., Stendahl, J., Olsson, B. A. (2018). Comparison of measured (XRPD) and modelled (A2M) mineralogies: A study of some Swedish forest soils in the context of weathering rate predictions. *Geoderma*, 310, 77-88.

II Casetou-Gustafson, S.,* Axselsson, C., Hillier, S., Olsson, B. A. (2019). The importance of mineral determinations to PROFILE base cation weathering release rates: A case study. *Biogeosciences*, 16, 1903-1920.

III Casetou-Gustafson, S.,* H., Hillier, S., Linder, S., Olsson, B. A., Simonsson, M. Current, steady-state and historical weathering rates of base cations at two sites in northern and southern Sweden: A comparison of three methods (submitted)

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* Corresponding author.

My contribution to the papers included in this thesis was as follows:

I Main author. Idea, field work, writing and analyses with co-authors.

II Main author. Questions, hypotheses, writing, and analyses with co-authors.

III Main author. Questions, hypotheses, writing, and analyses with co-authors.

Abbreviations

M_{XRPD}	Quantitative mineralogy based on XRPD (amount) and electron microprobe analysis (composition)
$M_{A2M\text{-}reg}$	Quantitative mineralogy calculated with the A2M model and using regional mineralogy
$M_{A2M\text{-}site}$	Quantitative mineralogy calculated with the A2M model and using site-specific mineralogy
W_{XRPD}	Weathering rate based on quantitative mineralogy determined by directly by XRPD and electron microprobe
W_{A2M}	Weathering rate based on quantitative mineralogy determined by the A2M model (unspecific mineralogy)
$W_{A2M\text{-}reg}$	Weathering rate based on quantitative mineralogy determined by the A2M model using regional mineralogy input
$W_{A2M\text{-}site}$	Weathering rate based on quantitative mineralogy determined by the A2M model using site-specific mineralogy input
$W_{depletion}$	Weathering rate based on calculation of loss of mobile elements since last deglaciation using the depletion method
$W_{profile}$	Weathering rate based on present-day steady-state PROFILE model weathering estimates
W_{bcb}	Weathering rate based on present-day dynamic weathering estimates using base the cation budget approach

1 Introduction

Weathering of minerals and release of elements such as potassium (K), magnesium (Mg) and calcium (Ca) from silicate minerals and phosphorus (P) from apatite is a key process in providing essential nutrients for primary production in all ecosystems. Weathering of silicate minerals and release of base cations (*e*.g. Ca^{2+}, Mg^{2+}, K^{+}, sodium (Na^{+})) is also a proton-consuming process that neutralises acidity produced by *e.g.* base cation uptake in biomass, leaching and accumulation of iron (Fe) and aluminium (Al) and acid deposition (van Breemen et al., 1983). The acid nature of Swedish forest soils derives mainly from the acidic, slowly weatherable silicate bedrock types of the basement, in combination with natural conditions that promote the development of acid forest soils. Such conditions include dominance of coniferous trees (Augusto et al., 2001), a humid and cold climate (precipitation > evapotranspiration) and acid deposition.

Acid Podsols, the dominant soil type in Swedish forests, are the product of weathering of minerals and other soil-forming processes that have taken place since the end of the last glaciation, *i.e.* approx. from 14.000 to less than 10.000 years ago in southern and northern Sweden, respectively. The soil-forming processes have also resulted in net export of base cations from the soil, causing natural acidification. Most of this historical depletion has been lost to runoff waters, which thereby provide an essential contribution to sustain primary production and alkalinity in downstream aquatic ecosystems over the long term. Another, much smaller, proportion of the base cations released by weathering is contained and recycled in forest biomass and soil organic matter. However, forest trees and other plants are not only recipients of weathering products, but also produce organic acids and carbon dioxide (CO_2) by root activity. Organic matter decomposition is another major driver of podsolisation. Thus the weathering process is an integral part of forest ecosystems.

Two processes induced or controlled by humans over the past century have accelerated the acidification and loss of base cations from forest soils. These are increased acid deposition and increased forest production and harvesting of forest biomass. Acid deposition has largely been caused by emissions of sulphur dioxide (SO_2) from combustion of fossil fuels, but also by nitrogen (N) deposition. The simultaneous input of a strong acid with the mobile sulphate ion in deposition resulted in increased leaching losses of base cations. The peak sulphur (S) deposition in Sweden occurred in the period 1960-1990 (Ferm et al., 2019). The ambition since 1990 to reduce sulphur emissions and deposition has been successful in most parts of Europe, but less successful in reducing deposition of nitrogen (De Wit et al., 2015). Agreements within the organisational framework of the United Nations (Convention on Long-Range Transboundary Air Pollution, CLRTAP) have been an important part of efforts to reduce acid deposition. An important tool for estimating emissions targets in the CLRTAP negotiation process was the concept of critical loads of acidity, which formed a bridge between scientists and policy-makers (Grennfelt & Hov, 2005). This concept defines the highest load of acidifying compounds that will not cause long-term damage to a particular ecosystem given best available knowledge (Nilsson & Grennfelt, 1988). In the early definitions, critical load calculations were mainly based on the molar ratio between base cations and aluminium in the soil solution (*i.e.* mass balance calculations of acidity), which in turn is inherently dependent on weathering rate calculations (Sverdrup, 1990). Since then, there have been many attempts to quantify weathering in acid-sensitive environments.

Surface waters are currently recovering from acidification as a consequence of reduced sulphur deposition (Akselsson et al., 2013). However, recent increases in forest production and harvesting rates in Sweden make forestry an important actor in the national environmental quality objective (EQO) of reducing the acid load to the environment (Objective 2017: “Only Natural Acidification”, Swedish Environmental Protection Agency). This change occurs simultaneously with other environmental trends, such as decreasing base cation deposition and climate change. The interest in understanding weathering and making accurate estimates of weathering rates has thus shifted towards long-term sustainable productivity of managed forests under changing environmental conditions and production targets.

Forest growth causes soil acidification through accumulation of base cation in biomass in excess of anion uptake. In theory, this acidification is reversed when trees die, the biomass is decomposed and base cations are released (Nilsson et al., 1982). Since only around one-third of the base cation stocks in aboveground tree biomass is contained in the stems, a change from stem-only to whole-tree harvesting results in much larger exports of base cations from forest sites. For this reason, the sustainability of whole-tree harvesting has been questioned in many studies.

Swedish field experiments have demonstrated that whole-tree harvesting can cause long-term depletion of extractable base cation stocks in the soil compared to stem-only harvesting, including lower soil pH and lower concentrations of calcium and magnesium in biomass of the following stand (Zetterberg et al., 2013; Brandtberg and Olsson, 2012; Olsson et al., 2000; Olsson et al., 1996). Calculations at the national level indicate that the supply of weathering products (*e.g.* Ca^{2+}, K^{+}) is not sufficient to sustain current levels of forest harvesting in large areas of Sweden (Akselsson et al., 2007). In the long-term and under future climate change scenarios, soil nutrient pools might become depleted, especially at sites that recover slowly from acidification (Iwald et al., 2013; Akselsson et al., 2013). For this reason, recyling of base cations and phosphorus with wood ash is recommended by the Swedish Forest Agency (Swedish Forest Agency, 2008).

Whole-tree harvesting is today notified for approximately half of the area of final fellings in Sweden, although the realized harvested area is lower (De Jong et al., 2017). The logging residues are used mostly for heat and power production in district heating plants, often in co-combustion with other woody fuels (sawdust, bark). The wood ash produced is used to some extent to recycle base cations and phosphorus, but the rate is far from that required to balance base cation and phosphorus export with harvested biomass (De Jong et al., 2017). The use of logging residues for energy, together with other biomass resources, is part of the Swedish energy policy aimed at replacing fossil fuels with renewable energy sources by 2045 (Swedish Environmental Protection Agency, 2017).

As outlined by Klaminder et al. (2011) and Paré and Thiffault (2016), defining sustainable levels of forest production and harvesting rates requires accurate estimation of nutrient budgets, which relies heavily on accurate estimation of weathering. In Sweden, regional weathering maps developed by Olsson et al. (1993), based on historical weathering estimates (produced using a climate regression model), and by Sverdrup and Rosén (1998) and Akselsson et al. (2004), based on steady-state weathering estimates (produced using the PROFILE model), have acted as important decision support tools.

There is a need to estimate weathering rates accurately for specific regions and site conditions. However, field weathering rates at the scale of a soil pedon cannot be measured directly, since they are the result of strong interactions between biotic and abiotic soil-forming factors and, not least, since soil formation and weathering are slow processes in cold climates (Palviainen et al., 2012; Augusto et al., 2001; Hatton et al., 1987). The latter has given rise to the historical weathering concept (Olsson & Melkerud, 2000; Olsson et al., 1993; Olsson & Melkerud, 1989), which is ultimately important for assessments of the long-term sustainability of ecosystems (*i.e.* sustainability under changing environmental conditions). Present-day weathering, on the other hand, is often estimated assuming steady-state conditions in the soil, *i.e.* that the soil solution chemistry is in balance with atmospheric inputs of base cations (Sverdrup & Warfvinge, 1993). In contrast to the steady-state concept, the dynamic version of the present-day weathering concept does not assume zero exchange in base saturation, long-term dynamics of mineral dissolution kinetics or average nutrient uptake over a forest rotation. Thus, the dynamic weathering concept takes account of short-term dynamics triggered by high nutrient demands in the active growing season of trees, which may be related to release of weathering products from secondary minerals (Kronnäs et al., 2019; Simonsson et al., 2015). As a consequence, several different methods are required to cover all conceptual views on weathering.

Use of multiple approaches has gained increasing attention during the past decade. While most previous studies have tried to compare at least two such approaches (*i.e.* present-day weathering and historical weathering), they are often applied at different physical scales (*e.g.* Augustin et al., 2016; Klaminder et al., 2011; Whitfield et al., 2006; Sverdrup et al., 1998; Starr et al., 1998; Ulén and Snäll, 1998). Futter et al. (2012) suggest overcoming these limitations through use of a so-called ‘ensemble approach’, where weathering estimates for a single site are compared using independent methods. There are in principle two different approaches for estimating present-day weathering rates: steady-state weathering based on the PROFILE model (Sverdrup, 1990) and current weathering estimates based on ecosystem base cation budgets or based on using the dynamic ecosystem model ForSAFE, an extended version of PROFILE (Wallman et al., 2005). Based on growing awareness of conceptual differences and improved quality of input data, and in line with Futter et al. (2012), at least three methods of estimation are required.

In mechanistic models used for estimating weathering rates, such as the PROFILE and ForSAFE models, accurate quantitative information on soil mineralogical composition is essential. Mineralogical composition in this regard refers to the identity of a mineral, including its element stoichiometry. Mineralogical information is essential because the PROFILE and ForSAFE models are built on the dissolution kinetics of specific minerals, determined *in vitro*, combined with data on specific element composition and dissolution rates and placing the kinetics in the context of the soil chemical and physical environment. The difference between PROFILE and ForSAFE is that the former calculates the steady-state weathering rates, assuming steady-state conditions in the soil, while the latter calculates dynamic changes in weathering and other processes at the ecosystem scale. The detailed information on mineralogical composition required to run these models is seldom available, despite the fact that uncertainties in weathering estimates are mainly related to data uncertainty. Recent attempts to interpolate B-horizon mineralogy from other horizons show that this can have a significant effect on model outcome, especially when soil layers contain minerals with high dissolution rates (Whitfield et al., 2018). However, "normative" methods are predominantly employed in PROFILE studies (Kronnäs et al., 2019; Stendahl et al., 2013; Philipps and Watmough, 2012). Normative mineralogy means that the mineralogical composition is calculated from geochemical data (*i.e.* the element concentration per unit dry mass) and assumed presence of specific minerals in a region. It is well known that minerals exhibit substantial variations in chemical compositions (Deer et al., 2013) and, hence, the exact composition may differ between sites. Another complicating factor hampering the use of generalised assumptions of mineral composition at a specific site is that glacial till soils may include soil minerals derived from different parent materials (Akselsson et al., 2006).

Another approach to estimating present-day weathering rates in the field is by the base cation budget, which estimates weathering from the difference between measured sources and sinks at the ecosystem scale (catchment or stand). This approach makes no assumption about the mechanisms underlying these processes, but can incorporate dynamic processes (indirect or direct) that occur in the rhizosphere, for example plant demand-driven or biological weathering (Finlay et al., 2009; Rosling et al., 2009). In this way, the base cation budget approach is unique and can give complementary information that is not captured by *e.g.* PROFILE. However, it is based on the prerequisite of reduced uncertainties in measured fluxes, as has been well described by Simonsson et al. (2015).

Approaches to estimating historical weathering rates are mostly based on theories by Brimhall et al. (1991), Brimhall and Dietrich (1987) and Kirkwood and Nesbitt (1991). Estimates obtained in this way are important, since they cover the average long-term dynamics of weathering and are fundamentally important for interpretation of present-day weathering rates. Although this could also be achieved in chronosequence studies, strong assumptions about the soil's history have to be made in such studies (*i.e.* soil profiles forming a chronosequence are exposed to constant soil-forming factors except for soil age) (Starr et al., 2006; Taylor and Blum, 1995; White et al., 1995).

In conclusion, there is a need to increase the accuracy and precision of estimation of base cation weathering rates, as a tool for defining sustainable forest production levels and critical loads of acidity. The ambition in this thesis work was to determine whether using better mineralogical data inputs to mechanistic models can help to improve weathering estimates, and how comparisons of different methods using the ensemble approach, made under best available conditions, can increase knowledge of base cation weathering in the context of forest ecosystems.

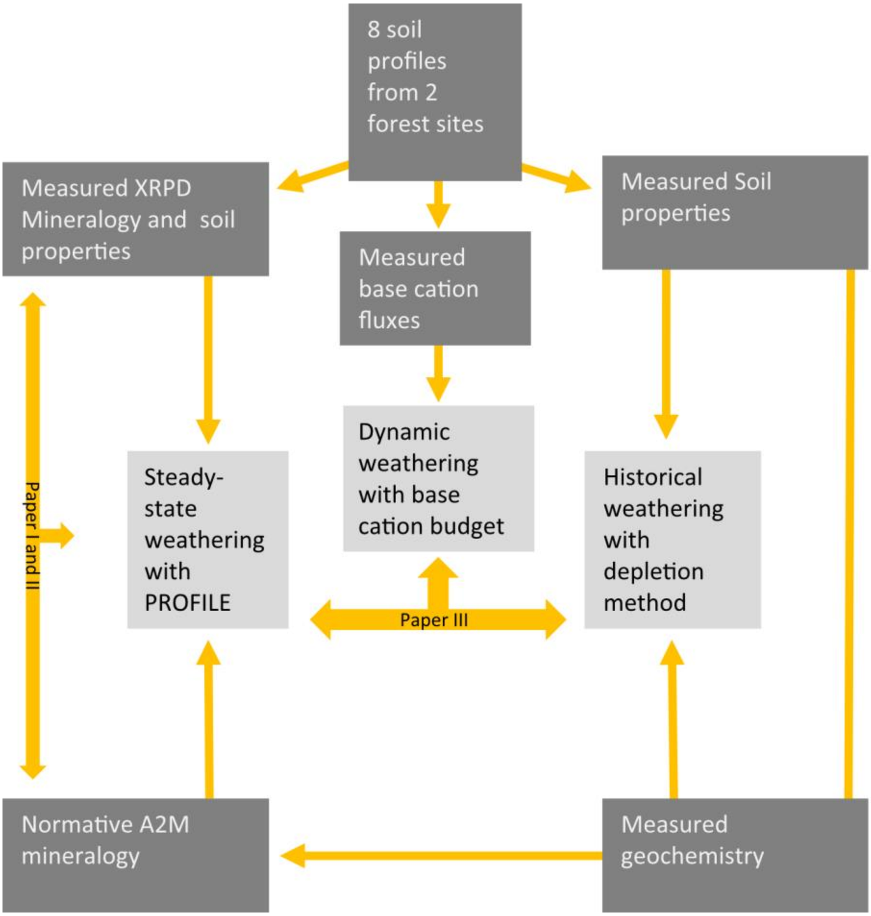


Figure 1. Schematic diagram showing a simplified view of the workflow in this thesis.

2 Aims and Objective

The overall aim of this thesis was to reduce uncertainties in weathering rate estimates. Specific objectives were to: i) evaluate different approaches for calculating quantitative normative mineralogies that are typically used for base cation weathering predictions with the PROFILE model (Papers I and II); ii) assess three complementary methods for obtaining quantitative weathering estimates (Paper III); and iii) make use of both empirical and model tools to estimate historical and present-day weathering rates in two aggrading forest ecosystems (Paper III).

This work comprised the following steps (Figure 1):

1. Quantitative determination and evaluation of normative mineralogy commonly used in PROFILE weathering studies (Paper I).
2. Examination of how different mineralogical inputs from Paper I affect PROFILE weathering estimates (Paper II).
3. Use of three methods for estimating weathering rates that differ conceptually and are applied at different scales, to cover all conceptual views, *i.e.* long-term pedogenesis, steady-state mineral dissolution and weathering in a mass balance perspective of a growing forest (Paper III).

3 Background

3.1 Mineral weathering in acidic forest soils

3.1.1 Soil profile-based weathering

Compared with the bedrock (consolidated regolith), soils are characterised by abiotic (unconsolidated regolith, water and air) and biotic material distributed in distinct soil layers. Dokuchaev (1967) and Jenny (1941) describe soil formation as being dependent on independent state factors, such as time, parent material, climate, organic activity, relief and dust deposition. It is well understood that both climate and erosion are predominant large-scale drivers of silicate mineral weathering (Riebe et al., 2017; Rasmussen et al., 2011; White et al., 1996; White and Brantley, 1995). However, at the scale of soil profile and minerals, both extrinsic and intrinsic factors interact and render the weathering processes more difficult to understand. This is exemplified by the strong regulating effect of plants on soil processes and properties, such as moisture, CO_2 pressure, and organic acid production (Kelly, 1998). Ultimately, the formation of soil profiles involves chemical transformation of parent material by reaction with water and water-soluble compounds, *i.e.* chemical weathering takes place by the attack of hydrogen ions (H^+) on silicate minerals and the consumption of carbon dioxide. Hydrolysis, the splitting of water and production of hydrogen ions, is the dominant process in humid climates that are characterised by net downward movement of water. Hydrolysis leads to incongruent dissolution of minerals via the movement of water through soil, whereby H^+ is consumed. Hydrogen ions are mainly provided through cation uptake and can also be provided by organic or inorganic acids. Organic acids affect weathering most intensively in the upper soil layers, through both H^+ attack and chelation.

Weathering in the upper soil horizons is most relevant for tree growth, and is thus also most relevant for forest management questions that rely on estimates about the long-term potential of mineral nutrient release in forest soils. The roots of most conifers are located in the upper 50 cm of the soil (Rosengren and Stjernquist, 2004), although weathering in deeper soil layers accessible to deeper roots could also be of relevance (Brantley et al., 2017).

Glacial till soils are formed by ice movement and are characterised as unsorted ice deposits. Around 75% of Swedish soils are classified as till soils (Fréden, 1994). Their main characteristic is presence of a mixture of all size classes of soil grains (Stendahl et al., 2009). On coarse-textured parent till material originating from the Precambrian Shield, Podsols are typically formed from the weathering of silicate minerals under the effect of a cold and humid climate and the acidifying influence of coniferous tree species (Iwald et al., 2013; Augusto et al., 1998). In Swedish field experiments, mineral dissolution has been shown to be elevated in the rhizosphere under Norway spruce (*Picea abies*) trees (Courchesne and Gobran, 1997). Podsols typically show strong vertical stratification into elluvial (typically E-horizons) and illuvial (typically B-horizons) horizons under a more or less distinct organic (O-) horizon. Natural acidification is an inherent process in granitic/gneissic soils formed under the cool, moist boreal climate and is caused by organic matter decomposition, plant uptake, respiration, reversed weathering and acidic atmospheric deposition (van Breemen et al., 1983).

3.1.2 Silicate mineral properties that determine weathering

Silicate minerals are the most abundant minerals in Swedish soils. Silicon-oxygen (Si-O) bonds are the principal structural entity of these minerals and, due to their covalent nature, are considered stronger than metal-oxygen bonds contained in the silicate structure. The degree of polymerisation of silicates and the affinity of the minerals for isomorphic substitution largely determines their resistance to weathering, *e.g.* the larger the Si-O molar ratio of the structural unit, the smaller the need for incorporation of metal ions to neutralise the oxygen anion (O^{2-}) charge (Sposito, 2008). Mineral weathering is also dependent on the environment to which the mineral is exposed, such as the residence time, supply of water and accumulation or removal of weathering products.

Primary silicate minerals are inherited from the parent material of a soil. Feldspar minerals are the most abundant group of silicate minerals in the Earth’s crust and the second most abundant mineral group in Swedish soils. Ionic substitution between aluminium and silicon (Si) is common in feldspars, accompanying substitutions of sodium and potassium in alkali feldspars and sodium and calcium in plagioclase feldspars, forming a range of feldspar minerals, *i.e.* solid solution series. There is a gradual change in chemical composition between members of a solid solution series (*e.g.* the plagioclases), which gives rise to different physical and chemical properties of the intermediates and the end minerals of the solid solution series. This variation increases the complexity of determining the rate-limiting step in mineral dissolution of feldspars. The linkage between silicate (SiO_4^{4-}) and aluminium oxide (AlO_4^{5-}) tetrahedra gives rise to three-dimensional framework structures of feldspars. It has been shown experimentally that the proportion of aluminium that substitutes for silicon at tetrahedral sites is exponentially related to the dissolution rate of plagioclase feldspars (*i.e.* the higher the fraction of Al at tetrahedral sites, the higher the dissolution rate) (Casey et al., 1991). Weathering mechanisms of primary minerals in acidic soils are mainly dependent on the pH of the soil solution, whereby hydrogen ions attack the crystal edges and binds to available oxygen anions.

Secondary silicate minerals originate from weathering processes by re-crystallisation and transformation, or may also be inherited, *e.g.* from sedimentary rocks. Secondary minerals include phyllo/layer-silicate minerals, such as clay minerals and amorphous minerals/paracrystalline minerals, but other non-silicate types of minerals such as hydroxides, oxyhydroxides, carbonates and sulphides may also occur. Clay minerals are by definition concentrated in the clay and fine silt fraction of soils, since the weathering of primary minerals is typically accompanied by a reduction in particle size. The abundance of phyllo-silicate minerals can give some insights into the weatherability/weathering degree of a sample, since they can usually be considered stable end products of weathering (Scheffer and Schachtschabel, 1992). In Swedish podsolic till soils derived from igneous rocks, primary micas are the most abundant phyllosilicates (Simonsson et al., 2016; Andrist-Rangel et al., 2006; Snäll and Ek, 2000). Like all micas, primary micas contain units of 2:1 layers (composed of two tetrahedral sheets and one octahedral sheet) held together by interlayer cations, most commonly potassium ions. However, the binding strength is greater for primary compared with secondary mica. Thus, these minerals play a vital role as an important reservoir of potassium, which becomes available to plants via complete dissolution (*i.e.* stoichiometric dissolution, which means that elements are released proportionally to their stoichiometric relationships in minerals) or by the reversible release of interlayer potassium (*i.e.* non-stoichiometric dissolution) where most of the 2:1 structure remains intact. Thus, a typical weathering reaction in Podsols is vermiculisation of mica via expansion and loss of interlayer potassium (Bain et al., 1993). These processes strongly depend on the soil solution equilibrium with regard to dissolved mineral species. The more conditions in the soil solution diverge from chemical equilibrium (changes may be triggered by low soil solution concentrations due to plant uptake or complexing agents), the faster chemical reactions, such as weathering, can occur. Vermiculite is only a stable weathering product as long as enough cations are released from primary minerals. As soon as the equilibrium for their formation is changed, vermiculite weathers and other secondary minerals are formed. The most stable end-products of weathering are minerals, such as kaolinite and iron and aluminium hydroxides (Sposito, 2008), which is why they are less abundant in young postglacial soils. Mareschal (2013) reported changes in clay mineral properties after 28 years of forest growth, even though weathering is considered a slow process.

From this comparison, it follows that plagioclase and expandable phyllosilicates are variable mineral groups. Courchesne and Gobran (1997) argue that minerals belonging to these groups are prone to plant-induced weathering. Moreover, the large abundance of plagioclase minerals in Swedish forest soils highlights the need for accurate determination of their abundance and stoichiometry.

3.1.3 Mineral determination

Since differences in the susceptibility of minerals to weathering ultimately depend on the properties of their crystalline structure, accurate quantitative mineralogical determination is essential for all methods that use mineralogical information to calculate weathering. Thus, the starting point of the experimental work in this thesis was evaluation of the input mineralogy used in the PROFILE model. The quality of mineralogy determination for weathering studies is based on both accurate identification and quantification of minerals and accurate determination of the stoichiometry of these minerals.

3.1.3.1 Direct methods (XRPD and EMPA analysis)

As summarised by Amonette (2002), quantification and identification of soil minerals relies on analysis of crystal mineral structures. Bish (1994) reported good performance of X-ray diffraction (XRD) as a non-destructive tool to determine mineral phases in a sample. The latter is based on Bragg's law:

$$n\lambda = 2dsin\theta \qquad Eq. 1$$

Where n denotes the order of reflection as an integer,
λ denotes the incident X-radiation wavelength (nm),
d denotes the spacing/distance between successive scattering planes in the

atomic lattice (nm), and θ is the angle between the incident X-radiation and the scattering plane (°).

However, while qualitative determination has a long history, quantitative analysis of X-ray diffraction data is more challenging, since peak intensities of different phases in a mixture cannot be directly translated into abundances of mineral phases. This challenge has also been identified by Bish (1994) and has stimulated the development of semi-quantitative, qualitative methods and indirect normative methods to determine soil mineralogical composition. In recent years, X-ray powder diffraction (XRPD) techniques have advanced most significantly in terms of sample preparation and quantitative analysis of diffraction data, and XRPD is now the preferred technique for quantitative analysis of material like soils. Among the different methods for quantitative analysis of diffraction data, the full pattern-fitting method has emerged as a powerful tool allowing quantitative determination not only of crystalline compounds, but also of amorphous and poorly ordered phases (Chipera and Bish, 2013). The uncertainty in quantitative estimates has been evaluated in ‘blind round robin’ tests, where the results are compared against the ‘true’ mineralogy of known samples (Omotoso et al., 2006; Kleeberg, 2005; McCarty, 2002). For samples of unknown composition, geochemical cross-validation (*e.g.* the mineralogical budgeting approach) can be applied to assess uncertainty (Andrist-Rangel et al., 2006). The latter approach can be used to define a reference mineralogy to which indirect methods such as the normative “Analysis to Mineralogy” (‘A2M’) method (Posch and Kurz, 2007) (see section 3.1.3.2) can be compared. In addition to the identification and quantification of the bulk mineralogical compositions of soils, microprobe techniques can be used to quantify the elemental concentrations of minerals. For example, electron microprobe analyser (EMPA) are able to achieve high analytical precision due to the use of wavelength dispersive spectrometers (Pownceby et al., 2007).

3.1.3.2 Indirect methods (A2M program)

Given the relative ease with which the bulk geochemical compositions of soils can be determined directly, compared to the difficulty of direct mineralogical analyses, the use of normative methods to determine soil mineralogies is still a common approach in many weathering studies, given the relative ease of determining bulk geochemical composition of soils. However, qualitative data on both the available minerals in the soil and their stoichiometry, *i.e.* their chemical composition, that are required for normative approaches are not routinely determined and as such are rarely available for a specific site. Therefore, indirect methods have been used, such as the regional classification scheme of soil mineralogies into four ‘norm’ mineralogical provinces in Sweden (Warfvinge and Sverdrup, 1995), which is the basis for many PROFILE-based weathering estimates in Sweden (*e.g.* Kronnäs et al., 2019; Akselsson et al., 2016; Stendahl et al., 2013; Akselsson et al., 2004). Compared with other normative methods that use various constraints to calculate quantitative mineralogy for weathering studies (*e.g.* Paktunc, 2001, 1998; Räisänen et al., 1995), the great advantage with the A2M program is that an unlimited number of minerals (as well as oxides) can be specified by the user, for which the A2M program calculates all possible solutions. Hence, given perfectly accurate bulk chemistry and mineralogy data (*i.e.* mineral identities and their chemical composition), the multidimensional solution space of A2M should include the ‘true’ mineral composition of a sample/site, but there is no way to know which composition it is.

3.2 Three methods to quantify weathering rates

The dynamic nature of weathering processes that are important for sustainable tree growth is reflected in a complex interplay of short-term and long-term dynamics from the microscopic level at the surface of a mineral to the macroscopic level encompassing the whole rooting zone of a forest stand. As a consequence, there are large conceptual differences between different methods for quantifying weathering rates, leading to different assumptions about soil history and the dominant process of mineral dissolution (Table 1). Thus all methods have advantages and disadvantages, as will be discussed in sections 3.2.1-3.2.3. The quantification of weathering rates in this thesis is based on the ecosystem concept. The core of this concept is that differences between ecosystem sinks and sources have to be balanced by weathering.

Table 1. Comparison of the PROFILE, depletion and base cation budget methods used in this thesis and the ForSAFE method (not used, but important in other respects). ForSAFE is a refined version of PROFILE model that models the effect of recovery from acidification and ecosystem response to climate change and forestry in order to estimate dynamic weathering rates (Kronnäs et al., 2019)

	PROFILE	Depletion	Base cation budget	ForSAFE
Concept	Steady-state	Historical	Dynamic	Dynamic
Time Scale	Average present-day weathering rates, simulated based on constant present-day environmental conditions	Average long-term weathering rates, based on soil age and fluctuations due to long-term environmental changes	Average present-day weathering rates, based on time period covered by measurements	Monthly weathering rates
Spatial scale	The ecosystem is represented by the soil profile	The ecosystem is represented by the soil profile	The ecosystem is represented by sink and source processes of base cations	The ecosystem is represented by the soil profile
Parameter representation/ measurement quality	All parameters are input to the model	Geochemistry and soil physical characteristics are measured	Base cation sinks and sources are measured	Several parameters are modelled from other input data
Weathering kinetics	Long-term kinetics are assumed	No assumption	No assumption	Long-term kinetics are assumed
Pedogenesis	No assumption	Assumption about zirconium immobility, homogeneous parent material	No assumption	No assumption

3.2.1 Steady-state weathering

Steady-state weathering does not consider seasonal variations in climate, soil and plant parameters. The concept assumes that a specific weathering rate is reached if all parameters are kept constant. The major reason for incorporating the steady-state concept into the mechanistic process-based soil model PROFILE was that, in the context of defining critical loads for acid-sensitive soils, a tool was required that would consider long-term sources and sinks of acidity (*i.e.* processes that are irreversible over several decades). Thus, Sverdrup et al. (1990) and Sverdrup and Warfvinge (1992) justified the use of long-term averages for input data (*i.e.* steady-state weathering is represented by the time period specified by the input data). The same authors also justified the use of long-term kinetics (*i.e.* steady-state kinetics) for mineral dissolution for young soils (such as Swedish soils). In the field, mineral dissolution is more complicated and goes through several processes (initial surface leaching, intermediate non-steady-state kinetics and long-term kinetics).

The structure of the PROFILE model follows the natural stratification of a soil into different soil horizons. For each soil horizon in PROFILE, chemical equilibrium reactions and weathering are calculated based on the properties of the soil layers. Chemical inputs/outputs of base cations to/from a specific soil layer (*i.e.* atmospheric inputs, litterfall, leaching and nutrient uptake) are determined by their steady-state mass balances (*i.e.* sources of alkalinity and acidity are balanced over time) and are critically dependent on water flux and volumetric soil water content. The constant flux leaving a soil layer is calculated based on annual average precipitation and runoff in relation to the relative base cation uptake in trees. Thus, for each soil horizon PROFILE applies several sub-models, *i.e.* nitrification, water chemistry, cation and nitrogen uptake, and weathering reactions are coupled and take place simultaneously and are all interconnected via the soil solution. Each soil layer consists of a chemically isotropic soil solution, which does not imply chemical equilibrium (*i.e.* zero net chemical reaction) (Warfvinge and Sverdrup, 1992). Central to the weathering rate sub-model are kinetic rate equations describing mineral dissolution based on transition state theory (Aagaard and Helgeson, 1982; Lasaga, 1981). Transition state theory postulates that the rate-determining step in mineral dissolution is the concentration of an activated surface complex (Warfvinge and Sverdrup, 1995) at the interface between solids and solution. The formation of this complex is a reversible process and is dependent on the sum of forward reactions minus the rate of backward reactions (*i.e.* secondary mineral precipitation). The decay of the activated surface complex is an irreversible process, *i.e.* when a threshold is overcome the release of cations due to complete mineral dissolution is irreversible (Sverdrup and Warfvinge, 1988) (Figure 2). The basic formula for base cation release rate, *r*, from each mineral, *j*, is (Warfvinge and Sverdrup, 1995):

$$r_j = \frac{k_H[H^+]^{n_H}}{f_H} + \frac{k_{H_2O}}{f_{H_2O}} + \frac{k_{CO_2}P_{CO_2}^{n_{CO_2}}}{f_{CO_2}} + \frac{k_R[R^-]^{n_R}}{f_R} \qquad Eq. 2$$

Where *k* denotes rate coefficients and *n* reaction rates and subscripts H, H_2O, CO_2 and R^- (organic acids) denote individual sub-reactions. Equation 2 is applied in equation 3 in order to calculate the weathering rate (R_W) for each soil horizon, i:

$$R_{W_i} = \frac{A_i \theta_i}{\Theta_i} \sum_{i=0}^{minerals} r_j x_j \qquad Eq.3$$

Where A denotes total exposed mineral surface area (m^2 m^{-3}), θ denotes soil moisture saturation, Θ denotes volumetric soil water content and x_j is the fraction of mineral j in soil horizon i. Equation 2 is based on constants and coefficients determined in laboratory experiments to assess the temperature-dependent reaction of different minerals with water (H_2O), carbon dioxide, hydrogen ions and organic acids. These constants and coefficients were evaluated by Sverdrup et al. (1990) on the basis of a literature study with the aim of making them universally applicable. The influence of trees and soil biota on mineral weathering integrates the effect of organic acids and carbon dioxide on the reaction rate coefficients, but also the indirect effect of dissolved organic carbon (DOC) through complexation with aluminium, the indirect effect through nutrient uptake and effects on soil wetness (Sverdrup and Warfvinge, 1993; Sverdrup, 2009). Equation 3 shows the dependency of reaction coefficients on reaction products. Weathering rates are product-inhibited, which means that high concentrations of dissolved base cations or aluminium act as retardation factors, but these effects are mineral-specific (*i.e.* minerals with high Al/base cation content are more affected by dissolved Al/base cations than those with low Al/base cation content; Sverdrup, 1990). Reaction products (*i.e.* ammonium (NH_4^+), nitrate (NO_3^-), base cations) are calculated using mass balance equations based on the acid neutralisation concept (ANC), whereas aluminium concentrations are calculated based on the assumption that solid phases of aluminium can be described by aluminium hydroxide. Equation 3 shows that the total weathering rate for a specific soil horizon is not only dependent on an activated surface complex (denoted by *r*), but is also described as a process that is proportional to the soil moisture saturation and exposed mineral surface areas. Soil moisture saturation is important, since PROFILE assumes that weathering reactions only occur on wetted surfaces.

As with all models, there are controversies about process representativeness since there are several contrasting concepts about the mechanism of mineral dissolution. In the past, diffusion-controlled mineral dissolution (incomplete dissolution) was believed to involve the formation of an alteration layer at the mineral surface and the rate-limiting step for mineral dissolution was thought to encompass the diffusion of ions through this alteration layer. However, in line with more recent insights on mineral dissolution based on laboratory dissolution experiments, surface-limited dissolution conditions (Chou and Wollast, 1985;

Aagard and Helgeson, 1982) are assumed in PROFILE based on transition state theory (Sverdrup, 1990), which has been acknowledged as a strong framework for weathering rate models (Hodson et al., 1997). With regard to the determination of reaction rate coefficients and reaction orders, Hodson et al. (1997) raised concerns about the fact that PROFILE assumes only congruent (*i.e.* stoichiometric) dissolution, whereas there is evidence of incongruent (non-stoichiometric) dissolution, *e.g.* for hornblende. Brantley et al. (2008) acknowledge that hornblende mineral dissolution does not reach a steady state. However, they also highlight the fact that for most silicates, non-stoichiometric dissolution occurs in the beginning of mineral dissolution, but dissolution eventually reaches steady state (Taylor et al., 2000; Stillings and Brantley, 1995).

Reducing input data uncertainty is considered most critical in narrowing the gap between dissolution rates determined in the laboratory and in the field. The sensitivity of the PROFILE model has been thoroughly evaluated in two studies (Hodson et al., 1996; Jönsson et al., 1995). Hodson et al. (1996) showed that PROFILE is predominantly sensitive to four different kinds of input data, *i.e.* soil mineralogy, exposed mineral surface area, soil moisture content and soil temperature. However, several recent Swedish studies dealing with the effect of increased temperature and soil moisture on base cation weathering rates have found overall similar results with ForSAFE and/or PROFILE (Belayzid et al., unpublished; Kronnäs et al., 2019; Akselsson et al., 2016). While a number of other studies have assessed the effect of different surface area measurements on model output (*e.g.* Whitfield et al., 2018; Hodson et al., 1998), the quality of mineralogical input data and the corresponding effect on PROFILE weathering rates has been largely neglected (Whitfield et al., 2018).

3.2.2 Historical weathering

In contrast to steady-state weathering, historical weathering calculates the long-term loss of mobile elements due to weathering (Brimhall et al., 1991; Kirkwood and Nesbitt, 1991; Chadwick et al., 1990; Brimhall and Dietrich, 1987; April et al., 1986) and compares it with the enrichment of immobile elements in weathered and unweathered soil (*i.e.* cumulative long-term changes). Immobile elements include zirconium (Zr), which is part of the weathering resistant mineral zircon (Chadwick et al., 1990; Harden et al., 1987) and titanium (Ti), which is part of the weathering resistant mineral anastase/rutile (Johnson et al., 1968). Zirconium is commonly used in weathering studies, since its distribution in the upper part of the soil profile is described as proportional to the gradual decrease in weathering of base cations. Thus, gradients in mobile and immobile element distribution are assumed to reflect mineral alteration over time (Melkerud, 2003; Brimhall et al., 1991). Inert elements help to quantify the loss of mobile elements since the beginning of soil formation (*e.g.* last deglaciation), which has led to the development of two methods, the pedological mass balance (PMB) method (Egli & Fitze, 2000) and the depletion method. However, both methods are derived from the same general mass balance function, as outlined in Brimhall et al. (1991):

$$\frac{V_p \rho_p C_{j,p}}{100} + m_{j,flux} = \frac{V_w \rho_w C_{j,w}}{100} \qquad Eq. 4$$

The mass of element j in the assumed unweathered rock (protolith), p, is given on the left side of equation 4. Where V denotes volume (cm^3), ρ is bulk density (g/cm^3), C denotes chemical concentration (wt. %) of element j, $m_{j,\,flux}$ denotes mass flux of element j out or into the protolith and w denotes the weathered material. The PMB approach has been applied less frequently (Augustin et al., 2016; Whitfield et al., 2011; Ouimet et al., 2005). It integrates changes in mass and volume (*i.e.* soil pedon height) through time (*i.e.* mass loss per unit volume), which makes it inherently difficult to interpret the results, since they could be influenced by either volume change or change in elemental mass. In this thesis, these two types of pedogenic changes were estimated separately. The depletion method has been applied to estimate elemental mass loss based on theories developed by Kirkwood and Nesbitt (1991) (Whitfield et al., 2011) or, alternatively, by theories developed by Brimhall and Dietrich (1987) and Brimhall et al. (1991). These have been adapted for Swedish deglaciated soils by Olsson and Melkerud (1989) and applied in Stendahl et al. (2013) under the term depletion method. Olsson and Melkerud (1989) redefined the historical weathering concept as the cumulative loss of an element divided by soil age:

$$W_i = \frac{d \cdot \rho}{100} \cdot \frac{X^p \cdot Zr^{w,i}}{Zr^p} - X^{w,i} \qquad Eq. 5$$

Where W denotes loss of the element (g m^{-2}) from soil layer i, d is layer depth (m), and ρ is bulk density (g m^{-3}), X denotes mobile element concentrations (%), Zr denotes immobile element concentrations (%), w denotes a weathered soil layer and p denotes the assumed unweathered reference layer. The calculated mean annual loss of elements for a soil profile is determined by dividing the total elemental loss by the age of the soil. In this way, field weathering is calculated as an integrated/accumulated change of elements over time. This concept is based on the assumption that the removal of base cations in nutrient uptake and the re-precipitation of calcium, magnesium, sodium and potassium into secondary minerals is negligible (Olsson and Melkerud, 1989). The distribution and/or enrichment of zirconium in the upper part of the soil is reported to be proportional to the gradual decrease in weathering of base cations (Melkerud et al., 2003). As such, initial and intermediate weathering processes that form the soil are taken into account. In contrast to the PROFILE model, the depletion method integrates both chemical and physical changes in the soil profile. The postglacial part of the Holocene was characterised by climatic conditions that, on average, were warmer than today (lasting until between *ca.* 10.000 to 4500 years ago in southern Sweden) and a change in vegetation cover (spruce and beech invaded southern and northern Sweden *ca.* 2500 years ago, which marked the start of a cooler climate) (Nilsson, 1990). Chronosequence studies based on granitic glacial deposits provide some evidence that weathering rates decline exponentially over time, since weatherable material is increasingly lost (Taylor and Blum, 1995; Bain et al., 1993). However, this also means that there can be large fluctuations, with both very high and low rates at any time during the history of soil formation, as well as at present (Hodson and Langan, 1999). Therefore, average annual long-term weathering and present weathering rates can be similar, but are not necessarily so. Further, Stendahl et al. (2013) and Sverdrup and Warfvinge (1988) argue that low historical weathering rates can be attributed to a low content of weatherable minerals, which can partly be attributed to the fact that Swedish till soils may also contain soil material from previous glaciations. One obstacle to the use of the depletion method is that stones and boulders may make up a large proportion by volume of Swedish till soils (Stendahl et al., 2009), a problem that has been neglected in many studies. The use of soil age to convert elemental loss into annual average release rates has also been criticised (Klaminder et al., 2011; Yoo & Mudd, 2008). In this thesis, the degree of change in a soil layer should thus be referred to as ‘loss’ or ‘change’, not ‘age’. Of course this means that using the depletion method involves an assumption that weathering has been more or less constant over time, which is not necessarily true since there is a gradual decline in weathering rate due to loss of minerals, formation of coatings *etc*. However, for the rather young soils of Sweden, the assumption is probably justified.

3.2.3 Dynamic weathering

The base cation budget approach can take account of biological weathering changes that occur over a period of intense growth and has the unique strength that it is based on measurements, without making assumptions about the dynamics of soil- and plant-driven processes and their interactions as required with the ForSAFE model (Table 2). Nutrient recycling is fundamentally important to sustain high nutrient demands during the rapid tree growth phase. This is especially important for elements that are characterised by a relatively high degree of openness of their ecosystem cycles (*i.e.* Mg, K, Ca) with regard to input/output fluxes to and from the ecosystem (Ågren and Andersson, 2012).

On a global scale, and in an evolutionary perspective, plants have accelerated mineral weathering (Berner, 1992), induced by their co-evolution with mycorrizal fungi (Taylor et al., 2009). Plants capture carbon dioxide, alter the water balance, capture atmospheric deposition and drive the release/movement of mineral nutrients via diffusion and mass flow. Observations on the short-term dynamics of plant-induced weathering changes in the field (Calvaruso et al., 2009; Courchesne and Gobran, 1997; Hinsinger et al., 1993) could be of high relevance for sustainable nutrient cycling at the stand scale. Courchesne and Gobran (1997) describe mineral weathering as the response to low pH, mediated through the dominant nutrient uptake of ammonium (and concurrent uptake of base cations) and the accumulation of organic matter. These early indications are in line with recent experimental evidence pointing towards nutrient uptake (*i.e.* reduction in transport limitation via nutrient uptake) as the main biological driver of mineral weathering rates (Rosenstock et al., unpublished (2019b)). Thus, there is a growing body of evidence that nutrient uptake reduces solute concentrations and thereby changes the dynamic soil solution equilibrium towards release of exchangeable, interlayer, or structural base cations. However, Rosenstock et al. (unpublished, 2019b) highlighted that while the latter has an effect on the weathering rate by affecting the rate-limiting step of mineral dissolution, the mechanism of biological weathering can be expected to be proton- and ligand-promoted.

During forest growth, trees acquire nutrients most intensively in the rapid tree growth phase, when nutrient accumulation in tree biomass is most intense (Bormann and Likens, 1979). These observations in the young phase of rapid growth contradict simple asymptotic models that predict a slow and constant increase until a steady state is reached, which is more in line with reports about the importance of biomass accumulation for mineral weathering and as a sink for base cations (Zetterberg et al., 2016; Simonsson et al., 2015; Bormann et al., 1998; Taylor and Velbel, 1991). Observations of diminishing soil base cation pools over time add further evidence that weathering is likely to be underestimated when derived from base cation balances under steady state conditions. Non-steady state conditions imply that all nutrient pools in the ecosystem are allowed to change over time and that weathering products can be accumulated or immobilised in different soil pools (Simonsson et al., 2015) (Figure 2). This is crucial, since calcium for example is to a large extent involved in organic matter complexes and clay-humus colloids. However, most mass balance studies are still based on steady-state assumptions, *i.e.* base cation accumulation in biomass and soil change is assumed to be negligible or zero (*e.g.* Klaminder et al., 2011). A few attempts have been made to account for plant uptake in mass balance studies, although these are based on simplified estimates/approximations (*e.g.* Kolka et al., 1996*)*. The base cation budget approach is based on the assumption that all ecosystem inputs equal outputs, which leads to the general equation:

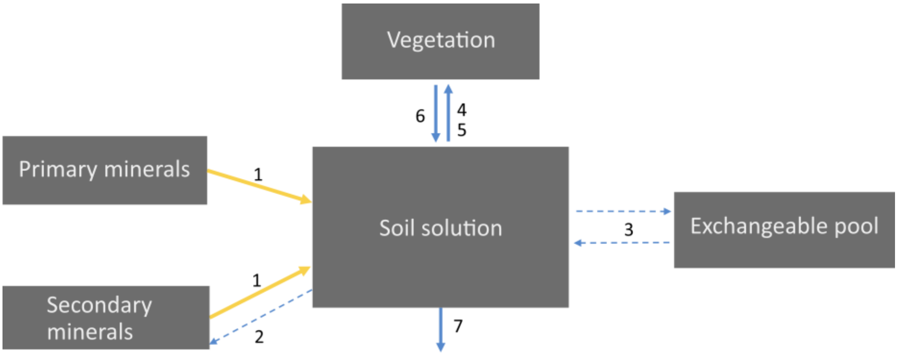
Weathering + Deposition + Negative soil change = Leaching + Net biomass accumulation + Positive soil change Eq. 6

Where 'negative soil change' and 'positive soil change' indicate that the soil is a sink and source for base cations, respectively. The basic principle underlying this equation is the conservation of mass, which implies that elements are recycled, but not destroyed or created, in any chemical reaction. The equation can be reformulated to estimate weathering:

Weathering = Leaching + Net biomass accumulation + Net soil change - Deposition Eq. 7

Equation 6 describes weathering as being dependent on the removal of base cations from the forest via leaching, biomass accumulation (plant uptake) and cation exchange, and the addition of base cation via weathering, cation exchange and atmospheric deposition. Although non-exchangeable pools are not measured, they are indirectly included in the weathering estimate. This creates the opportunity to replace the weathering term with weathering estimates derived using the base cation budget method (equation 7) or estimates based on PROFILE or the historical weathering (depletion method) approach. Thus, three different mass balances can be formulated, each based on a different weathering estimate. Doing so can provide a stronger understanding of the links between the mineralogical compartment and the biology compartment, ultimately dependent on stoichiometric characteristics (*i.e.* in terms of minerals) and demands (*i.e.*, in terms of trees). As Brantley et al. (2011) point out, only a few studies have tried to link biological demands with changes in mineralogy due to weathering.

Uncertainties of the base cation balance method when applied to rapidly growing forest under non-steady-state conditions have been described extensively by Simonsson et al. (2015). Each term of the mass balance contributes to the combined/overall uncertainty of the weathering estimate in proportion to the magnitude of each term. A quantitatively important, but uncertain, term might therefore contribute significantly more to the overall uncertainty in weathering estimates.



1. Irreversible weathering release: Taken into account directly by PROFILE and indirectly by the depletion method and the base cation approach
2. Reversible weathering: Taken into account indirectly by the base cation budget approach and the depletion method
3. Adsorption/Desorption: Taken into account directly by the base cation budget approach and indirectly by the depletion method
4. Net nutrient uptake: Taken into account directly and in a dynamic way by the base cation budget approach and indirectly by the depletion method and PROFILE
5. Gross nutrient uptake (Sum of net uptake and nutrient cycling): Taken into account directly by PROFILE (net uptake+litterfall) and indirectly by the base cation approach and the depletion method (net uptake+litterfall+canopy exchange+net mineralization)
6. Total deposition: Taken into account directly by the base cation budget approach and PROFILE and indirectly by the depletion method
7. Leaching: Taken into account directly by the base cation budget approach and PROFILE and indirectly by the depletion method

Figure 2. Simplified illustration of processes that may (*e.g.* irreversible weathering) or may not (*e.g.* reversible weathering) be represented by the three different methods used in this study (PROFILE model, depletion method, base cation method) or may be represented in different ways (*e.g.* nutrient uptake).

4 Methods

4.1 Long-term field experiments

Long-term experimental forest plots were established in a 12-year-old Norway spruce stand at Asa in southern Sweden in 1987 and in a 23-year-old Norway spruce stand at Flakaliden in northern Sweden in 1986. The original purpose of the experimental design was to identify the requirements for optimal nutrient growth of Norway spruce stands (Bergh, 2005, 1999; Linder, 1995). Both the Asa and Flakaliden experiments were set up as randomised block designs, with four different treatments (control, fertilisation, irrigation and liquid irrigation). Of these, only control plots and fertilised plots were included in the analyses in Papers I-III of this thesis, to study the importance of mineral weathering for base cation cycling in two aggrading Norway spruce stands.

Table 2. *Characteristics of the study sites*

	Asa	*Flakaliden*
Coordinates[a]	57°08'N, 14°45'E	64°07'N, 19°27'E
Altitude (m a.s.l.)[a]	225-250	310-320
Mean annual precipitation (mm)[b]	688	523
Mean annual temperature (°C)[b]	5.5	1.2
Mean atmospheric total deposition (mmol$_c$/m^2/year)	27.0 (SO_4^{2-}); 38.3 (Cl^-); 30.7 (NO^-_3); 21.6 (NH_4^+); 7.2 (Ca^{2+}); 6.8 (Mg^{2+}); 1.9 (K^+); 31.5 (Na^+)	13.1 (SO_4^{2-}); 5.6 (Cl^-); 10.5 (NO^-_3); 9.9 (NH_4^+); 5.2 (Ca^{2+}); 1.9 (Mg^{2+}); 1.1 (K^+); 5.6 (Na^+)
Dominant tree species[a]	Norway spruce	Norway spruce
Forest type[c]	Mesic grass	Mesic dwarf-shrub
Bedrock[d]	Acidic intrusive rock	Quartz-feldspar-rich sedimentary rock
Soil type[e]	Spodosol	Spodosol
Soil texture[f]	Sandy loam	Sandy loam
Type of quartenary deposit[f]	Sandy loamy till	Sandy loamy till
Mean stone and boulder content (%$_{vol}$)	28	39
Soil age (calendar years)[g]	14 300	10 150
Site productivity (m^3/ha/yr)[a]	10.8	3.2

[a]Bergh et al. (2005), [b]Long-term averages of annual precipitation and temperature data (1961-1990) from the nearest SMHI meteorological station (Asa: Berg; Flakaliden: Kulbäcksliden), [c]Flakaliden: Kellner (1993) and Strengbom et al. (2011); Asa: Strengbom et al. (2011), [d]SGU bedrock map (1:50 000), [e]USDA Soil Conservation Service (2014), [f]Soil texture based on own particle size distribution analysis by wet sieving according to ISO 11277, [g]Fréden (2009).

4.2 Study site description

The study sites are situated along a strong climate gradient of decreasing temperature, precipitation and atmospheric deposition from the south to the north. Site productivity also decreases from the south to the north (Table 2). Moreover, Asa in the south has historically received more anthropogenic deposition than Flakaliden in the north of Sweden. Soils at Flakaliden are well buffered, which is characterised by higher base saturation in both the organic and mineral soil (Fröberg, J., unpublished data). The harsher climate at Flakaliden affects decomposition processes negatively and is exemplified by a thicker humus layer at Flakaliden compared to Asa. The soils at Flakaliden and Asa are well-drained Udic Spodosols. Both sites are characterised by felsic bedrock, which is the case for most areas in Sweden, whereas carbonate bedrock is only expected in the Caledonian mountain range in the north and carbonate-bearing till is expected close to the Caledonian mountains and in some other confined areas where sedimentary bedrock occurs (*e.g.* Gotland). The bedrock of the Flakaliden site belongs to the Svecokarelian province and the bedrock of the Asa site belongs to the Transscandinavian Granite-porphyry belt (Fréden, 2009). Both study sites are located above the highest Quartenary coastline, which indicates that soil mineralogy and particle size distribution have not been changed due to wave action.

4.2.1 Soil sampling

Soil sampling was performed in October 2013 at Flakaliden, using a rotary drill to extract intact soil cores in the border zone of a total of four plots (two control plots (10B and 14B) and two fertilised plots (15A, 11B)). The depth of each soil core varied as a function of the high frequency of large boulders. In March 2014, the same rotary drill was applied in one of two control plots (K1) at Asa and in the remaining control plot (K4) and two fertilised plots (F3, F4), soil pits were dug by hand due to inaccessible terrain for forest machinery. Soil samples were taken from the mineral soil at 10-cm depth intervals. At both study sites and for all soil plots, a soil profile description was made in the field. For the purpose of quantitative mineralogical analyses, representative samples were selected from each soil layer based on the soil splitting technique, where a composite sample was split using a riffle splitter. The maximum rooting depth was estimated visually. Prior to chemical analysis, soil samples from each 10-cm soil layer were dried at 30-40 °C and sieved (2 mm mesh).

4.2.2 Repeated sampling

Prior to the start of the experimental treatments, the organic layer and the mineral soil were sampled to 40 cm or deeper, in 1986 at Flakaliden and in 1988 at Asa. A second sampling was performed in 1998 at Flakaliden and in 2004 at Asa. In order to extract soil samples for chemical analysis, a 5.6 cm diameter corer was used for the organic layer and a 2.5 cm diameter corer for the mineral soil in the border zone of the control plots at Flakaliden and Asa. For each soil, 25 samples were pooled to one soil sample for each soil layer (*i.e.* the entire humus layer and then 10-cm layers down to at most 40 cm in the mineral soil).

Nutrient concentrations in harvested Norway spruce trees were determined on two occasions at Asa (1993 and 1998) and Flakaliden (1992 and 1997) (S. Linder, unpublished data). It was assumed that the values obtained were valid for growth measurements performed between 1987 and 2003. At both sites, total element concentrations were sampled on the same tree parts as were used for biomass sampling in 1993 and 1998.

Soil water was sampled during 14-16 years of measurements (*i.e.* 1988-2004 at Flakaliden and 1990-2004 at Asa) once in the spring and once in the autumn of each year, since soil water chemistry is known to vary most significantly between these seasons (as a function of soil water residence time, biological uptake *etc.*), *i.e.* soil water content is low during forest growing seasons and during summer droughts.

4.3 Soil analyses

4.3.1 Mineralogical analysis of bulk mineralogy (XRPD)

4.3.1.1 Sample preparation

Random powder specimens were prepared using the procedure described by Hillier (1999). The first step was to produce a concentrated aqueous suspension of 3 g of sieved (<2 mm) soil sample in ethanol (ethanol:soil ratio 3:1), which allowed spray-drying at low temperatures. The slurry was then micronised in a McCrone mill for 12 minutes and poured undiluted into a glass bottle mounted on an air-brush. The samples were spray-dried through the air-brush into a heated chamber (60 °C). An advantage of the technique described in Hillier (1999) is the high recovery rate of sample and the avoidance of large droplets that would move too fast through the chamber. The resulting air-dried samples, consisting of small and evenly distributed spheres (50-60 µm in diameter), were collected at the bottom of the chamber on a large piece of paper. The spray dried specimens were top loaded into circular sample holders and run in a Bruker D8 diffractometer with copper (Cu) K-α radiation. Powder patterns were recorded from 4-70°2θ and counting for 96 s per 0.01945 step with a Lynxeye XE position-sensitive detector.

4.3.1.2 Analysis

For qualitative analysis of the samples (mineral identification), visual analysis of the diffraction patterns was performed using the EVA DIFFRAC software (Brucker, 2006) and reference patterns from the International Center for Diffraction Data (ICDD) Powder Diffraction File (PDF-4, 2016). Quantitative mineralogical analysis by XRPD was performed using the full pattern-fitting approach detailed by participant 18 (Hillier) in Omotoso et al. (2006). Calculations were performed in an EXCEL spreadsheet using the SOLVER add-in to optimise the fit between the observed diffraction pattern and a pattern based on a sum of single-phase (mineral) reference patterns. This method makes use of a sequence of fitting steps (based on least squares optimisation). No internal standard was used and mineral abundances were computed from the proportion of all reference patterns needed to achieve a good fit between observed and modelled patterns and the full pattern reference intensity ratios were measured for each standard pattern (Omotoso et al., 2006; Hillier, 2003).

4.3.2 Total chemical analysis

All mineral soil samples were dried (30-40 °C) and sieved using a 2-mm mesh. Fine-particle samples of the mineral soil were analysed for total carbon using a LECO element analyser according to ISO 10694. They were analysed for bulk chemistry by milling 1 g sample and igniting it at 1000 °C for 75 min prior to fusion of 0.105 g of the ignited sample with $LiBO_2$ at 1000 °C and solvation in nitric acid (HNO_3). The resulting solutions were analysed by inductively coupled plasma mass spectrometry (ICP-MS). Additionally, extraction of aluminium, silicon and iron was performed for the two soil profiles using 0.2 M ammonium oxalate (pH 3) in darkness (Van Reewijk, 1995; McKeague & Day, 1966) and centrifugation of the extracts at 3000 rpm for 20 min. The aluminium, silicon and iron concentrations were measured by ICP-SFMS (Element 2, ThermoScientific) after sample dilution. The presence of imogolite/allophane-type materials was examined according to Gustafsson et al. (1998). A LECO elemental analyser was used and total carbon was determined in accordance with ISO 10694.

4.3.3 Mineral budgeting approach

By combining information about mineral identity from XRPD (section 4.3.1.2) with information on the site-specific chemical compositions of minerals determined by EMPA (section 4.3.4.4), the geochemistry of the Asa and Flakaliden soils was estimated according to the mineralogical budgeting approach advocated by Andrist-Rangel et al. (2006) in a normative calculation procedure. In a next step, the predicted geochemistry was compared with the directly measured geochemical compositions (see section 4.3.2) for all soil samples.

4.3.4 Mineralogical modelling by the Analysis to Mineralogy (A2M) program

In Paper I, all quantitative estimates of calculated soil mineralogies were based on the arithmetic mean output of the A2M program (centre of gravity of the A2M solution space), as is common practice in PROFILE-based weathering studies. Since A2M does not provide one unique mineralogical solution, in Paper II it was used to calculate 1000 random mineralogical solutions for each soil unit, in order to include the full space of quantitative mineralogies, all equally possible A2M solutions. A corresponding number of PROFILE runs was made to estimate the corresponding range of weathering rates. Two approaches, a regional approach and a site-specific approach, were chosen to calculate normative quantitative mineralogy with A2M for Paper I and Paper II.

4.3.4.1 Regional approach

In the regional approach used in this thesis, ‘region’ refers to the regional mineralogical input to A2M, where mineral identification and mineral stoichiometry (see section 4.4.1) were based on four norm provinces (Warfvinge and Sverdrup, 1995). The regional A2M mineralogy was calculated based on the regional mineralogical input described above and on an anhydrous version of the weight percentages of element oxides calculated from the geochemical analysis described in section 4.3.2.

4.3.4.2 Site-specific approach

In the site-specific approach, site-specific mineralogical input to A2M was used, determined in terms of the minerals identified (information from the XRPD analysis) and the chemical composition (see section 4.3.4.4) of these minerals, but not determined (directly) in terms of the abundance of these minerals. The site-specific A2M mineralogy was calculated based on the site-specific mineralogical input described above and based on an anhydrous version of the weight percentages of element oxides calculated from the geochemical analysis described in section 4.3.2.

4.3.4.3 Correction for hydrous minerals and minerals that contain Fe^{2+}

The A2M output on estimated A2M mineralogy needed some correction, since it was calculated from anhydrous geochemical analyses but some of the minerals modelled are hydrous (or contain other volatiles that contribute to loss on ignition) and since all iron in the geochemical analyses was expressed only in one oxidation state, Fe^{3+}, when in some minerals it actually occurs as Fe^{2+}. Recalculation factors were based on a sample calculation using hypothetical soil geochemistry applied to a synthetic mineral mixture (chlorite, corundum, periclase, hematite and quartz). Since the synthetic mineral mixture was kept simple (*i.e.* the only mineral in the synthetic mixture that contained H_2O and FeO was chlorite), it was possible to calculate an anhydrous geochemical composition from the synthetic mineral mixture. The latter was then applied to let A2M model a corresponding soil mineralogy. It was found that the outcome was not identical with that obtained using the synthetic mineral mixture, which justified the use of correction factors.

4.3.4.4 Mineral stoichiometry determination by electron microprobe analysis (EMPA)

Site-specific mineral stoichiometries were determined at two soil depths per soil profile, as a means to represent the full range of composition that could be expected in the soils at Asa and Flakaliden. Determination of chemical composition based on electron microprobe analysis of different minerals in terms of major, minor and trace elements was performed on a Jeol JXA-8530F Hyperprobe. An accelerating voltage of 15-20 kV and a beam current of 10 nA were applied, based on a counting time of 10 s on peaks and 5 s on upper and lower background positions. Raw data were corrected based on a technique described by Pouchou and Pichior (1985). Mineral standards were used for the different elements. The results of the chemical analysis were reported in weight percentages of the element oxides. Mineral formulae were calculated from the chemical analyses. Because all iron was reported as FeO in the chemical analyses and because site-specific mineral formulae calculations should be based on the same principles of formula calculations as used by Warfvinge and Sverdrup (1995) (*i.e.* in order to allow a comparison of regional and site-specific quantitative mineralogies), all iron was re-calculated as ferric iron (Fe_2O_3)

4.3.5 Soil physical property determination: Particle size distribution, soil bulk density and estimated stoniness

In accordance with ISO 11277, particle size distribution was analysed by sedimentation (pipette method) and wet sieving. The penetration method described by Viro (1952) was used to determine the volume of stones and boulders to a maximum depth of 30 cm for each plot at the two study sites, and by applying the fitted function described by Stendahl et al. (2009).

Except for some plots and density measurements that were not possible below a certain soil depth (plots F3, K4 and F4 at Asa) or where a large and sudden decrease in bulk density with increasing soil depth was observed (plots 11B and 15A at Flakaliden), bulk density of soil <2 mm was estimated using an exponential model including total organic carbon and bulk density as variables. The latter were based on measured data.

4.4 Quantifying mineral weathering rates

4.4.1 PROFILE

4.4.1.1 Total deposition

Monthly precipitation data, throughfall data and bulk deposition data from Aneboda (near Asa) for the period 1996-2005 and from Gammtratten (near Flakaliden) for the period 1999-2005 were used (for sampling and analysis details, see ICP Forest (2010)). By multiplying base cation concentrations with precipitation amounts, bulk deposition and throughfall deposition were calculated. Atmospheric deposition measured under the tree canopy (*i.e.* throughfall deposition) is composed of dry deposition, canopy exchange and wet deposition. In order to distinguish canopy exchange from dry deposition for calcium, magnesium and potassium, sodium was used as a tracer ion. Dry deposition for sodium and chlorine (Cl^{-}) was calculated as the difference between wet and throughfall deposition. Wet deposition for all elements was calculated as outlined by Zetterberg et al. (2016), *i.e.* correcting bulk deposition for dry deposition using wet-only to bulk deposition ratio. Finally, total deposition for all elements was estimated by summing up dry deposition and wet deposition.

4.4.1.2 Aluminium solubility

A function was developed from previously published data (Simonsson & Berggren, 1998) and total carbon (C_{tot}) and oxalate-extractable aluminium (Al_{ox}) measured at the field sites in order to estimate the aluminium solubility coefficient needed for solution equilibrium reactions, defined as $\log\{Al^{3+}\}$+3pH. It was assumed that the Al_{ox}/C_{tot} ratio, instead of the molar ratio of aluminium to carbon in pyrophosphate extract (Al_p/C_p ratio), could be used. The function is related to findings by Simonsson and Berggren (1998) that aluminium solubility in the upper B-horizon of Podsols is controlled by organic complexation and that below a threshold value of 0.1, aluminium solubility increases with Al_p/C_p ratio (*i.e.* pyrophosphate extractable Al to C ratio). In soil layers where $Al_{ox}/C_{tot} < 0.1$, aluminium solubility cannot be explained by obvious factors, and therefore default values given by Warfvinge and Sverdrup (1995) were used in this thesis. The latter are based on the simple gibbsite equilibrium.

4.4.1.3 Dissolved organic carbon concentrations

Dissolved organic carbon (DOC) concentrations in leachate under the O-horizon were taken from Fröberg et al. (2006), while data on DOC concentrations in leachates under the B-horizon (at 50 cm depth) were available for two plots at each site (H. Grip, unpublished data). Mean values for Flakaliden were compared to published data in Fröberg et al. (2013). Data for the B-horizon were also applied for the C-horizon.

4.4.1.4 Temperature and precipitation

In Paper II, temperature and precipitation data were based on averages of long-term measurements (1961-1990) obtained from nearby SMHI meteorological stations (*i.e.* Berg near Asa and Kulbäcksliden near Flakaliden). In Paper III, site-specific meteorological data for the period 1990-2003 were available for the Asa and Flakaliden sites (S. Linder, unpublished data).

4.4.1.5 Exposed mineral surface area

Soil bulk density and soil texture data were used to calculate exposed mineral surface area according to the algorithm specified in Warfvinge and Sverdrup (1995).

4.4.1.6 Net base cation and nitrogen uptake

The average accumulation rate over a 100-year stand rotation length at Flakaliden and a 73-year stand rotation length at Asa was calculated based on measured nutrient concentrations in aboveground biomass (*i.e.* bark, stemwood, needles and branches (dead and living)) multiplied by predicted biomass at final felling. The biomass values were calculated based on Heureka simulations (StandWise) (Wikström et al., 2011).

4.4.1.7 *Purely estimated parameters*

The moisture classification scheme described in Warfvinge and Sverdrup (1995) was used to estimate volumetric field soil water content for each soil pit in Flakaliden and Asa. Each soil layer was assigned the same value, 0.25 m^3m^{-3}. In addition, partial CO_2 pressure in the soil was estimated based on a default value in Warfvinge and Sverdrup (1995).

4.4.2 Depletion method

Equation 5 requires information about the concentrations of immobile and mobile elements in unweathered soil, which were derived from a reference layer chosen based on the condition that it was located in the unweathered C-horizon and that zirconium was enriched compared with other elements (*i.e.* base cations) above this layer. It was also assumed that zirconium gradient and zirconium/base cation (Zr/BC) ratio are constant below the reference layer. The reference soil layer was defined based on Zr/BC ratio and if there were heterogeneities in the profile the reference layer was chosen above this heterogeneity. The latter was not possible for soil profile 11B, where zirconium gradient and Zr/BC ratio peaked just below the B-horizon (*i.e.* at 50-60 cm). Further, both zirconium and titanium are enriched towards the soil surface, so their ratio was used to assess the uniformity of parent material (as described by Law et al., 1991) in the soils at Asa and Flakaliden. This was the case for all plots at Asa except for plot K1, where zirconium concentrations decreased towards the soil surface. Therefore, titanium was used as the immobile element instead of zirconium for that plot. At Flakaliden, the zirconium and titanium gradients increased significantly with soil depth in plots 11B and 15A, so those soil profiles were excluded from further analysis.

Fractional volume change (Vp) was calculated according to White et al. (1996) in order to identify soil profiles with unrealistic volume changes in the mineral soil. Since all values were close to zero below 30-40 cm soil depth at Asa and Flakaliden, it was concluded that no major volumetric change had occurred in those soil profiles.

4.4.3 Mass balance

4.4.3.1 Nutrient uptake

For determination of nutrient uptake, the net ‘biomass accumulation’ term that is part of equation 6 and 7 was calculated by multiplying annual increments in aboveground biomass by nutrient concentrations of different tree compartments (*i.e.* living and dead branches, needles, stemwood, stem bark).

Biomass increment in aboveground biomass of Norway spruce was estimated based on site-specific allometric functions developed by Albaugh et al. (2009). These site-specific functions were derived from biomass measurements based on destructive sampling of 180 trees on seven occasions between 1986 and 2003 at Flakaliden, and on 93 trees sampled on three occasions between 1993 and 2003 at Asa. The functions were compared against published biomass expansion functions (Lehtonen et al., 2004; Wirth et al., 2004). Biomass increment in belowground biomass of the Norway spruce stand at Flakaliden was derived from data for Svartberget (Hellsten et al., 2013), while data were directly available for Asa (Hellsten et al., 2013).

Annual increment in belowground biomass (*i.e.* roots and stumps) was estimated from general allometric functions for Norway spruce in Sweden (Marklund, 1988). A correction factor was applied (11%) that accounts for underestimation of belowground biomass using Marklund’s functions (Petersson & Ståhl, 2006). Annual increment in fine roots was estimated based on data from Helmisaari et al. (2007), by assuming it to be proportional to 20% of needle biomass at Asa and 33% at Flakaliden.

Analyses of element concentrations were performed based on acid wet digestion in nitric acid and perchloric acid ($HClO_4$) and subsequent element determination by inductively coupled plasma-atomic emission spectrophotometry (ICP-AES)

(Jobin Yvon JY-70 Plus). Measurements of nutrient concentrations in belowground biomass fractions were derived from Hellsten et al. (2013).

4.4.3.2 Leaching

Each experimental plot was equipped with five ceramic tension lysimeters (Ceramic P80 cups; Staatliche Porzellanmanufaktur, Berlin). The lysimeters were operated with an initial tension of -70 kPa and left overnight at transient vacuum. Base cation leaching at 6-month intervals was estimated based on base cation concentrations at 50 cm soil depth, measured (by ICP-AES analysis of frozen samples) in two pooled (by linear interpolation) soil water samples per plot and year multiplied by modelled runoff (*i.e.* sum of daily fluxes per plot and year) at the same depth. Mean annual base cation leaching was calculated for the period 1988-2004. Modelled runoff calculations were based on the Coup model (Jansson, 2012), which takes into account measured hydraulic soil properties and measured climate variables (*i.e.* daily mean global radiation, wind speed, air temperature and humidity) in order to calculate vertical heat and water flux. In a calibration procedure, parameters were slightly adjusted to achieve highest agreement between measured and calculated soil water content.

4.4.3.3 Deposition

Total deposition was calculated as described in section 4.4.1.1.

4.4.3.4 Change in exchangeable soil pools

A percolation method (where 100 mL of solution was percolated through 2.5 g of sample at a rate of around 20 mL/h) was used for the Flakaliden samples and for the first Asa samples taken in 1988. Extractions were performed on dry samples with 1M NH_4Cl and base cation amounts were analysed by atomic absorption spectrophotometry (AAS). An exception to this was the Asa samples from 2004, where extractions were performed using the same extractant, but in a batch extraction method, followed by ICP analysis. In order to compare the yield of the percolation and batch extraction methods, a laboratory test was performed on soil samples from each site. Due to inconclusive results, no correction factors could be determined.

The change in extractable base cation stocks in the soil was taken as the difference between two soil samplings (section 4.2.2). The calculations were based on the amount of fine soil (<2 mm) per unit area, which was derived from the volume of fine soil in the soil profiles and the average bulk density of the soil in the 0-10, 10-20 and 20-40 cm layers. Bulk density and volume proportion of stoniness at Flakaliden were determined from samplings in 1986 in 20 soil profiles (0.5 m x 0.5 m and about 0.5 m deep) outside plots. At Asa, stoniness and bulk density were determined as detailed in section 4.3.5.

4.4.3.5 Judgement of data quality

The quality of estimate of each individual term in equation 7 was assessed based on the measurement quality of each term and its spatial and temporal scale. Estimates of deposition, leaching and accumulation in biomass were thus considered to be of moderate to high quality, whereas measurements of changes in extractable soil pools were considered to be of lower quality because of potential bias in methods of repeated measurements. The latter could lead to significant uncertainty if soil changes are of quantitative importance in the base cation budget. For this reason, estimates of weathering obtained by the PROFILE and depletion methods in additional base cation budget calculations (*i.e.* where the change in soil was determined from the base cation budget) were compared to weathering estimates based on equation 7.

4.5 Statistical analysis

In Paper I, the overall accuracy of the normative A2M program was evaluated based on the assumption that the XRPD mineralogy constitutes the ‘true’ mineralogy of each site and sample (for justification, see section 5.1) It was hypothesized that normative quantitative A2M mineralogy calculated using the site-specific approach (see section 4.3.4.2) is in closer agreement with quantitative XRPD mineralogy than A2M mineralogy derived from the regional approach (see section 4.3.4.1). Discrepancies were determined based on three statistical error measures: bias, root-mean square error (RMSE) and relative error. A positive bias was interpreted as an average overestimate of the ‘true’ mineral content and a negative bias as an average underestimate. The overall accuracy of the predicted geochemical analyses was evaluated in a similar manner, by assuming that the measured geochemistry constitutes the ‘true geochemistry’ of each site and sample.

In Paper II, PROFILE weathering estimates based on measured XRPD mineralogy were taken as the ‘reference’ weathering rates. The statistical analyses of data were performed in a similar way as in Paper I, with two statistical measures (RMSE and relative error) used to establish discrepancies between PROFILE runs based on measured and modelled mineralogies. In addition, RMSE was calculated in two different ways, in order to establish (i) whether there were differences in total PROFILE weathering rates per element in the 0-50 cm soil profile (*i.e.* it was hypothesised that the PROFILE weathering rates based on XRPD mineralogy would be closer to those based on site-specific mineralogy rather than on regional mineralogy); and/or (ii) whether minerals contributed differently to the overall weathering rates per element (*i.e.* it was hypothesised that over- and underestimation of specific base cation weathering rates could be directly related to over- and underestimation of specific mineral concentrations in the A2M mineralogy). Differences in PROFILE weathering rates were also evaluated by comparison of the entire A2M solution space with XRPD measurements. In this, a significant discrepancy was defined as a scenario in which PROFILE weathering rates based on XPRD were not contained in the A2M solution space.

In Paper III, in order to compare three different weathering estimates derived from three conceptually different methods, standard errors were calculated. With regard to weathering estimates based on the PROFILE model and the depletion method ($W_{depletion}$), standard errors were calculated based on all soil profiles (except for Flakaliden, where only two soil profiles were included). Standard errors of weathering estimates based on the base cation budget (W_{bcb}) were based on the four control plots. Estimates of uncertainty associated with each term in the base cation budget were based on confidence intervals calculated from measured between-plot variation (n=4) with regard to leaching and soil change and on estimated confidence intervals derived from Simonsson et al. (2015) for biomass accumulation and deposition. The 95% confidence intervals based on the combined uncertainties were estimated for each base cation.

5 Results and Discussion

5.1 Paper I

The primary aim in Paper I was to determine the accuracy of quantitative A2M mineralogy, since it is by far the most frequently applied normative input used in PROFILE weathering studies. Two different A2M mineralogies were calculated based on a common approach (regional mineralogical input to A2M) and a new approach (site-specific mineralogical input to A2M). This comparative work was done to be able to in depth determine the accuracy of the modelled soil mineralogy. The results provide a benchmark for future weathering studies as regards how refinements of mineralogical input data can improve the accuracy in modelled mineralogies.

The XRPD-measured mineralogies of the Asa and Flakaliden till soils were found to be similar and in line with the composition expected for soils formed from parent material belonging to the Baltic Shield. In the soil mineralogical analyses performed using XRPD, quartz was the dominant mineral, followed by plagioclase and K-feldspars. Although all plagioclases were assessed as a single class, a more refined evaluation of the diffraction patterns revealed that calcic anorthitic plagioclases were relatively more abundant at Flakaliden (56 calcic and 44 sodic plagioclases), while the Asa site had higher proportions of sodic albitic plagioclases (37 calcic and 63 sodic plagioclases). This difference was confirmed by electron microprobe analysis, which validates the quality of the data generated by the XRPD analysis. Other differences in minerals observed between the sites were that amphiboles and phyllosilicates were more abundant at Flakaliden, while epidote, ilmenite and hematite were more abundant at Asa. Further, from the electron microprobe results it was possible to see that the composition not only of plagioclases, but also of epidote (variation in iron content) and dioctahedral mica, differed between the two sites. Trends in mineral abundance with respect to depth were apparent at both sites, *i.e.* increasing trends with depth for plagioclase, chlorite and hydrobiotite. In addition, at Flakaliden, amphibole and dioctahedral mica showed a tendency to increase with soil depth. There is good reason to believe that these trends reflect weathering processes that could be expected in acidic till soils, where the measured accumulation of imogolite/allophane and ferrihydrite in the B-horizon was a further confirmation of the accuracy of the full pattern-fitting XRPD method.

In addition, Paper I successfully validated the reliability of mineralogical analysis by the budgeting approach and use of the quantitative measured XRPD mineralogy as a reference data set to which quantitative normative A2M mineralogy could be compared. When comparing measured and predicted geochemical bulk compositions of soil samples at Asa, a few elements were slightly overestimated (silicon and iron) and a few were marginally underestimated (aluminium, magnesium and calcium). Overall, at Flakaliden, calculated and measured geochemistry were in slightly better agreement compared to Asa. The larger spread in geochemical compositions at Flakaliden, was most likely a reflection of the variation in mineral abundance as a function of depth rather than a variation between different plots. Measured oxalate-extractable aluminium, iron and silicon concentrations also agreed well with the XRPD predicted distribution of imogolite/allophane and ferrihydrite. In summary, the mineralogical budgeting approach aided in validating the XRPD results, further strengthening its use as a reference mineralogy.

To determine whether the ‘regional’ approach is useful or not, A2M mineralogy was compared with XRPD mineralogy. Interestingly, regional mineralogical input to A2M showed the largest inaccuracies for two potassium-bearing minerals, K-feldspar and dioctahedral mica. At Flakaliden, the only dioctahedral mica listed/included in the regional mineralogy was illite. There are many reports on illite in the literature, explaining its modification via expansion to form more stable end products of weathering. Given the relatively young age of the soils studied in this thesis, it is unlikely to observe amounts of illite at the Flakaliden site that amount on average to 16.2 wt.-%, compared with 9.3 wt.-% of K-feldspar (Figure 3a-b). Andrist-Rangel et al. (2008) showed for agricultural till soils that the contribution of potassium from K-feldspar was dominant except for one site with fine-textured soil. The exact speciation of potassium between different potassium-bearing minerals seems also to be important, since K-feldspar is the most sensitive mineral to changes in PROFILE input data (Hodson et al., 1995).

In Paper I, applying the refined ‘site-specific’ approach, using minerals quantified by XRPD and composition derived from electron microprobe analysis (except for quartz, vermiculite, kaolinite and iron/titanium oxides) as input to A2M proved applicable for both Asa and Flakaliden (Figure 3c-d). As anticipated, on using these ‘site-specific’ parameters the outcome of the A2M model was enhanced, although a large number of statistically significant biases still persisted. This was somewhat more apparent for the Asa site, with RMSE > 3 wt.-% for quartz and total plagioclase, which is comparable to the range of error reported in other studies (Posch and Kurz, 2007; Sverdrup and Warfvinge, 1995). However, in terms of the 95% confidence level for accurate XRPD analysis (Hillier, 2003), approximately 22% of the site-specific estimates fell outside this analytical confidence area. Nevertheless, it must be underlined that normative mineralogy always involves a simplification of the actual variability of mineral composition in soils, which is better described by ranges rather than mean values.

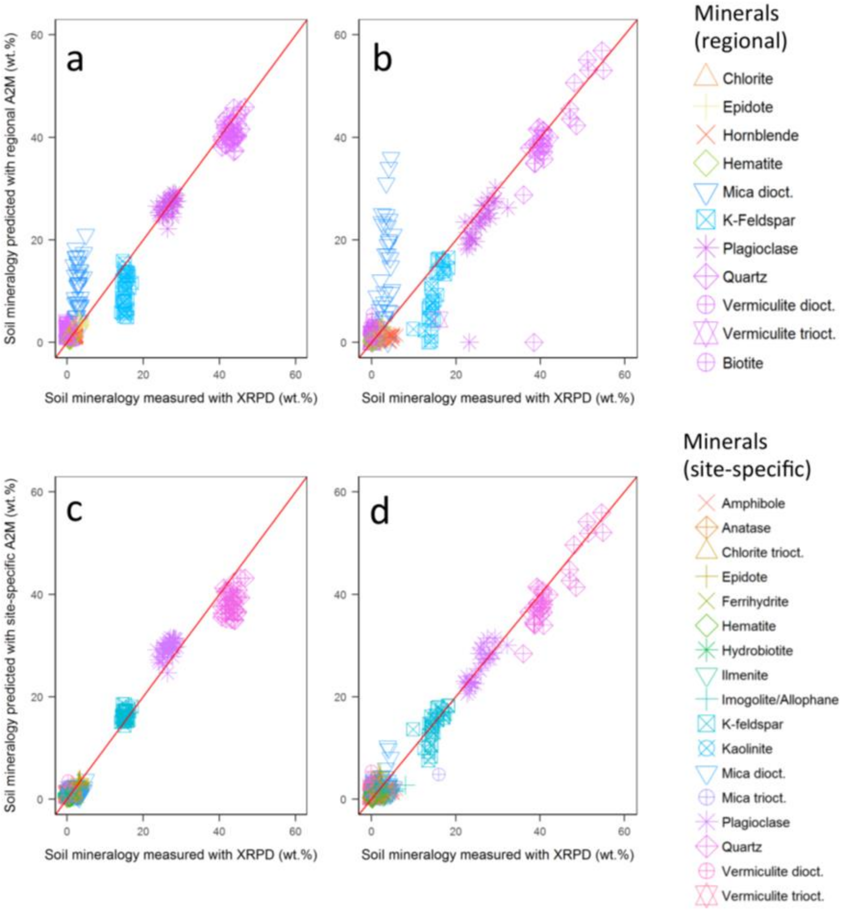


Figure 3: a-b: Comparison of mineral contents predicted with regional A2M (wt. %) and those measured directly by XRPD (wt. %) for: (a) soils at Asa and (b) soils at Flakaliden. c-d: Comparison of mineral contents predicted with site-specific A2M (wt. %) and those measured directly by XRPD (wt. %) for: (c) soils at Asa and (d) soils at Flakaliden. The figure is based on: http://dx.doi.org/10.1016/j.geoderma.2017.09.004.

5.2 Paper II

Paper II sought to overcome the shortcoming that mineralogical input to one of the most used weathering estimation methods had never been evaluated, although it had been identified as a key variable, since the structure of the model is strongly focused around mineral-based dissolution kinetics (see section 3.2.1 and Sverdrup, 1990). In order to gain a better understanding of the relative importance of different normative mineralogies on PROFILE release rates of different base cations, PROFILE results based on normative input mineralogies were compared against PROFILE results based on reference mineralogies (*i.e.* the ‘true mineralogy’ as defined in Paper I using direct measurements derived from XRPD and EMPA). Thus, PROFILE weathering rate estimates were based on three different mineralogical input data (*i.e.* XRPD reference mineralogy, site-specific A2M mineralogy and regional A2M mineralogy). Figure 9 shows how errors from paper I are propagated to paper II and illustrates the largest and most significant deviations between A2M-based weathering estimates compared with those based on XRPD, expressed as total weathering per element and depicted in detail in Figure 4a. Figure 4b shows the sum of significant deviations between A2M and XRPD based on comparing individual mineral contributions to total weathering per element.

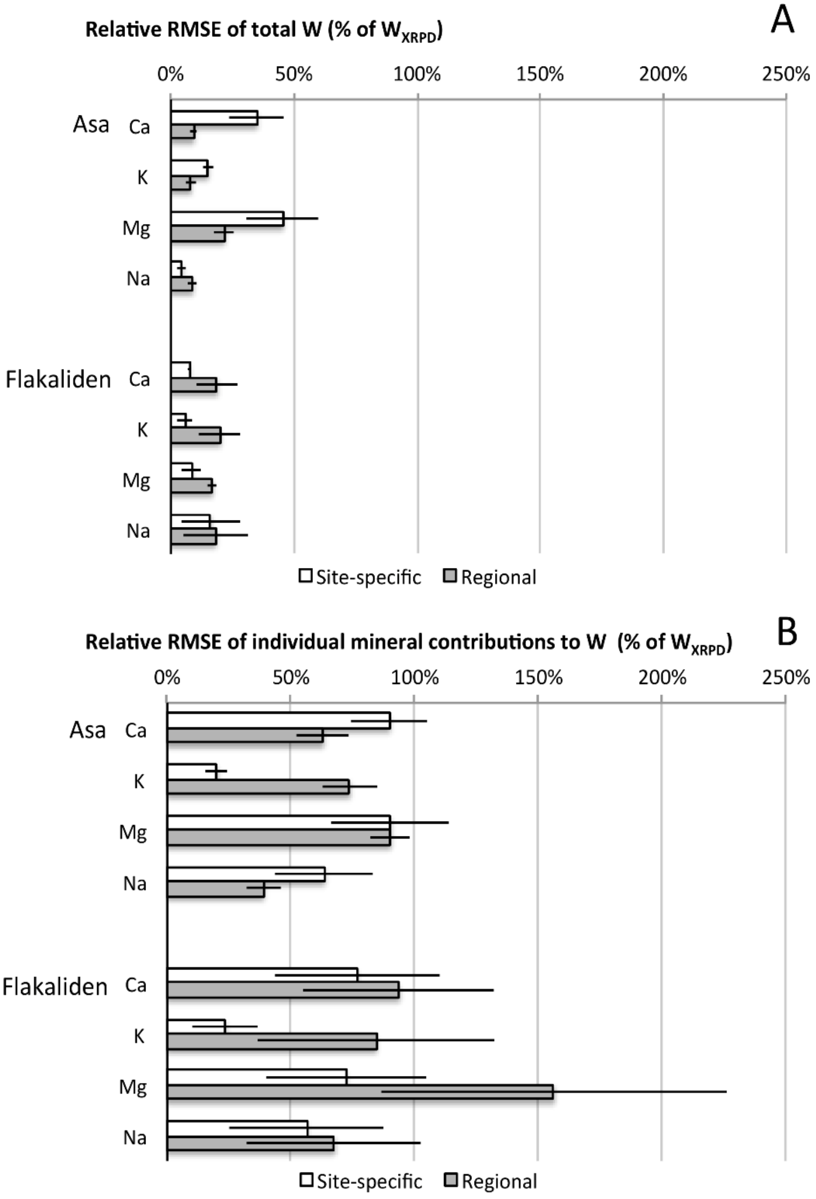


Figure 4. Significant deviations between A2M-based weathering estimates (W) compared with those based on XRPD for the soils at Asa and Flakaliden, based on A) total weathering per element and and B) mineral specific weathering per element (expressed as sum per element). RMSE = root mean square error. The figure is based on: https://doi.org/10.5194/bg-16-1903-2019.

It was expected in Paper II that PROFILE results based on site-specific mineralogy would deliver overall closest agreement with PROFILE results based on XRPD. In reality, the calcium and magnesium weathering rates at Asa based on PROFILE using site-specific A2M mineralogy (*i.e.* $W_{A2M\text{-}site}$) diverged most significantly from PROFILE weathering estimates based on XRPD mineralogy (i.e. W_{XRPD}) (Figure 4a). In line with the second hypothesis of Paper II, the overestimation of calcium was directly related to the overestimation of calcic plagioclase in quantitative A2M estimates based on site-specific mineralogical input data (i.e. $M_{A2M\text{-}site}$) and magnesium overestimates (Figure 5) were directly linked to overestimation of hydrobiotite (bias = 0.7 wt.-%) and biotite in $M_{A2M\text{-}site}$ (bias = 1.6 wt.-%) (Figure 9). Although the uncertainties in plagioclase determination based on M_{A2M} compared with M_{XRPD} were judged to be relatively small (bias = 2.7 wt.-% for $A2M_{site}$ at Asa and -2.1 wt.-% for A2M based on the regional approach ($A2M_{reg}$) at Flakaliden), the detailed character of the relative contribution of calcic to sodic plagioclase on PROFILE weathering estimates was more complicated. This is also reflected in the relatively large contribution of sodic plagioclase to the overestimation of sodium weathering rates using regional A2M mineralogy ($W_{A2M\text{-}reg}$) at Flakaliden (Figure 5 and 9). The same applied for $W_{A2M\text{-}site}$ of magnesium at Asa and Flakaliden, where relatively small error in $M_{AM\text{-}site}$ for biotite and hydrobiotite (Figure 3c-d), respectively, led to relatively large uncertainties in $W_{A2M\text{-}site}$. Surprisingly, these effects, although very similar, were reflected very differently in deviations of W_{XRPD} and $W_{A2M\text{-}site}$ with regard to individual mineral contributions to the total weathering rates per element at Asa compared with Flakaliden (Figure 4b). A plausible explanation for this observation is that minerals tend to compensate for each other in terms of relative contribution to the overall weathering rate per element (*i.e.* ‘compensatory effect’).

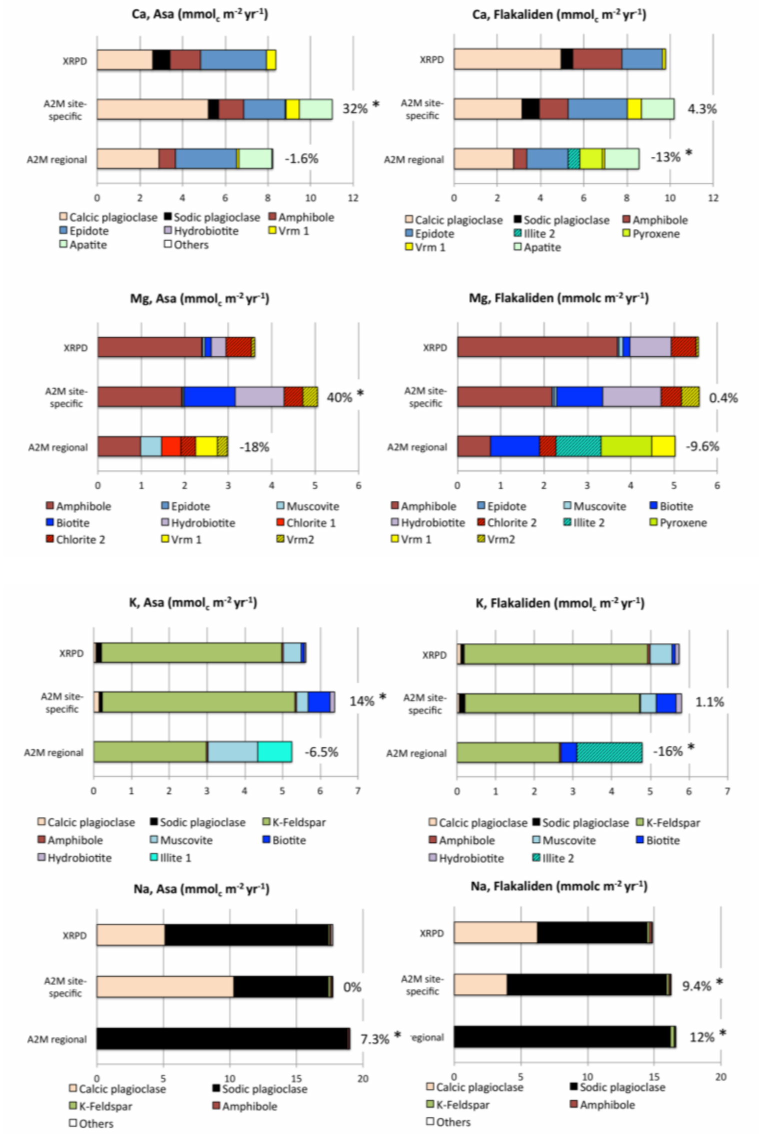


Figure 5. PROFILE base cation weathering rate based on XRPD mineralogy and the average PROFILE base cation weathering rate (*i.e.* based on one thousands input A2M mineralogies per mineral) according to the two normative mineralogical methods. The comparison is done for different minerals in the upper mineral soil (0-50 cm) and for each study site (i.e. Asa site-sepcific, Flakaliden site-specific, Asa regional, Flakaliden regional). Relative error (% of W_{XRPD} estimate) are given at the end of each bar (for W_{A2M}) to show the average deviation of W_{A2M} and W_{XRPD} in the upper mineral soil. *=significant discrepancy as defined in section 4.5. Vrm1=Trioctahedral vermiculite; Vrm2=Dioctahdreal vermiculite.

The identification of a compensatory effect made it possible to answer the question that arises when comparing W_{A2M} with W_{XRPD}, *i.e.* why the total PROFILE weathering estimates based on regional mineralogy ($W_{A2M\text{-}reg}$) at Asa and Flakaliden and based on site-specific mineralogy ($W_{A2M\text{-}site}$) for Flakaliden were relatively closely related to W_{XRPD} (deviation <20% (Figure 4a and 5) as suggested by Jönsson et al., 1995). Interestingly, the answer was that there was no systematic pattern that could explain these differences, since the relative contribution of different minerals to the total weathering rates at Asa compared to Flakaliden were both very similar (for $W_{A2M\text{-}site}$ of Mg and K, for $W_{A2M\text{-}reg}$ of Na) and rather different (for $W_{A2M\text{-}reg}$ of Ca, Mg and K, for $W_{A2M\text{-}site}$ of Na and Ca) (Figure 5). Root mean square errors were large regardless of the method used to determine A2M mineralogies (with the exception of $W_{A2M\text{-}site}$ for K at both sites) (Figure 4b). This was most apparent for magnesium. In each case, specific minerals added a large contribution of uncertainty to the overall/total weathering rates (*i.e.* apatite for Ca, pyroxene for Mg, K-feldspar/mica for K) (Figure 5), which has been to different sources of uncertainty (grey and red arrows) that are propagated from paper II to paper III (Figure 9). Apart from apatite, it was speculated that calcite could have fallen under the XRPD detection limit of <1 wt.-%. Whereas apatite might indeed contribute up to a maximum of 0.3 wt.% (total apatite content modelled based on total phosphorus minus the likely contributions of different phosphorous (P) phases (organic P, phosphate (PO_4^{3-}) bound to clays and Al and Fe hydroxides or precipitated asCa, Al and Fe phosphates)) in soils to the overall calcium weathering rate, there is good reason to believe that calcite does not contribute to calcium weathering rates in the studied soils (see section 4.2). The second unexpected finding in Paper II was that inaccuracies in quantitative determination of K-feldspar and micas did not affect PROFILE weathering rates significantly as long as the dissolution rate coefficients for these minerals were kept the same (uncertainty highlighted in Figure 9 (red arrows)). Owing to the basic difference in crystalline structure between micas and K-feldspar, potassium ions are held in their binding positions with different strengths (K-feldspar > mica). Furthermore, minerals are weathered congruently according to PROFILE but this does not reflect natural conditions, where a large proportion of silicate minerals release elements preferentially through transformation. A true and significant difference in the dissolution rates of K-feldspar and mica can therefore be expected under natural conditions (Simonsson et al., 2016; Thompson & Ukrainczyk, 2002).

Based on the W_{XRPD} data, base cation weathering was in quantitative terms predominantly derived from plagioclases, followed by K-feldspar and amphibole at Flakaliden and epidote at Asa. This is partly in line with previous findings by Sverdrup and Warfvinge (1993). Contrary to these findings, the magnesium and calcium release rates in the regional application of PROFILE at Flakaliden proved to be affected by several minerals with high dissolution rates. Of these, apatite was classified as the most influential mineral for calcium release, due to its low mineral dissolution rate coefficient used in PROFILE for the reaction with water. As described by Holmqvist et al. (2003), the reaction of mineral surfaces with water (hydrolysis) in PROFILE dominates over the other reactions (*i.e.* 50% or more reactions are based on H_2O, 25-30% on CO_2, 10-15% on organic ligands and 5-10% on H^+ reaction).

5.3 Paper III

Current forestry practices are strongly dependent on reliable estimates of current weathering rates at the pedon scale. In Paper III, an important first step to achieving this goal was to cross-validate current weathering estimates based on the PROFILE model against average long-term weathering rates based on the depletion method.

First, comparison of both methods in the upper mineral soil (0-50 cm), showed that historical magnesium losses estimated by the depletion method ($W_{depletion}$) at Flakaliden were higher (12.9 $mmol_c/m^2$/year) than those estimated by PROFILE ($W_{profile}$) (6.7 $mmol_c/m^2$/year). Since the comparison was made in a harmonised way in terms of boundary conditions and quality of common input data, these differences could be interpreted as a reflection of the conceptual differences between the methods. This interpretation is in line with common theories of a decline in weathering rates over time (Hodson & Langan, 1999; White et al., 1996; Taylor and Blum, 1995). Apart from magnesium at Flakaliden, $W_{profile}$ was generally higher than $W_{depletion}$ in both the 0-50 cm and 0-100 cm soil profile. Moreover, both current and historical estimates were higher at Flakaliden than at Asa, However, historical weathering rates at Asa could have be underestimated, owing to relatively flat zirconium gradients for all soil profiles, which may have resulted from various disturbances in the past (*i.e.* soil scarification, bioturbation or small-scale agriculture).

A second test of the reliability of current weathering rates based on PROFILE was made by comparing similarities between predicted and calculated weathering rate gradients with soil depth for the 0-100 cm mineral soil. Contrary to PROFILE, estimates based on the depletion method predicted a decline in the loss of elements with increasing soil depth (Figure 6), which is in line with the common view on soil formation and mineral ageing. Based on this evidence, which confirmed that the depletion method gives results that are in line with general expectations about historical soil development over time, it was possible to calculate the hypothetical time needed for the PROFILE-based current weathering rates to accomplish the historical element losses determined with the depletion method. Accordingly, maximum PROFILE weathering rates observed at 80 cm (Asa) or 60 cm (Flakaliden) depth (Figure 6) appeared to achieve historical losses in unreasonably short time spans (Figure 7a,b). It could not be argued that this intense weathering was due to the weathering front moving through the soil (Yoo & Mudd, 2008), which would mean that PROFILE-predicted, soil depth-related weathering gradients could be explained by the progressive depletion of soil minerals throughout the soil. An evaluation of the sensitivity of the PROFILE model with regard to variation in important input parameters showed that the model was most sensitive to within-soil profile variability of exposed mineral surface area and soil bulk density, and rather insensitive to soil depth-related changes in mineralogical composition. The latter was a strong reason to reject the hypothesis of a moving weathering front passing through the soil.

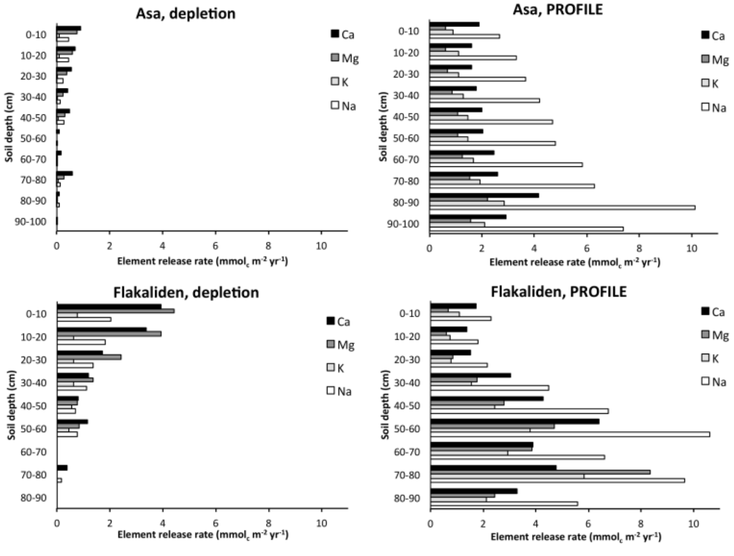


Figure 6: Shown are historical weathering rate of base cations (mmol$_C$ m^{-2} yr^{-1}) estimated by the depletion method (left) and steady-state weathering rate estimated by the PROFILE model (right) in different soil layers at Asa and Flakaliden.

Contrary to what was observed at the Asa site (Figure 7b), the results for Flakaliden (Figure 7a) suggested that the hypothetical time needed to achieve historical losses of magnesium and calcium based on minimum PROFILE weathering rates was ‘sustainable’ (Figure 7a), which was regarded as a validation of $W_{profile}$ (Figure 9). Thus they exceeded the age of the soil for both elements in the shallow soil horizons and for magnesium this was the case even in the deeper soil horizons (*i.e.* 0-60 cm layer for Mg). However, the opposite was revealed for potassium and sodium, at both Asa and Flakaliden. Even when minimum PROFILE weathering rates observed in the shallow soil horizons were applied, these rates were still too high and achieved a historical weathering loss in less than half the time of the respective soil age at Asa. The increase in PROFILE weathering intensity with increasing soil depth was strongly correlated (R^2 = 0.65-0.89) to an increase in exposed mineral surface area. Increases in weathering rates with soil depth have also been observed in buried test (rock) mineral studies (Palviainen et al., 2012) and can be explained by a decrease in ionic strength and acidity of the soil solution. Hodson and Langan (1999) applied the PROFILE model for two chronosequences and showed that soil density and surface area explained the increase in PROFILE predicted weathering rates with soil age. Average historical weathering rates predicted with the depletion method could be explained by the loss of reactive minerals and the development of etch pits and secondary precipitates over time. Thus, in Paper III the criticism was made that PROFILE normalises mineral dissolution to total surface area instead of reactive surface area, and does this under the assumption that reaction coefficients are constant. These general findings might lend support for overestimated rather than underestimated PROFILE weathering rates. Furthermore, PROFILE predicted the highest weathering rates for sodium, followed in order by calcium, magnesium and potassium at Flakaliden and calcium, potassium and magnesium at Asa. In line with previous studies in northern Sweden (Olsson & Melkerud, 2000), at Flakaliden the historical average element loss based on the depletion method in both the upper mineral soil (0-50 cm) and the entire mineral soil (0-100 cm) was highest for magnesium, followed in order by calcium, sodium and potassium. Further indications that support this ranking is the geochemical composition of Flakaliden soils, showing strong vertical patterns for magnesium, with an increase in magnesium concentrations with depth in the soil profile. Similar vertical patterns have been reported by Olsson et al. (1993) and Olsson and Melkerud (1989). As pointed out by Bain et al. (1993), the mobility of an element can be indicated by the ratio of the weathering rates and the concentration of the respective element in the C-horizon. Accordingly, magnesium was the most mobile element at Flakaliden and Asa, as exemplified by an increase in amphibole and chlorite with increasing soil depth. Strong historical mobility of magnesium has also been reported by Olsson and Melkerud (2000), Ulén and Snäll (1998) and Bain et al. (1993).

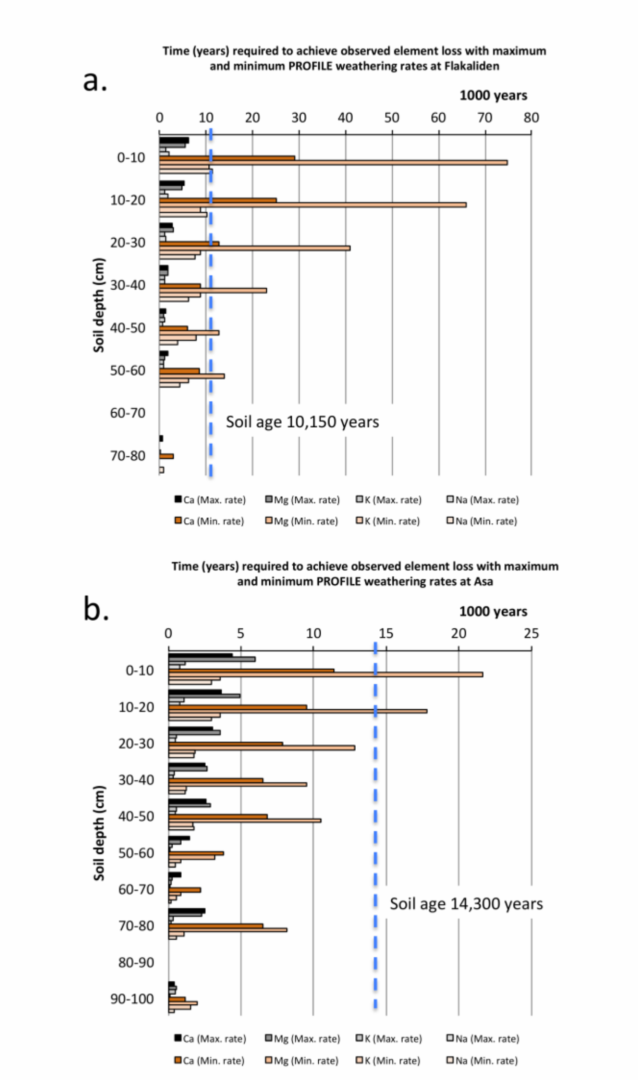


Figure 7: Bars represent the measured historical element loss in different soil layers predicted with maximum or minimum PROFILE weathering rates at (a) Flakaliden and (b) Asa. The dashed vertical line represents the time (years) that is needed to achieve this historical loss of base cations (*i.e.* 10.150 years for Flakaliden and 14.300 years for Asa).

In terms of comparing all three weathering estimates in a base cation budget in the 0-50 cm soil layer (Figure 8), it was found in Paper III that weathering based on the depletion method ($W_{depletion}$) and the PROFILE model ($W_{profile}$) played a minor role in the overall base cation cycle at the two study sites compared with weathering rates estimated from the base cation budget (W_{bcb}). However, uncertainties in W_{bcb} were most likely underestimated when based on standard error of site mean values of weathering, especially for potassium. Weathering of potassium was mostly influenced by the nutrient uptake term in the base cation budget, which was based on site measurements rather than plot-wise measurements. Regardless of these uncertainties in estimated weathering rates, net nutrient uptake was a dominant sink in all three base cation budgets, most specifically for calcium. These findings are in line with the general notion that, in an aggrading forest soil, nutrient return to the soil is lower than nutrient uptake (Yanai et al., 2005; Kelly et al., 1998). Moreover, in most cases, large biomass uptake of base cations needs to be balanced by sources of base cations in the soil, either by estimated soil change in the budgets based on $W_{depletion}$ and $W_{profile}$ or by W_{bcb}. Estimated soil change and W_{bcb} might both consist of different bioavailable pools, such as Ca-oxalate complexes (Dauer et al., 2014), fixed or interlayer potassium (Simonsson et al., 2016) or base cations fixed in microbial biomass of forest soils.

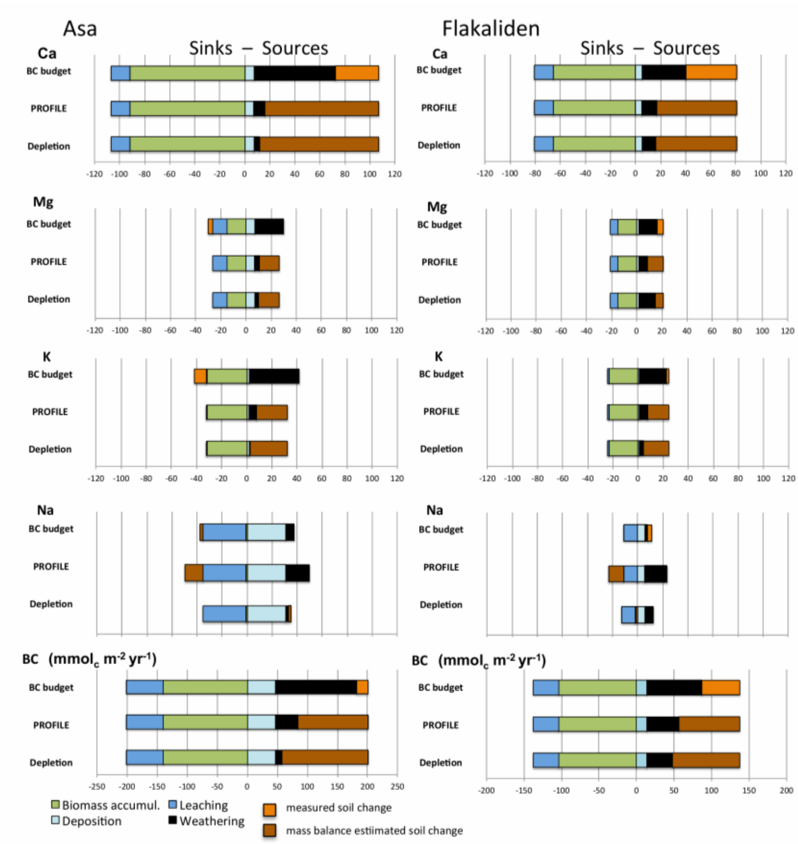


Figure 8: Shown are sinks (left) and sources (right) of base cations in net ecosystem fluxes at Asa and Flakaliden. The soil is considered a net source of base cations if stocks decrease and a net sink if they increase. 'BC budget' = present-day dynamic base cation weathering rate (W_{bcb}) estimated with the base cation budget method, including measured changes in soil extractable base cation stocks; 'PROFILE' = present-day steady-state weathering rate ($W_{profile}$) estimated using PROFILE, where soil extractable pools are estimated from the base cation budget; 'Historical' = historical weathering rate ($W_{depletion}$) by the depletion method, where soil extractable pools are estimated from the base cation budget;. ‘Base cation budget estimated soil change’ and ‘Measured soil change’ indicate that equation 7 and 6 were used to estimate weathering rate or the soil change, respectively.

Indeed, for W_{bcb} of calcium, relatively large estimated combined uncertainties (93.3 and 64.4 mmol$_c$/m^2/year for Asa and Flakaliden, respectively) (*i.e.* depicted in Figure 9 as overall largest uncertainty associated with base cation budget approach (W_{bcb}) in this thesis) were related to the 95% confidence intervals of bioaccumulation, which suggests that there is some uncertainty as to whether W_{bcb} only comprises mineral weathering products. In several previous studies, the exchangeable cation pool could not account for the intense nutrient uptake in growing forests (Brandtberg and Olsson, 2012;

Bélanger et al., 2004; Yanai et al., 1999). Furthermore, compared with calcium, lower estimated combined uncertainties were suggested for W_{bcb} of potassium at both study sites (32.3 and 22.2 $mmol_c/m^2$/year for Asa and Flakaliden, respectively). The relatively small measured soil change in potassium at both study sites could be explained by the observation that pools of exchangeable potassium are relatively stable (Bengt Olsson, unpublished data; van der Heijden et al., 2013). Surprisingly, for potassium and magnesium, W_{bcb} exceeded nutrient uptake rates at Asa (Figure 8). These results are in line with those reported by Bormann et al. (1998) for magnesium. However, there is no support in the literature for the results for potassium presented in Paper III. Although the quality of most terms in the potassium budgets based on W_{bcb} was considered relatively high, biomass accumulation constituted a relatively large uncertainty in the overall potassium budget. In combination with its quantitative importance in the potassium budget, this most likely contributed to W_{bcb} overestimates of potassium.

Base cation budget weathering estimates of sodium could simply be derived from the sum of atmospheric deposition and weathering, minus the removal of sodium from the soil via leaching (Figure 8). These estimates were seen as relatively robust, since estimated combined uncertainties for sodium were low (23.6 and 6.1 $mmol_c/m^2$/year for Asa and Flakaliden, respectively), especially at Flakaliden. Similarities in the sodium base cation budget based on W_{bcb} and $W_{depletion}$ were interpreted as reflecting conservative behaviour of sodium in forest ecosystems (Ågren and Andersson, 2012) and was regarded as a validation of $W_{depletion}$ in paper III (Figure 9). This means in turn that PROFILE overestimates sodium weathering rates, as previously postulated by Houle et al. (2012), Philipps and Watmough (2012) and Stendahl et al. (2013). Similarly to the approach in Paper III, Philipps and Watmough (2012) tried to validate their PROFILE model results with regard to sodium by making use of the simplified mass balance, *i.e.* by comparison of sodium exports and inputs (*i.e.* deposition and leaching).

Comparing all three budgets (*i.e.* $W_{depletion}$, $W_{profile}$ and W_{bcb}) for calcium, magnesium and potassium showed that they agreed better at Flakaliden (as illustrated by the budget for the sum of all base cations) than at Asa (Figure 8). At Asa, a plausible reason is the more intense tree uptake of calcium, magnesium and potassium at this southern Swedish site and a smaller change in measured exchangeable base cations. The geographical differences in base cation fluxes of calcium observed in this thesis are in line with recent findings by Zetterberg et al. (2016). They are also supported by findings in other studies of small pools of exchangeable calcium and magnesium pools in acid forest soils (van der Heijden, 2017). However, W_{bcb} at Flakaliden was still overestimated for calcium and, most significantly, for potassium. Thus it is possible that W_{bcb} comprises other soil sources of base cations and underestimated portions of exchangeable base cations at Asa and Flakaliden not captured by measurements of salt-extractable base cations (Olofsson, 2016). However, Rosenstock et al. (unpublished (2019a)) showed that strong acids such as hydrochloric acid (HCl) can dissolve silicate minerals. Moreover, rapid turnover of exchangeable soil pools of base cations in spruce forest soil, as described by Simonsson et al. (2015) and Yanai et al. (2005), could be an explanation for the relatively large contribution of soil depletion to the combined uncertainty in W_{bcbc} of potassium and calcium. Many studies have reported the important role of recycling of divalent cations released from mineralisation of organic matter in organic soil, which may be a strategy by coniferous tree species to overcome nutrient limitation (Hobbie et al., 2007; Dijkstra & Smits, 2002). Moreover, van der Heijden et al. (2017) identified a non-crystalline transition pool of calcium and magnesium in acidic forest soils, which was shown to be more important for calcium than for magnesium. It was hypothesised that the latter was caused by historically stronger depletion of magnesium than of calcium soil pools (in their case in the Breuil-Chenue experimental mountain forest ecosystem, Burgundy, France). With regard to potassium, Simonsson et al. (2016) showed in a rubidium isotope study that the mineral soil is an important source of the proportion of potassium that is taken up by trees (approximately 25%). It has previously been shown that potassium accumulates in secondary minerals in soils (Andrist-Rangel et al., 2006) and is tightly biocycled (James et al., 2016; Ågren and Andersson, 2012), which explains the negligible losses of potassium from soils due to leaching. Watmough et al. (2005) found that watershed mass balances were nearly balanced when weathering was included. At least for calcium and magnesium, W_{bcb} could comprise base cations taken up from the deeper mineral soil and could explain the gap between nutrient uptake and depletion of base cations from the upper mineral soil (*i.e.* 0-50 cm). James et al. (2016) showed that low exchangeable calcium and magnesium pools are related to leaching with dissolved organic matter in wet and cold climates and that exchangeable calcium and magnesium increase significantly with increasing soil depth. This is in contrast with the trend of decreasing soil carbon with depth, whereas soil exchangeable potassium is less deeply distributed owing to the higher biological control over potassium distribution in soils. Joggaby and Jackson (2001) concluded that higher upward transport of nutrients from deeper soil layers is triggered by a high ratio of plant uptake to soil supply.

6 Conclusions

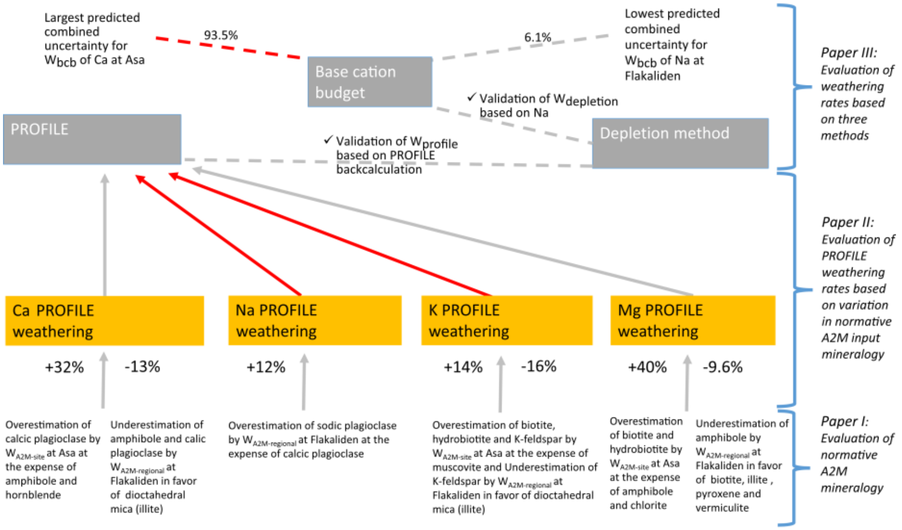


Figure 9. Summary of the findings in this thesis. The diagram should be read from bottom to top, where major findings from Paper I influenced Paper II significantly. For example, trading of elements between calcium (Ca)- and magnesium (Mg)-bearing minerals strongly affected over- and underestimation of normative A2M quantitative mineralogy compared with trading of elements with potassium (K)-bearing minerals (Paper I). These results caused large average overestimation of PROFILE weathering rates for Ca and Mg (the relative error (% of 'true' W_{XRPD} estimate) illustrates the average deviation of W_{A2M} from W_{XRPD} in the upper mineral soil (0-50 cm)). However, these results for Ca and Mg were shown to be "coincidental". Uncertainties relating mainly to the presence or absence of specific minerals with high dissolution rates (grey arrows) were apparent in both the normative A2M mineralogy and the XRPD mineralogy. Weathering results for K and sodium (Na) were mainly related to uncertainties in mineral dissolution rate coefficients (red arrows). These uncertainties identified in Paper II might have affected the weathering results in Paper III, which were based on PROFILE using XRPD mineralogy. A validation of PROFILE weathering results was therefore performed based on two approaches. The first one involved a back-calculation (*i.e.* calculating the time that is required to achieve historical weathering losses using PROFILE weathering rates) and the second a validation of the depletion method based on comparison of historical Na weathering estimates and dynamic Na weathering

rates derived from applying the base cation budget approach (the latter was possible due to a low predicted combined uncertainty of Na weathering rates estimated with the base cation approach).

6.1 Important ways to reduce uncertainties in estimating Ca and Mg weathering rates

Paper I confirmed the accuracy in direct measurements of soil mineralogy (*e.g.* XRPD and electron microprobe) and showed that quantitative mineralogies calculated by A2M using the two different approaches were in relatively close agreement with measured XRPD mineralogy. However, trading of elements between minerals (including minerals that weather relatively rapidly) led to significant discrepancies between PROFILE weathering rates in Paper II.

More importantly, the results in Paper II showed that discrepancies of some magnitude between PROFILE weathering rates for calcium and magnesium are likely to occur whatever the type of mineralogical input data used. Four minerals (apatite, pyroxene, illite and calcite) that added the largest uncertainties to PROFILE weathering rates were identified. In in-depth future analyses of uncertainties in weathering rates due to mineralogical input, a first step should be to constrain the allocation of phosphorus to apatite in normative A2M input data, making use of knowledge of how phosphorus is speciated in soil profiles. Similarly, measured mineralogy could be improved by trying to characterise minerals that fall below the detection limit of the XRPD method (calcite, apatite, pyroxene). These adjustments are likely to improve PROFILE weathering estimates and could be regarded as a refinement of the results obtained in Paper III, since the suggested rates for calcium and magnesium estimated by PROFILE using measured mineralogy were reasonably accurate. By calculating the time needed for PROFILE weathering rates to achieve historical losses predicted by the depletion method, it proved possible to validate the PROFILE model results for calcium in shallow soil layers and for magnesium in all soil layers at the Flakaliden site. Similarities in historical losses of calcium and magnesium at the Flakaliden site are strong indicators of similarities in the overall biogeochemical cycles of these elements. As confirmed by the XRPD measurements in Paper I, the easily weatherable mineral amphibole was the most abundant calcium- and magnesium-containing mineral at Flakaliden, and its abundance increased significantly with soil depth.

6.2 Important ways to reduce uncertainties in estimating Na and K weathering rates

Surprisingly, high uncertainties in quantitative mineralogy estimated using the regional normative A2M mineralogy compared to the measured quantitative XPRD mineralogy had small effects on calculated PROFILE weathering rates for potassium. Uncertainties arising on comparing PROFILE weathering rates based on reference mineralogy derived from XRPD measurements and on normative mineralogy calculated by the A2M program were lower for sodium and potassium (<20%) compared with magnesium and calcium (Paper II). However, these results do not reflect differences in dissolution rates of major sodium- and potassium-bearing minerals in natural environments.

The use of updated mineral dissolution rate coefficients in future PROFILE weathering studies for major sodium- and potassium-bearing minerals (*i.e.* the plagioclase feldspars, K-feldspar and dioctahedral micas) are likely to contribute to larger differences between the PROFILE weathering rates based on direct measurements of mineralogy and those based on regional A2M mineralogy, since the latter assumes a large contribution of mica to overall potassium weathering rate.

In Paper III, it was shown that the depletion method underestimated rather than overestimated sodium and potassium weathering rates. At the Flakaliden site, there was relatively large between-plot variability in zirconium gradients, showing that an improved understanding of the method can only be achieved by using a large number of soil profiles per study site. A first step in testing the suitability of a soil profile to be used for historical weathering calculations should be to verify that zirconium shows a net trend of enrichment towards the soil surface. This should be one of the first criteria in future studies to decide whether or not to exclude a soil profile from further analysis. A second test should be to compare titanium and zirconium gradients in deeper soil horizons. Furthermore, in future studies it could be of interest to determine historical weathering rates with at least two methods (*e.g.* the pedological mass balance approach and the depletion method). There is a need to validate historical weathering estimates. Overestimation rather than underestimation of sodium and potassium could be justified (a) based on back-calculations of historical weathering losses and (b) based on comparison of weathering rates to sodium input and output fluxes. Applying at least two validation tools to evaluate the reliability of current weathering estimates seems to be crucial in assessment of sustainable forest harvesting practices.

6.3 Weathering in a base cation budget perspective

Given accurate local input data, the base cation budget approach proved to be a crucial tool for comparison of weathering rates estimated by other approaches, *e.g.* to validate the reliability of current weathering estimates against historical weathering estimates. However, it was not a suitable tool for estimating calcium, magnesium and potassium weathering rates, due to the difficulty in distinguishing between exchangeable stocks and other plant-available soil sources of base cations.

The base cation budgets showed that the soil was the most important source of base cations accumulated in trees, since atmospheric deposition of calcium, magnesium and potassium constituted a very small part of the overall base cation cycling. For calcium and potassium, weathering of primary minerals played a minor role compared with depletion of exchangeable stocks or the possible contribution from other unidentified sources in the soil. For magnesium at Flakaliden, on the other hand, weathering was more important for the uptake in trees.

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Popular science summary

Base cations are essential nutrients for plants, since they are involved in photosynthesis (magnesium) and regulation of gas exchange through opening and closing of stomata (potassium), are integral parts of plant tissues (calcium and magnesium) and are regulators of the ion balance in plant cells (potassium).

A major concern for forest managers and policy makers in Sweden is identification of sustainable forest production levels and loads of acidity, so that progressive nutrient losses from soils and forests can be avoided without addition of fertiliser. However, large uncertainties about the absolute release rates of calcium, magnesium, potassium and sodium from soil minerals cause uncertainties in defining levels of sustainable forest production and harvests.

Atmospheric deposition of base cations and weathering of soil minerals are the only long-term sources of nutrients to forest ecosystems. Weathering involves the breakdown of minerals into smaller components (physical weathering) and changes in their composition (chemical weathering). Chemical weathering leads to the release of base cations into soil water, where they can be taken up by plant roots, accumulate (incorporated into new or existing minerals, build complexes with amorphous soil material, adsorb to soil particle surfaces) or be flushed away by leaching from the main root zone in soils (*i.e.* 0-50 cm depth). Net inputs (deposition and weathering) and outputs (tree uptake and leaching) of base cations can be compared in ecosystem base cation budgets. This thesis shows that high rates of tree uptake of base cations from the ecosystem need to be balanced almost entirely by soil sources other than weathering. This finding is reliable, since it was confirmed using three different estimates of base cation release rates. Each method differed conceptually, since no method can calculate all three aspects of weathering, *i.e.* long-term (weathering since the beginning of soil formation, usually calculated by the depletion method), short-term (dynamic present-day weathering response to increased nutrient uptake in soils, usually based on the base cation budget approach) and constant (weathering response to present-day environmental conditions, usually calculated based on the PROFILE model). In this thesis, the methods were compared in a harmonised way (*e.g.* uniform data use and sampling location), which allowed true or conceptual similarities and dissimilarities between the methods to be identified for the first time. The results showed that dynamic weathering values based on the base cation budget approach (*i.e.* the difference between ecosystem input and output fluxes of base cations) were largely overestimated for calcium, magnesium and potassium. For calcium and magnesium, the depletion method and PROFILE model gave reasonably accurate results. For potassium and sodium, weathering rates were overestimated by the PROFILE model.

The results indicate that dissolution rate kinetics for important potassium- and sodium-bearing minerals should be changed in future applications of the model. The PROFILE weathering rates for calcium and magnesium were also found to be uncertain, due to lack of knowledge about the presence or absence of highly weatherable minerals. This new knowledge about uncertainties in the content of highly weatherable minerals can be used to refine direct mineralogy quantified by X-ray powder diffraction (XRPD) for future use in applications of the PROFILE model. However, the results also indicate that PROFILE weathering rates are not strongly affected by uncertainties related to minerals occurring under the detection limit of the XRPD mineralogy (apatite, pyroxene and calcite). The use of quantitative XRPD mineralogy as the ‘true’ mineralogy of the soil at the study sites was justified based on the accuracy of the measurements, whereas the more simple and inexpensive tools that are commonly used in PROFILE applications to estimate quantitative mineralogy (the normative “Analysis to Mineralogy” (‘A2M’) program) need better input data. Overall, this thesis demonstrated the potential of two conceptually different methods (PROFILE model and depletion method) to estimate weathering rates, provided that: (i) it is confirmed that the depletion method gives reasonable results, which requires careful assumption testing for every soil profile for which weathering rates are to be calculated; (ii) PROFILE weathering rate kinetics for major potassium- and sodium-bearing minerals are improved; and (iii) validation tools for both methods are improved.

Populärvetenskaplig sammanfattning

Baskatjoner är essentiella näringsämnen för växter, eftersom de är nödvändiga för fotosyntesen (magnesium), reglerar växtens gasutbyte genom klyvöppningarna (kalium), är integrerade delar av vävnader (kalcium och magnesium) och är viktiga för att reglera växters jonbalans (kalium).

I Sverige har skogen en viktig roll att spela i omställningen till ett fossilfritt samhälle. Det ställer stora krav på förmågan att öka produktionen av biomassa från skogen på ett hållbart sätt, *t.ex.* så att ökade näringsförluster från skogsmarken kan undvikas utan särskild näringskompensation. Osäkerhet om i vilken takt marken kan leverera baskatjoner för att skapa hållbar skogsproduktion skapar därmed osäkerhet kring vilka skördenivåer som kan betraktas som hållbara.

Atmosfäriskt nedfall av och vittring av mineral i marken är de enda källorna som på lång sikt tillför baskatjoner till skogsekosystem. Vittring innebär att mineral bryts ner i mindre beståndsdelar (fysisk vittring) och förändrar sin kemiska sammansättning (kemisk vittring). Kemisk vittring leder till frigörelse av baskatjoner till markvattnet där de kan tas upp av växtrötter, ackumuleras (byggas in i nya eller befintliga mineral, eller i amorfa mineral i marken, adsorberas till markpartiklarnas ytor), eller lakas ut från den huvudsakliga rotzonen i marken (*d.v.s.* 0–50 cm markdjup). Nettoinflöden (nedfall och vittring) och nettoutflöden (upptag i träd och utlakning) av baskatjoner kan jämföras i form av baskatjonbudgetar för ekosystem. Denna avhandling har visat att det stora upptaget av baskatjoner som sker när trädens tillväxttakt är hög måste balanseras till största delen av andra källor i marken än vittring. Slutsatsen baseras på resultat från tre olika metoder att mäta frigörelsen av baskatjoner genom vittring, vilket gör den pålitlig. Mätmetoderna som användes var olika till sin natur, och gav sinsemellan olika mått på vittringshastigheten i tid och rum: Den långsiktiga vittringen (den som skett sedan slutet av istiden när jordlagren bildades, som vanligen mäts genom beräkning av historiska 'massförluster', den kortsiktiga (den dynamiska, aktuella vittringen som avspeglar kortsiktiga markkemiska förändringar genom t ex näringsupptag, som ofta mäts med baskatjonbudgetar), och den konstanta (den aktuella vittringen beräknad med antagande om en konstant kemisk miljö i marken, ofta beräknad med PROFILE-modellen). I denna avhandling beräknades vittringen med olika metoder men med enhetliga förutsättningar, *t.ex.* samma fysiska avgränsningar och enhetliga databas, för att ge bättre möjlighet att identifiera likheter och olikheter mellan metoderna än i tidigare studier. Resultaten visade att den dynamiska vittringen, som baserades på baskatjonbudgeten (*dvs.* skillnaden mellan ekosystemets in- och utflöden av baskatjoner) var tydligt överskattad för kalcium, magnesium och kalium. PROFILE-modellen och skattningar av förluster av baskatjoner i markprofilen bedömdes ge rimliga skattningar av den aktuella respektive långsiktiga vittringen av kalcium och magnesium.

Resultaten visade att kunskap om upplösningshastigheten av mineral som är viktiga för kalium- och natrium-vittringen behöver korrigeras för framtida användning i PROFILE-modellen. Det fanns även en osäkerhet i PROFILE-modellens beräkning av frigörelsen av kalcium- och magnesium som berodde på att lättvittrade mineral som är rika på dessa baskatjoner är svåra att kvantifiera när de förekommer i små mängder i marken. Ny kunskap om dessa lättvittrade mineral skulle kunna förbättra bestämningen av kvantitativ mineralogi med röntgendiffraktionsanalyser baserade på pulvriserade mineral (X-ray powder diffraction, XRPD), som sedan används i PROFILE-modellen. Osäker bestämning av lättvittrade mineral som ofta förekommer under detektionsgränsen för XRPD, som apatit, peroxen och kalcit, har dock ingen stor effekt på PROFILE-modellens bestämning av vittringen. XRPD-analyser av den kvantitativa mineralogin har i denna studie betraktats som den "sanna" mineralogin. En “normativ” metod för att beräkna kvantitativ mineralogi som ofta har använts i PROFILE-modellen är kalkylprogrammet ‘A2M’ (“Analysis to Mineralogy”). Programmet använder billigare och enklare geokemiska analyser av mineral än XRPD, men resultaten visar att det finns behov av att förbättra kvaliteten på data som används i A2M. Avhandlingen har visat att PROFILE-modellen och massförlustmetoden har potential har ge pålitliga skattningar av vittringen givet vissa förutsättningar. För mätning av långsiktig vittring med massförlustmetoden är det av central betydelse att alla kriterier för metoden är uppfyllda. För PROFILE-modellen är förbättrad kunskap om viktiga kalium- och natriumhaltiga minerals upplösning särskilt viktig, och för båda angreppsätten är det viktigt att förbättra metoder för att validera dem.

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