Current, steady-state and historical weathering rates of base cations at two forest sites in northern and southern Sweden: A comparison of three methods

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Abstract

Reliable and accurate methods for estimating soil mineral weathering rates are required tools in evaluating the sustainability of increased harvesting of forest biomass. A variety of methods that differ in concept, temporal and spatial scale and data requirements are available for measuring weathering rates. In this study, release rates of base cations through weathering were estimated in podsolised glacial tills at two experimental forest sites, Asa and Flakaliden, in southern and northern Sweden, respectively. Three different methods were used: (i) historical weathering since deglaciation estimated with the depletion method, using Zr as assumed inert reference; (ii) steady-state weathering rate estimated with the PROFILE model, based on quantitative analysis of soil mineralogy; and (iii) base cation budget at stand scale, using measured deposition, leaching and changes in base cation stocks in biomass and soil over a period of 12 years.

In the 0–50 cm soil layer at Asa, historical weathering of Ca, Mg, K and Na estimated by the depletion method was 4.7, 3.1, 0.8 and 2.0 $mmol_c\ m^{-2}\ yr^{-1,}$ respectively. Corresponding values at Flakaliden were 11.0, 12.9, 3.2 and 7.0 $mmol_c\ m^{-2}\ yr^{-1}$, respectively. Steady state weathering rate for Ca, Mg, K and Na estimated with PROFILE was 8.9, 3.8, 5.9 and 18.5 $mmol_c\ m^{-2}\ yr^{-1}$, respectively, at Asa and 11.9, 6.7, 6.6 and 17.5 $mmol_c\ m^{-2}\ yr^{-1}$, respectively, at Flakaliden. At both sites, the PROFILE results indicated that steady-state weathering rate increased with soil depth as a function of exposed mineral surface area, reaching a maximum rate at 80 cm (Asa) and 60 cm (Flakaliden). In contrast, the depletion method indicated that the largest postglacial losses were in upper soil layers, particularly at Flakaliden.

With the exception of Mg and Ca in shallow soil layers, PROFILE appeared to produce consistently higher weathering rates than the depletion method, particularly of K and Na in deeper soil layers. In contrast, the depletion method appeared to produce consistently lower rather than higher weathering rates, due to natural and anthropogenic variability in Zr gradients. The base cation budget approach produced significantly higher weathering rates of Ca, Mg, and K (65, 23, 40 $mmol_c\ m^{-2}\ yr^{-1}$at Asa and 35, 14 and 22 $mmol_c\ m^{-2}\ yr^{-1}$at Flakaliden), but lower Na weathering rates similar to the depletion method (6.6 and 2.2 $mmol_c\ m^{-2}\ yr^{-1}$at Asa and Flakaliden). The large discrepancy in weathering rates for Ca, Mg and K between the base cation budget approach and the other methods suggest that there were additional sources for tree uptake in the soil besides weathering and measured depletion in exchangeable base cations.

Keywords. Weathering; minerals; soil layers; nutrient mass-balance; *Picea abies*; PROFILE model; depletion; base cation budget approach

Definitions and abbreviations

Mineralogy = The identity and stoichiometry of minerals present in a certain geographical unit, a particular site (*site-specific mineralogy*) or a larger geographical province (*regional mineralogy*)

Quantitative mineralogy or mineral composition = Quantitative information (wt.%) on the abundance of specific minerals in the soil.

Weathering rate = Weathering of a mineral resulting in release of a base cations per unit area per unit time.

Definitions:

$W_{depletion}$ = Historical weathering rate based on calculation of loss of mobile elements since last deglaciation

$W_{profile}$ = Steady-state weathering rate estimated using the PROFILE model

W_{budget} = Current weathering rate based on base cation budget calculations

1. Introduction

Silicate weathering is the major long-term source of base cations in forest ecosystems (Sverdrup et al., 1988) and is therefore crucial for sustainable plant production and for proton consumption, counteracting soil and water acidification (Nilsson et al., 1982; Hedin et al., 1994; Likens et al., 1998; Bailey et al., 2003). These effects of weathering are important in areas where in the past high sulphur (S) deposition has caused severe acidification of forest soils and waters (Reuss and Johnson, 1986), for example in southern Scandinavia where felsic igneous bedrock and less readily weatherable soils are abundant (Likens and Bormann, 1974). By 1990 in most European countries, the trend of increasing S emissions since the 1950s started to abate (Grennfelt and Hov, 2005) and forest and accumulation of base cations in tree biomass in excess of anion uptake has become a more important source of acidity to the soil (Nilsson et al., 1982). Whole-tree harvesting can thus result in more acid, base cation-depleted soils than stem-only harvesting (Olsson et al., 1996; Zetterberg et al., 2013). The combined effect of increased productivity of forests in Sweden, resulting in increased stocks of forest biomass, and increased use of whole-tree harvesting for energy purposes can therefore impede recovery from acidification and place increasing demands on nutrient supply.

In society there is a need to know if current forestry practices are sustainable, that is if current weathering provides enough base cations to at least balance their export by forestry. The role of weathering in maintaining base cation balance in Swedish forest soils has been examined in several previous studies (Sverdrup and Rosén, 1998; Akselsson et al., 2007). A regional-scale study on Swedish forest soils found that, in parts of Sweden, base cation losses can occur at rates that lead to very low base saturation of the soils, possibly leading to negative effects on e.g. soil fertility and runoff water quality within one forest rotation (Akselsson et al., 2007). Base cation depletion in the soil was found to be more frequent after whole-tree harvesting than stem-only harvesting, especially for Norway spruce, with deficits being more common in southern than in northern (boreal) Sweden.

In regional assessments of the sustainability of different harvesting regimes, the estimated weathering rate has a strong influence on the base cation balance. Klaminder et al. (2011) found that different approaches to estimating weathering rates yielded results that differed substantially, and that uncertainties in the methods had a great influence on the predicted sustainability of different harvesting practices. Futter et al. (2012) compiled weathering rates estimated at 82 sites, using different methods, and found both large between-site as well as within-site differences in the values. Differences in input data can be attributed to different time scales used when acquiring different input data, challenges determining accurate mineralogical compositions and the use of field data compared with laboratory data (Van der Salm, 2001; Futter et al., 2012). Thus, they recommend that at least three different approaches be applied per study site to evaluate the precision in weathering estimates. The approaches examined in the present paper include (1) 'historical weathering' based on geochemical investigation of the soil profile, (2) modelled present weathering rate and (3) present weathering rate based on cation balances at the ecosystem level. The choice of methods is primarily based on the fact that rates of weathering may vary over time (Klaminder et al., 2011; Stendahl et al., 2013). The average weathering under long-term environmental change, i.e. 'historical weathering', is thus different from the weathering potential under present-day environmental

conditions, i.e. 'present-day weathering', which is why we need to be able to consider historical weathering when assessing current/present-day weathering rates. Moreover, present-day weathering rates estimated based on the steady-state concept, which lacks the dimension of time, may differ from dynamic estimates of weathering rates derived from measured base cation budgets. These three different concepts of estimating weathering cannot be covered by a single method (Klaminder et al., 2011; Futter et al., 2012). Weathering estimates based on these concepts have often differed largely from pedon to catchment scale, whereas truly harmonized comparisons of methods require that methods are tested uniformly at the same spatial scale. This spatial scale can be the pedon, which also contains the major part of the mineral nutrient sources in the soil available for forest growth. To our knowledge, Kolka et al. (1996) is the only study to have previously used this approach.

The first approach, the depletion method, makes use of soil profile based mass balances (Chadwick et al., 1990; Brimhall et al., 1991) to estimate total base cation losses in the soil above a reference soil depth. An element in a weathering-resistant mineral is used as a standard, most commonly zirconium (Zr, present in e.g. zircon) or titanium (Ti, present in e.g. rutile) (Sudom and St.Arnaud, 1971; Harden et al., 1987; Chadwick et al., 1990; Bain et al., 1994), due to their stability at low temperatures (Schützel et al., 1963). To yield an annual average weathering rate ($mmol_c\ m^{-2}$), calculated element losses are commonly divided by an estimated soil age. In Nordic glacial tills situated above the marine limit, soil age is conventionally considered to be the number of years lapsed since the site of interest was finally deglaciated at the end of the Weichselian. Since the rate of weathering may vary over time (Klaminder et al., 2011; Stendahl et al., 2013), the average 'historical weathering' rate may differ from the present-day weathering rate. The depletion method is most widely used in Sweden to estimate weathering rates, specifically at the regional scale (Olsson et al., 1993).

The second approach commonly involves the mechanistic PROFILE model, by which release rates of base cations are estimated based on the dissolution kinetics of a user-defined set of minerals present in the soil, and the physical and chemical conditions that drive the dissolution of minerals. Since it is a mechanistic model, its strength is its transparency, while its main weakness is the difficulty in setting values of model parameters and input variables to which it may have high sensitivity. Akselsson et al. (*this issue*) concluded that the most important way to reduce uncertainties in modelled weathering rates is to reduce input data uncertainties, e.g. regarding soil texture, although there is still a need to improve process descriptions of e.g. biological weathering and weathering brakes (e.g. Erlandsson Lampa et al., *this issue*). The sensitivity of PROFILE to variations in soil physical parameters (e.g. soil texture, soil bulk density) and mineral composition was discussed by Jönsson et al. (1995) and Hodson et al. (1996), while the importance of the ability to determine the precise identity and quantity of the minerals was analysed by Casetou-Gustafson et al. (*this issue*).

The third approach to estimating weathering rate is the base cation budget approach (Velbel, 1985; Likens et al., 1998). This method has been applied to estimate current weathering rates at various temporal and spatial scales, and components of the budget approach have been used in different ways in some models, e.g. MAGIC (Cosby et al., 1985). The weathering rate is estimated indirectly as the difference between other sinks and sources of base cations, which are measured within a system with defined boundaries. The missing source in the mass balance

equation is assumed to represent the weathering. The base cation budget approach is most reliable when based on long-term data from well-defined systems, although even then estimated weathering rates suffer from large uncertainties, as errors in the sinks and sources accumulate in the mass balance equation (Simonsson et al., 2015). The base cation budget approach has mostly been applied under conditions where accumulation in biomass were not directly measured but estimated to be small, or base cation stocks in the soil were assumed to be at steady-state (e.g. Kolka et al., 1996; Sverdrup et al., 1998; Whitfield et al., 2006). Consequently, at the pedon scale, the PROFILE model and the depletion method are the most frequently used methods in Sweden to estimate weathering rates.

In this study, we applied the three conceptually different methods of estimating weathering on two well-defined forest ecosystems, Asa and Flakaliden in southern and northern Sweden, to allow a harmonized comparison of methods, and to place weathering in the context of other base cation fluxes in aggrading Norway spruce forests. The base cation budgets were estimated at the period of stand development when nutrient demand was expected to peak. In combination with access to highly accurate data on biomass production, these conditions also provided opportunities to relate weathering to base cation accumulation in biomass at high nutrient uptake rates, and possible simultaneous depletions of extractable base cation stocks in the soil. Furthermore, input data to PROFILE were characterised by high quality quantitative mineralogical data, measured directly by X-ray powder diffraction (XRPD), as previously discussed by Casetou-Gustafson et al. (2018).

Three test criteria were used to examine the outputs of the depletion method and PROFILE model: (1) similarity in weathering estimates for the 0-50 cm soil profile; (2) similarity in depth gradients in weathering for the 0-100 cm soil profile; and (3) similarity in ranking order of the base cations released.

2. Materials and methods

2. 1 Study sites

Two forest sites planted with Norway spruce (*Picea abies* (L.) Karst) were chosen for the study, Flakaliden in northern Sweden (64°07'N, 19°27'E) and Asa in southern Sweden (57°08'N, 14°45'E), because they have been used for long-term experimental studies on the effects of climate and nutrient and water supply on tree growth and element cycling (Linder, 1995; Bergh et al., 1999; Ryan, 2013).

The experiment at Flakaliden was established in 1986 in a 23-year-old Norway spruce stand, planted in 1963 with four-year-old seedlings of local provenance after prescribed burning and soil scarification (Bergh et al., 1999). The experiment at Asa was established one year later (1987), in a 12-year-old Norway spruce stand planted in 1975 with two-year-old seedlings after clear-felling and soil scarification. The experimental design was similar at both sites and included control, irrigation and two nutrient optimisation treatments (Bergh et al., 1999). All treatments were replicated in 50 m x 50 m plots, arranged in a randomised block design. Only two of the four treatments were used in the present study; the control (C) and plots receiving an annual dose of an optimised mix of solid fertiliser (F), which among other elements per year contained about 10 kg ha^{-1} Ca, 8 kg ha^{-1} Mg and 45 kg ha^{-1} K (Linder, 1995).

198
199 Flakaliden is located in the central boreal sub-zone with a harsh climate, with long cool days in summer and short
200 cold days in winter. Mean annual temperature for the period 1990-2009 was 2.5 °C, and mean monthly
201 temperature varied from -7.5 °C in February to 14.5 °C in July. Mean annual precipitation in the period was ~650
202 mm, with approximately one-third falling as snow, which usually covers the frozen ground from mid-October to
203 early May. Mean length of the growing season (daily mean temperature ≥ 5 °C) was 148 days, but with large
204 between-year variations (Table 1) (cf. Sigurdsson et al., 2013).
205
206 Asa is located in the hemi-boreal zone, where the climate is milder than at Flakaliden, which is reflected in a
207 longer growing season (193 days). Mean annual temperature (1990-2009) was 6.3 °C, mean monthly temperature
208 varied from -1.9 °C in February to 16.0 °C in July and mean annual precipitation was ~750 mm. The soil is
209 periodically frozen in winter. The difference in climate is reflected in differences in site productivity, which
210 broadly follows climate gradients in Sweden (Bergh et al., 2005).
211
212 The soils at Asa and Flakaliden differ in age due to differences in the time since deglaciation (Table 1), from
213 approximately 14,300 years at Asa and 10,150 years at Flakaliden (estimated from Fredén, 2009). The soil type
214 at both sites is an Udic Spodosol, with a mor humus layer overlying glacial till derived from felsic bedrock. The
215 soil texture is classified as sandy loam. The transition between the B- and C-horizons is mostly located at 50 cm
216 depth at Flakaliden and 50-60 cm depth at Asa. The natural ground vegetation at Flakaliden is dominated by
217 *Vaccinium myrtillus* (L.) and *V. vitis-idaea* (L.) dwarf-shrubs, lichens and mosses (Kellner, 1993; Strengbom et
218 al., 2011). The ground vegetation at Asa is dominated by *Deschampisa flexuosa,* (L.) and mosses (Strengbom et
219 al., 2011; Hedwall et al., 2013).

220 **2.2. Soil sampling and analyses of geochemistry and mineralogy**

221 A detailed description of soil sampling, geochemical analyses and determination of mineralogy can be found in
222 Casetou-Gustafson et al. (2018). The procedures are summarised below.

223 Sampling was performed in untreated control plots (K1 and K4 at Asa and 10B and 14B at Flakaliden) and
224 fertilised (F) plots (F3, F4 at Asa and 15A and 11B at Flakaliden) in October 2013 (Flakaliden) and March 2014
225 (Asa), in the border zone of four plots at each site. One intact soil core per plot at Flakaliden and in plot K1 at Asa
226 was extracted using a rotary drill (17 cm inner diameter). In plots K4, F3 and F4 at Asa, soil samples were instead
227 taken from 1 m deep manually dug soil pits, due to inaccessible terrain for the rotary drill machinery. Maximum
228 soil depth was shallower at Flakaliden (70-90 cm) than at Asa (90-100 cm). The volume of stones and boulders
229 was determined for each plot at the two study sites using the penetration method described by Viro (1952) to a
230 maximum depth of 30 cm and by applying the fitted function described by Stendahl et al. (2009). Mean stone and
231 bolder content was higher at Flakaliden (39%$_{vol}$) than at Asa (28%$_{vol}$).

232 Soil samples were taken from each 10-cm soil layer. Prior to chemical analysis, these samples were dried at 30-
233 40 °C and sieved to <2 mm. Analysis of particle size distribution was performed by wet sieving and sedimentation

(pipette method) in accordance with ISO 11277. Geochemical analyses were conducted by ALS Scandinavia AB and comprised inductively coupled plasma-mass spectrometry (ICP-MS) on HNO_3 extracts of fused samples that were milled and ignited (1000 °C) prior to fusion with $LiBO_2$.

Quantitative soil mineralogy was determined with the X-ray powder diffraction (XRPD) technique (Hillier 1999, 2003). Samples for measurement of XRPD patterns were prepared by spray drying slurries of soil samples (<2 mm) micronised in ethanol. A full pattern fitting approach was used for quantitative mineralogical analysis of the diffraction data (Omotoso et al., 2006). This fitting process involved the modelling of the measured diffraction pattern as a weighted sum of previously measured and verified standard reference patterns of the identified mineral components. The determination of chemical compositions of various minerals present in the soils was conducted by electron microprobe analysis (EMPA) of mineral grains subsampled from the sifted (< 2 mm) soil samples.

2.3 Historical weathering determined with the depletion method

2.3.1 Method description

The depletion method (Table 2), as defined by Marshall and Haseman (1943) and Brimhall et al. (1991), estimates the accumulated mass loss since soil formation (last deglaciation for our sites) as a function of loss of a mobile (weatherable) element and enrichment of an immobile (weathering resistant) element according to the following general function introduced by Olsson and Melkerud (1989) and based on the same theories as the mass transfer function described in Brimhall et al. (1991):

$$W_{\mathrm{depletion},i} = \frac{d \cdot \rho}{100} \cdot \frac{X_c \cdot Zr_{w,i}}{Zr_c} - X_{w,i} \quad (1)$$

where W denotes loss of the ith element (g m^{-2}), X denotes mobile element concentrations (%), Zr denotes immobile element concentrations (%), w and c denote a weathered soil layer and the assumed unweathered reference layer, respectively, d is layer thickness (m), and ρ is bulk density (g m^{-3}). Zirconium is commonly used as the immobile element due to the inert nature of the mineral zircon ($ZrSiO_4$), although Ti is sometimes used due to the resistance of the Ti-containing minerals anatase and rutile (TiO_2) to weathering (Olsson and Melkerud, 1989). The unweathered reference layer is located in the C horizon, and has X to Zr ratios that are assumed to represent pristine conditions of the presently weathered layers above it. In the weathered layers, X to Zr ratios are smaller; that is, Zr is enriched compared with the mobile elements (i.e. the base cations). The method is based on the assumptions that Zr, hosted in zircon, was uniformly distributed throughout the soil profile at the time of deglaciation, that weathering only occurs above the reference layer and that zircon does not weather. The latter implies that Zr concentrations and Zr/base cation ratios are constant below the reference layer. Table 3 shows the reference depths for different base cations compared with Zr, which were used as the depths of immobile element concentrations. The Zr/base cation ratio (Fig. S3) was used to help select the reference soil layer as it highlights heterogeneities in parent material with depth. In cases of heterogeneities in the profile, the reference layer was chosen above this heterogeneity. This choice was precluded for soil profile 11B, where Zr concentrations and Zr/base cation ratios peaked directly below the B-horizon (i.e. at 50-60 cm).

2.3.2. Application

Prior to calculating base cation weathering rates with the depletion method, fractional volume change (Vp) was calculated according to White et al. (1996) in order to assess if there were any large volume changes (collapse) in the mineral soil with implications for which depth the weathering should be calculated to. Similar to White et al. (1996), it was assumed that values close to zero indicate no volumetric change, which was the case below 30-40 cm of soil depth at both sites (Table S5). The homogeneity of the parent material was also evaluated (Fig. 1) using the criterion that the ratio of Ti to Zr should be more or less stable with depth in an originally homogeneous material. Use of the ratio of two immobile elements to establish uniformity of parent material has been suggested previously (Sudom and St.Arnaud, 1971; Starr et al., 2014). The homogeneity criterion was not met using Zr in plot K1 at Asa (i.e. the Zr concentrations decreased towards the soil surface; Fig. 2); here Ti was used as the immobile element instead. Furthermore, the plots 15A and 11B at Flakaliden had to be eliminated from the calculations, because relatively large variability in both the Zr and Ti gradients was observed. These large heterogeneities led to an overall gain of base cations in the rooting zone, which is opposite to what would be expected (i.e. that losses and gains can occur at specific soil depths due to eluviation and illuviation processes in podzolic soils). For this reason, soil profiles 15A and 11B were eliminated from further consideration in calculations of historical weathering rates using the depletion method. Thus, apart from heterogeneities, transportation processes (eluviation and illuviation) and/or erratic Zr or Ti gradients could lead to "negative" weathering, i.e. leading to a calculated relative accumulation of elements. Such negative values were not considered in the calculation of historical weathering losses.

Bulk density was estimated for each soil layer except in some plots where density measurements could not be made below a certain soil depth. Bulk density in these cases was estimated using an exponential model for total organic carbon (TOC) and bulk density (BD, g/cm^3) based on our own data. For Asa (soil layers F3: 70-90 cm; F4: 0-10, 30-40, 50-60, 60-70, 70-80, 80-90, 90-100 cm; and K4: 70-80, 80-90, 90-100 cm), the following function was used:

$$\rho = 1.3\, e^{-0.1\, x} \quad (2)$$

where x is TOC content (% of dry matter).

For Flakaliden (soil layers 14B: 80-90cm; 10B: 60-70 cm; and 11B: 40-70 cm), the function used was:

$$\rho = 1.8\, e^{-0.2\, x} \quad (3)$$

2.4 The PROFILE model

2.4.1 Model description

The steady state weathering of soil profiles was estimated using the biogeochemical PROFILE model (Table 2), where weathering of the *i*th base cation ($W_{\text{profile, i}}$) is described by long-term mineral dissolution kinetics at the interface of wetted mineral surfaces and the soil solution. PROFILE is a multilayer model, where parameters are specified for each soil layer based on field measurements and estimation methods (Warfvinge and Sverdrup, 1995).

2.4.2 PROFILE parameter estimation

A detailed description of the application of the PROFILE model to the soils and sites in the present study can be found in Casetou-Gustafson et al. (*this issue*). The parameters used are listed in Table 4.

Exposed mineral surface areas were estimated from soil bulk density and texture data using the algorithm specified in Warfvinge and Sverdrup (1995). Volumetric soil water content for each soil profile in Flakaliden and Asa was estimated to be 0.25 $m^3\,m^{-3}$ according to the moisture classification scheme described in Warfvinge and Sverdrup (1995) (Table S4).

The aluminium (Al) solubility coefficient, a soil chemical parameter needed for solution equilibrium reactions, was defined as $\log\{Al^{3+}\}+3pH$. It was estimated by applying a function developed from previously published data (Simonsson and Berggren, 1998) and existing total carbon and oxalate-extractable Al measurements for our sites (Casetou-Gustafson et al., 2018) (Table S4). For partial CO_2 pressure in the soil, the default value of Warfvinge and Sverdrup (1995) was used. Data on measured dissolved organic carbon (DOC) in the soil solution at 50 cm depth were available for plots K4 and K1 at Asa and plots 10B and 14B at Flakaliden, and these values were also applied for deeper soil horizons. Shallower horizons (0-50 cm) were characterised by higher DOC values, based on previous findings (Fröberg et al., 2006, 2013) and the DOC classification scheme in Warfvinge and Sverdrup (1995) (Table S4).

The site-specific parameters used were evapotranspiration, temperature, atmospheric deposition, precipitation, runoff and nutrient uptake in biomass (Table 4). Mean evapotranspiration per site was estimated from mean annual precipitation and runoff data, using a general water balance equation.

Total deposition was calculated using deposition data from two sites of the Swedish ICP Integrated Monitoring catchments, Aneboda (for Asa) and Gammtratten (for Flakaliden) (Löfgren et al., 2011). Na was used as a tracer ion in order to distinguish canopy exchange from dry deposition for Ca, Mg and K. Dry deposition for Na and Cl was calculated as the difference between wet and throughfall deposition. As outlined in Zetterberg et al. (2016), wet deposition for all elements was calculated by correcting bulk deposition for dry deposition using wet-only to bulk deposition ratio. Wet deposition was estimated based on the contribution of dry deposition to bulk deposition, both for base cations and anions, using dry deposition factors from Karlsson et al. (2012,2013). Finally, total deposition for all elements was calculated from the sum of dry and wet deposition.

Net base cation and nitrogen uptake in aboveground tree biomass (i.e. bark, stemwood, living and dead branches, needles) was estimated as mean accumulation rate over a 100-year rotation period in Flakaliden and a 73-year rotation period in Asa. These calculations were based on Heureka simulations using the StandWise application (Wikström et al., 2011) for biomass estimates, in combination with measured nutrient concentrations in aboveground biomass as described in section 2.5.4 below (Linder, unpubl. data).

2.4.3 PROFILE sensitivity analysis

The sensitivity of PROFILE to changes in soil physical and mineralogical input was analysed, to test to what extent the depth gradients of weathering rates as predicted by PROFILE were affected primarily by soil physical properties or by soil mineralogy. Independent PROFILE runs were performed, after replacing horizon-specific input values with soil profile average values regarding either (1) soil bulk density and specific exposed mineral surface area ('homogenous soil physics'), or (2) soil mineral percentages ('homogenous mineralogy'), or (3) both ('homogenous soil physics and mineralogy'). In each scenario, the squared deviation in weathering rate was calculated for each base cation and horizon, compared to the normal simulation based on horizon-specific inputs for soil physics and soil mineralogy. The sum of squares over base cations and horizons was used as a measure of the overall error caused by the 'homogenous' input data. The ratios of sum of squares, of scenario (1) over (3) and of scenario (2) over (3), was used to estimate the percent contribution of soil physics and soil mineralogy, respectively, to the overall weathering gradients in the soil profile.

2.5 The base cation budget approach

2.5.1. General concepts of the base cation budget approach

The average weathering rate of the *i*th base cation according to base cation budget, $W_{\text{budget, }i}$, over a period of time can be estimated with base cation budgets (Table 2) using the base cation budget approach, which assumes that total deposition (TD_i) and weathering are the major sources of mobile and plant-available base cations in the soil, and that leaching (L_i) and accumulation of base cations in biomass (ΔB_i) are the major sinks. A change in the extractable soil stocks of base cations over time (ΔS_i) ar considered as a sink if stocks have increased, or as a source if stocks have been depleted (Simonsson et al., 2015). Each of these terms is measured independently over a specific period of time. Hence,

$$W_{\text{budget, }i} = L_i + \Delta B_i + \Delta S_i - TD_i \quad (4)$$

2.5.2 Atmospheric deposition, TD_i

The same estimates of total atmospheric deposition as used in parameter setting of the PROFILE model (section 2.4.2) were used in the base cation budget, Eq. (4).

2.5.3. Changes in exchangeable soil pools, ΔS_i

Changes in extractable base cation stocks in the soil were calculated from the difference between two soil samplings, performed in 1986 and 1998 at Flakaliden, and in 1988 and 2004 at Asa. The organic layer was sampled with a 5.6 cm diameter corer, whereas a 2.5 cm diameter corer was used to sample 10 cm sections to 40 cm depth in the mineral soil. For each plot and layer, 25 cores were combined into one sample.

Exchangeable base cation content in the soil (<2 mm) all Flakaliden samples in Asa samples from 1988 was determined by extraction of dry samples with 1 M NH_4Cl using a percolation method, where 2.5 g of sample was leached with 100 mL of extractant at a rate of 20 mL h^{-1}. The base cations were analysed by atomic absorption spectrophotometry (AAS). For the Asa samples from 2004, batch extraction was performed using the same

extractant, and the base cations were determined with ICP. A separate test was made to compare the yield of the percolation and batch extraction methods. No consistent difference between the methods was observed.

The amount of fine soil (<2 mm) per unit area was calculated from the volume of fine earth (<2 mm) 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 was determined with the penetration method of Stendahl et al. (2009) and the bulk density of soil <2 mm was calculated using a pedotransfer function that included soil depth and measured carbon concentrations as variables.

2.5.4 Net uptake in biomass, ΔB_i

Accumulation of base cations in tree biomass, i.e. net uptake of base cations, was calculated as a mean value of control plots over the period 1989-2003, based on increments in aboveground biomass at Asa and Flakaliden for this period and on the concentrations of elements in different tree parts. The increment in aboveground biomass was based on measurements of stem diameter at breast height (DBH) of all individual trees in the plots, and applying DBH data to allometric functions developed for Norway spruce at the sites (Albaugh et al., 2009, 2012). The allometric functions were based on destructive samplings (1987 - 2003) of 93 and 180 trees at Asa and Flakaliden respectively. The increment in belowground biomass was estimated from general allometric functions for Norway spruce stumps and roots in Sweden (Marklund, 1988). Since Marklund's functions (1988) underestimate belowground biomass by 11%, a factor to correct for this was included (Petersson and Ståhl, 2006). Furthermore, the finest root fraction (≤2 mm), which is not included in the functions of Marklund (1988) and Petersson and Ståhl (2006), was assumed to be 20% of needle biomass at Asa and 33% at Flakaliden, respectively, based on data from Helmisaari et al. (2007).

Data on element concentrations in biomass were available from measurements on harvested trees (S. Linder, unpublished data). At Flakaliden, total element concentrations were analysed in trees sampled for biomass determination in 1992 and 1997. Analyses of needles and branches (dead and live) were conducted on the same tree parts in the biomass sampled in 1993 and 1998. Base cation concentrations in biomass were determined from acid wet digestion in HNO_3 and $HClO_4$, followed by determination of elements by ICP-atomic emission spectrophotometry (ICP-AES) (Jobin Yvon JY-70 Plus).

Data on element concentrations in belowground biomass fractions were taken from literature from the Nordic countries (Hellsten et al., 2013). Specifically, data on stump and root biomass of Norway spruce were available for Asa and data from Svartberget was used for Flakaliden (Table 7 in Hellsten et al., 2013).

2.5.5. Leaching, L_i

Base cation leaching was quantified in six-month intervals from modelled daily runoff multiplied by average element concentrations in soil water collected with tension lysimeters at 50 cm soil depth.

Soil water was collected from five ceramic tension lysimeters (P80) installed at 50 cm depth in each experimental plot. Soil water was collected during frost-free seasons, applying an initial tension of 70 kPa in 250 mL sampling bottles, and left overnight. These soil water samples were pooled by plot. The base cation concentration in the soil solution was determined with ICP-AES. Soil water sampling was performed twice every year, i.e. in the spring and in the autumn, which are the periods of highest water flux and which means that the most important leaching events were covered. The spring samples were collected soon after the snowmelt and depending on the weather in a specific year this meant that the yearly spring sampling date varied between the last week of April and the last week of May. The autumn samples were collected when frost risk increased. That meant that the autumn sampling dates varied from year to year, i.e. from the first week in September to mid-November. The seasonal variation in soil water chemistry is shown in Fig. S4).

The drainage flux out of the profile was calculated by the CoupModel (Jansson, 2012). The model was parameterised based on hydraulic soil properties measured at the sites. The model was run with hourly mean values of locally measured climate variables (precipitation, global radiation, wind speed, air temperature and humidity) and model outcomes were tested against tensiometer data, i.e. bi-weekly tensiometer readings at 15, 30 and 45 cm depth were used for model calibration. The parameters were then adjusted slightly to obtain good agreement between measured and calculated soil water content. Annual precipitation varied considerably during the period 1990-2002, ranging from 906 to 504 mm at Flakaliden (mean 649 mm) and from 888 to 575 mm at Asa (mean 736 mm). Annual evapotranspiration increased by about 50 mm at both sites, during the period 1987-2003 at Flakaliden and 1990-2002 at Asa, due to the increment in tree leaf area. Monthly means and standard deviation of drainage (mm) at 50 cm depth in the soil of control plots at Asa during 1990 – 2004 and at Flakaliden during 1988-2004 are shown in Fig. S5.

2.5.6. Assessment of data quality in base cation budget

The precision and accuracy of a base cation budget estimate of $W_{budget,\,i}$ was determined by the quality of estimates of each individual term in Eq. (3), in proportion to the magnitude of each term (Simonsson et al., 2015). Significant uncertainty in the estimate of a quantitatively important term will therefore dominate the overall uncertainty in estimates of W_{budget}. Firstly, the quality of data for each term in Eq. (3) was assessed based on the spatial and temporal scales of measurements and the quality of measurements (Table 5). Using these criteria, we consider the estimates of deposition, leaching and accumulation in biomass to be of moderate to high quality. The measurements of changes in extractable soil pools were of lower quality because extraction methods were not identical for samples collected 1986/1988 and 1998/2004, which would cause significant uncertainty if soil changes were an important part of the element budget. To partly overcome this uncertainty, we used the estimates obtained by the PROFILE ($W_{profile,\,i}$) and depletion method ($W_{depletion,\,i}$) in additional base cation budget calculations where the change in soil was determined from the base cation budget. These additional base cation budget estimates, which are conceptually analogous to the regional mass balances presented by Akselsson et al. (2007), were also used to place the PROFILE and depletion method estimates of W_i in the context of other base cation fluxes at the ecosystem scale.

444

445 **2.6 Statistical analyses**

446 Site mean values and standard error (SE) of $W_{depletion}$, $W_{profile}$ were calculated based on the four (or two) soil profiles
447 studied at each site. For W_{budget} an average based on the four control plots at each site was calculated as well as a
448 combined standard uncertainty. The latter was partly based on standard errors derived from plot-wise replicated
449 data of the present experiments (for leaching and changes in exchangeable soil pools, SE(L_i) and SE(ΔS_i),
450 respectively), partly on standard uncertainties (u) derived from Simonsson et al. 2015, where replicated data were
451 missing in the present study (for accumulation in biomass and total deposition, $u(\Delta B_i)$ and $u(TD_i)$, respectively).
452 Because total deposition and bioaccumulation differed substantially from those in the study of Simonsson et al.
453 2015, relative standard uncertainties were derived from that study, and multiplied with the average deposition and
454 bioaccumulation rates at Asa and Flakaliden, respectively, to yield realistic standard uncertainties for the present
455 sites. For the weathering rate of the *i*th base cation according to Eq. (4), a combined standard uncertainty (u_c) was
456 calculated as:

457 $$u_c\left(W_{budget,\ i}\right) = \sqrt{\left(SE(L_i)\right)^2 + \left(u(\Delta B_i)\right)^2 + \left(SE(\Delta S_i)\right)^2 + \left(u(TD_i)\right)^2} \quad (5)$$

458 Confidence intervals were calculated by multiplying the combined standard uncertainties with a coverage factor
459 of 3.

460

461 **3. Results**

462 **3.1 Depletion method estimates of historical weathering rates**

463 At both Asa and Flakaliden, historical weathering rates estimated with the depletion method ($W_{depletion}$) were
464 highest in the upper soil layers and showed a gradual decrease down to the reference depth, which was defined at
465 60-70 cm at Flakaliden and for most plots at 80-90 cm at Asa (Fig. 3). Flakaliden had a higher historical annual
466 weathering rate to 90 cm soil depth, 37.8 $mmol_c\ m^{-2}yr^{-1}$, than Asa, 12.8 $mmol_c\ m^{-2}yr^{-1}$; the corresponding value
467 for 0-50 cm depth was 34.1 $mmol_c\ m^{-2}yr^{-1}$ at Flakaliden and 10.5 $mmol_c\ m^{-2}yr^{-1}$ at Asa. The gradients with depth
468 showed that $W_{depletion}$ increased towards the surface, although this trend was more pronounced at Flakaliden than
469 at Asa. At Flakaliden, $W_{depletion}$ was highest for Mg, followed by Ca, Na and K (Figs. 3 and 4); at Asa, it was
470 highest for Ca, closely followed by Mg, Na and K (Figs. 3 and 4).

471 **3.2 PROFILE model estimates of steady state weathering rates**

472 The steady state weathering rate estimated by the PROFILE model ($W_{profile}$) differed from the historical rate with
473 respect to all three test criteria, i.e. (1) total weathering rate in the 0-50 cm soil layer, (2) variation in weathering
474 with depth and (3) ranking order of base cations (Figs. 3 and 4). Firstly, regarding base cation weathering rate in
475 the upper 50 cm of the mineral soil, $W_{profile}$ estimates for Asa and Flakaliden (Asa: 37.1 $mmol_c\ m^{-2}yr^{-1}$, Flakaliden:
476 42.7 $mmol_c\ m^{-2}yr^{-1}$) were around 3.5 and 1.3-fold higher than $W_{depletion}$ estimates, respectively. Secondly, the total

modelled base cation weathering rate for the soil profile down to 90 cm was around 7-fold higher than the rate estimated using the depletion method at Asa (89.4 $mmol_c\ m^{-2}yr^{-1}$), and 3.4-fold higher at Flakaliden (127.6 $mmol_c\ m^{-2}yr^{-1}$). Unlike the historical weathering based on the depletion method, PROFILE predicted that weathering rates increased with soil depth at both sites. At Flakaliden, high contents of K- and Mg-bearing tri-octahedral mica (Casetou-Gustafson et al., 2018) gave rise to particularly high weathering rates at 70-80 cm. Thirdly, as opposed to $W_{depletion}$, $W_{profile}$ was largest for Na at both sites, followed by Ca. However, $W_{profile}$ was larger for K than for Mg at Asa, while the reverse was true at Flakaliden.

The sensitivity analysis of the PROFILE model using homogeneous soil physical and/or mineralogical properties demonstrated that the variations in soil physical properties (i.e. soil bulk density and specific exposed mineral surface area) with depth had a greater influence than mineralogy on the observed change in $W_{profile}$ with soil depth. In terms of the ratios of sums of squares, the 'homogenous soil physics' of scenario (1) produced 75% or more of the error obtained with 'homogenous soil physics and mineralogy' (scenario (3)), leaving a mere 25% or less to the 'homogenous mineralogy' of scenario (2); also see Tables S1 and S2. The soil physical inputs that were more important for PROFILE weathering rates are indicated in Figs. S1 and S2. There was a strong linear and positive relationship between exposed mineral surface area and $W_{profile}$ for all elements at both sites, with R^2 values ranging from 0.65 to 0.89 (Fig. S1). The relationship between bulk density and $W_{profile}$ was also strong and showed the same linear response, although R^2 values were lower, 0.40-0.70 (Fig. S2).

3.3 Base cation budget estimates of current weathering rates

A comparison of weathering rates estimated by base cation budgets (W_{budget}), $W_{profile}$ and $W_{depletion}$ was made for the 0-50 cm soil layer. It was found that, for most elements, W_{budget} in the 0-50 cm layer was higher, or much higher, than $W_{profile}$ (Fig. 4). Compared with the PROFILE model estimates, the base cation budget estimates of weathering were 6- to 7-fold higher for Ca, Mg and K weathering at Asa, and about 2- to 3-fold higher for Ca, Mg and K at Flakaliden. At Asa, the sum of base cations was on average 13-fold and 3.6-fold larger than $W_{depletion}$ and $W_{profile}$, respectively. The closest resemblance between methods was found between $W_{depletion}$ and W_{budget} for Na. The budget calculations suggested that weathering was a dominant source of K and Mg, but contributed a somewhat smaller proportion of Ca (61% at Asa and 43% at Flakaliden).

As to the fluxes (terms) of the base cation budget, Na showed patterns different from those of K, Mg and Ca (Fig. 5). For Na, uptake in biomass was negligible and leaching was the dominant sink. For the latter three elements, accumulation in biomass was the dominant sink. Loss by leaching was negligible for K, but significant for Mg and Na. Deposition generally represented only a small input, except for Na at Asa. The measured decreases in soil stocks of exchangeable base cations indicated that a change in this pool was a particularly important source of Ca. There were minor increases in exchangeable stocks for Na, K and Mg at Asa. The combined uncertainty of W_{budget} was larger for Ca and K, both dominated by the bioaccumulation term in Eq. (4), than for Na and Mg (Table 6). In relation to the mean W_{budget}, the combined uncertainty was of the same order of magnitude for Na, about the half for Ca, one-third for K, and lower for Mg.

By using the weathering estimates obtained with PROFILE and the depletion method in the base cation budget equation, Eq. (4), in combination with measured estimates of deposition, leaching and uptake in biomass, alternative soil balances were estimated (Fig. 5). Since the base cation budget method predicted much higher weathering rates than the other methods, a balance of sources and sinks consequently required more marked decreases in exchangeable soil stocks for K, Ca and Mg when weathering rates were based on PROFILE or the depletion method. Furthermore, as a consequence of the substantially higher $W_{profile}$ for Na, the PROFILE based base cation budget suggested substantial increases in exchangeable Na stocks.

4. Discussion

4.1 Comparison of conceptually different methods

A number of studies have used multiple approaches to estimate weathering rates, with the aim of validating methods and finding a best estimate for a particular site or catchment (Langan et al., 1995; Kolka et al., 1996; Sverdrup et al., 1998; Futter et al., 2012). A common problem encountered is that differences in quantities, are not only complicated by conceptual differences between the approaches, but also by the fact that the comparisons are not carried out in a harmonized way, i.e. at the same scale (pedon/catchment), using identical sampling locations and methods for common input data, and consistent assumptions about the weathering zone (i.e. 0-50 cm or 0-100 cm). Concerning the spatial scale, the base cation approach has more commonly been applied at the catchment and forest stand scale, whereas the depletion method and the PROFILE model are normally applied at the pedon scale. In the present study, the base cation budget approach included data at stand level over a period when the stand showed a high nutrient demand. Concerning the temporal scale, the concepts of the depletion method and the PROFILE model are conceptually different, although they can be applied at similar spatial scale. In the present study, these two methods are based on direct measurements of soil properties, i.e. quantitative mineralogy, soil bulk density and soil stone content, which was rarely the case in previous comparable studies. Since the three approaches used here do not measure similar quantities at spatial and temporal scale, and all of them have obvious weaknesses, no estimate can be taken as the "true" weathering rate. However, the conceptual differences between the three approaches are an asset, as they provide complementary information about weathering at different scales that helps to identify strengths and weaknesses of each method and establish reasons as to why these methods tend to vary in estimated weathering rates of particular elements.

4.2 Depletion method estimates versus PROFILE model estimates

Modelled ($W_{profile}$) and historical ($W_{depletion}$) base cation weathering rates were within the range of recently published data for similar forest sites on podzolised glacial till (Stendahl et al., 2013). However, the historical weathering rates at Asa were similar to the lowest historical weathering rate observed by Stendahl et al. (2013) and the historical weathering rates for Flakaliden were similar to their highest rates, at least with regard to Ca and Mg.

Our first test criterion was the overall weathering rate over 0-50 cm depth in the soil profile. A major finding was that $W_{profile}$ was higher than $W_{depletion}$ for Na and K. Similarly, high ratios of $W_{profile}/W_{depletion}$ of 4 were found at

catchment scale by Augustin et al. (2016). At the pedon scale, Stendahl et al. (2013) found $W_{profile}/W_{depletion}$ ratios of on average 2.7 for 16 Swedish study sites (with average max. and min. ratios of 7.9 and 0.4, respectively); this ratio was larger than the one found for Flakaliden in our study (1.5) and lower than the one found for Asa (5.1). Similar to Flakaliden, low ratios have been reported for the Lake Gårdsjön site situated in south-western Sweden (Sverdrup et al., 1998; Stendahl et al., 2013). An exception to the general trend of higher steady-state PROFILE weathering rates compared to historical rates calculated by the depletion method, was found for Mg at the Flakaliden site, where $W_{depletion}$ was 1.9-fold greater than $W_{profile}$ in the upper mineral soil, but only at Flakaliden. This exception with regard to Mg was also found by Stendahl et al. (2013) for all of their 16 study sites.

However, the estimated weathering rates are relevant for different temporal scales. Several studies have concluded that the average historical weathering rate should generally be higher than the present weathering rate, since soil development involves loss of easily weatherable minerals and ageing of mineral surfaces (Bain et al., 1993; Taylor and Blum, 1995; White et al., 1996). In a study using the Historic-SAFE model, applied to the Lake Gårdsjön catchment in southwestern Sweden, Sverdrup et al. (1998) predicted a decline in weathering rates due to assumed disappearance of fine particles and loss of minerals. Their results suggested an increase in weathering rates from deglaciation 12,000 years B.P. towards a peak at 9000 years B.P., followed by a gradual decrease to below initial levels.

With this background, it may not seem surprising that our second test, postulating similarity between methods concerning the weathering rate gradient with soil depth, was not fulfilled. We may imagine a front of intense weathering moving downward through the soil profile over the millennia. Each horizon would undergo an episode, limited in time, of intense weathering followed by slower weathering in the ageing material. The sensitivity test performed with PROFILE revealed that the model output was only little affected by the differences in mineralogy between horizons. Therefore, if processes are correctly modelled with PROFILE, the notion of a weathering front should primarily be associated with changes in bulk density and exposed mineral surface area, as also suggested by the positive correlation between $W_{profile}$ and exposed mineral surface area and bulk density (Figs. S1-S2) and by the findings of Jönsson et al. (1995).

The intense weathering at depth simulated by PROFILE is obviously in contrast with the classic notion of weathering rates being highest in the A- or E-horizon of podzolised soils (Tamm, 1931). To test whether the high $W_{profile}$ values were possible to reconcile with the observed historical weathering, the hypothetical time needed for the PROFILE weathering rates to accomplish the element losses determined with the depletion method was calculated. The highest weathering rate, presently prevailing at approximately 80 cm (Asa) or 60 cm (Flakaliden) depth according to PROFILE (Fig. 2), would cause the observed depletion losses within less than half of the soil age ('max rates' in Fig. 6), potentially in concert with the concept of a weathering front. However, the calculation also showed that the present minimum weathering rate, presently simulated for the topmost 1-3 layers (Fig. 2), would often result in a more severe base cation depletion within less than the postglacial period than observed by the depletion method ('min rates' in Fig. 6), particularly at Flakaliden, and for K and Na also at Asa. Provided

that the current weathering rate did not substantially exceed the historical average, this suggests a positive bias in $W_{profile}$ at the investigated sites.

The weathering rates of PROFILE may also be criticized based on discrepancies in the ranking order of weathering of elements, compared to historical weathering; this is our third test criterion. PROFILE predicted the highest steady-state weathering for Na at both sites. However, historical weathering at Asa was greatest for Ca among the base cation elements, whereas Mg was the most abundant element released at Flakaliden. The latter was also found by Olsson and Melkerud (2000), who reported the same ranking order of individual base cation weathering (i.e. Mg>Ca>Na>K) for other sites in northern Sweden. At the mineralogical level, Casetou-Gustafson et al. (*this issue*) demonstrates that K-feldspar was the dominant source of all steady state PROFILE weathering of K and there are indications that the dissolution rate for K-feldspar is too high compared with mica. For example, Thompson and Ukrainczyk (2002) described differences in the plant availability of K via weathering from these two mineral groups. In addition, Simonsson et al. (2016) found that, although K-feldspar contained approximately 90% of the bulk K in the soil, 25-50% of the weathering of K had occurred in mica. Furthermore, and in more general terms, Hodson and Langan (1999) suggested that the PROFILE model overestimates weathering rates because it does not consider the decrease in mineral reactivity that has taken place over time and because it assumes that all mineral surface areas are reactive. If this is not accounted for, PROFILE can be expected to overestimate base cation weathering rates.

As to possible bias in the historical weathering rates, underestimates are possible at Asa, where the low values of $W_{depletion}$ can be attributed to the low gradient of Zr in the soil (Fig. 5). This might, in turn, be the result of soil mixing by different means. Mechanical soil scarification was carried out at both Asa and Flakaliden prior to planting of the present stand, which would at least have caused partial mixing or inversion of surficial soil layers. In addition, clearance cairns of unknown age were found in the experimental area at Asa, indicating small-scale agriculture in the past. Moreover, if burrowing earthworms have been abundant in the past, they might have produced soil mixing in the upper soil horizons (Taylor et al., 2019), resulting in a disturbed Zr gradient (Fig. 2) and in low estimates of historical weathering in the rooting zone (Whitfield et al. 2011). High or near-neutral soil pH and deciduous litter can promote high population densities of burrowing earthworms following forest clearing and agriculture; partly deciduous vegetation dominated at Asa until only 1000-2000 years BP, with species such as *Corylus avellana* (L.), *Betula* spp., *Quercus* spp. and *Tilia* spp. (Greisman et al., 2009).

Apart from disturbances, natural variability in weathering rates can likely be attributed to differences in soil texture (i.e. exposed mineral surface area), climate (i.e. temperature and water percolation rate) and mineralogy. At Flakaliden, it was reasoned that heterogeneous Zr gradients (Fig. 2) and Zr/base cation ratios (Fig. S3) disqualified two soil profiles from further analysis, which would have otherwise indicated unreasonable net gains of elements in the rooting zone (0-50 cm) (i.e. for soil profile 15A for all elements and for soil profile 11B with regard to Na and K). Whitfield et al. (2011) used the same argument for excluding single profiles from their calculations, emphasizing that overall gains in the rooting zone are not expected without external additions of base cations to the soil profiles. Several alternative reasons could have contributed to the observed peaks of Zr in

627 the B/C-horizon at Flakaliden, such as local heterogeneities of the deposited till, which was suggested by the
628 unstable Ti/Zr ratio in soil profile 15A and 11B. However, the observed peaks in the Ti/Zr gradients were only
629 explained by irregularities in Ti gradients (i.e. increases in the Ti/Zr ratio indicate that Ti concentrations are
630 increasing) the latter has to be treated carefully since in cases where both Zr and Ti show inconsistent patterns
631 with soil depth, the Ti/Zr ratio will still be stable and hereby overshadows heterogeneities observed with soil depth
632 for both elements (Fig. 1, 2). Thus, heterogeneities in Zr gradients observed in the B/C horizon can be attributed
633 to local heterogeneities of the parent material irrespective of if the Ti/Zr gradients are stable at these depths.
634
635 Regardless of errors in the Zr gradients, both $W_{depletion}$ and $W_{profile}$ showed more marked gradients with soil depth
636 at Flakaliden compared to Asa. This could be expected based on the more well-developed podzol profile at
637 Flakaliden. It has been postulated that the formation of podzols is enhanced by long duration and great depth of
638 snow cover (Jauhiainen, 1973; Schaetzl and Isard, 1996), which would imply that soil formation had progressed
639 further at Flakaliden than at Asa (Lundström et al., 2000). At Flakaliden, the average mass loss of Ca and Mg was
640 4.0-fold larger in the E-horizon than in the B-horizon, which is similar to findings by Olsson and Melkerud (2000)
641 of a 5-fold higher ratio between losses of base cations in the E- compared with the B-horizon.

642 **4.3 Weathering in a base cation budget perspective**

643 The base cation budget approach consistently resulted in much higher weathering rates than PROFILE and the
644 depletion method for all base cations except Na. However, as was shown by the large combined uncertainties
645 given in Table 6, base cation budget estimates of weathering are associated with substantial uncertainties from
646 different sources. Similar large uncertainties associated with estimates of W_{budget} were observed by Simonsson et
647 al. (2015) for the Skogaby site in south-western Sweden, a Norway spruce site of similar stand age and soil
648 condition as Asa.. Accounting for all sources of uncertainty, they found that the 95% confidence interval in
649 estimates of base cation weathering was 2.6 times the mean (33 $mmol_c\ m^{-2}\ yr^{-1}$).

650 Despite the considerable uncertainties in W_{budget} estimates, the base cation budget approach illustrated that
651 accumulation in biomass was a dominant sink for all base cation elements except Na. This is in line with findings
652 by Nykvist (2000) for two Norway spruce sites in Sweden and the study by Simonsson et al. (2015). However, it
653 contrasts to conditions in other studies of no change in soil and tree biomass stocks of base cations (e.g. Sverdrup
654 et al., 1998). The higher estimates of weathering rate at Asa reflected the higher productivity and nutrient demand
655 of the stand at this site (Bergh et al., 1999), which has resulted in 1.4-fold greater accumulation of base cations in
656 biomass than at Flakaliden.

657 The Na fluxes differed from those of the other base cations, probably because Ca, Mg and K are important plant
658 nutrients whereas Na is not. Calcium and Mg uptake in forest trees is considered to be more or less passive flow
659 driven by transpiration fluxes, whereas K uptake is an energy-demanding active process (Nieves-Cordones et al.,
660 2014). Considering that Na was the dominant base cation in the soil solution at 50 cm soil depth (Fig. 5), the
661 negligible accumulation of Na in tree biomass suggests that Na uptake in trees is physiologically blocked. Low
662 concentrations of Na seem to be a general feature of terrestrial plants in boreal forests, in contrast to aquatic plants,

663 which explains why the latter are considered important Na sources for large herbivores like moose (Ohlson and
664 Staaland, 2001). Thus, the negligible Na accumulation in tree biomass and the particularly low deposition at
665 Flakaliden simplify the Na budget to only three major counterbalancing fluxes: weathering, deposition and
666 leaching. Since $W_{depletion}$ and W_{budget} of Na were fairly similar, and were much lower than $W_{profile}$, our results provide
667 additional support for the claim that the PROFILE model produced consistently too high Na weathering.

668 Accumulation of Ca, Mg and K in biomass made up the dominant sink. Since deposition and measured depletion
669 of extractable Ca, K and Mg in the soil did not balance this sink, substantial missing sources, here estimated as
670 an apparent weathering rate, were needed to reach a balance. Using the alternative weathering estimates by
671 PROFILE and the depletion method in the base cation budget resulted in even larger estimated depletion in the
672 soil to balance the sinks than was actually measured. Uncertainties in estimating soil changes were probably
673 significant, since the estimates of soil depletion were based on two single measurements over 12 years and the
674 extraction procedures were not identical over time. Nevertheless, the changes observed in extractable Ca stocks
675 in the soil are in line with observations over 22 years of aggrading Norway spruce forests by Zetterberg et al.
676 (2016), who reported exchangeable Ca depletion rates of 5-11 and 23-39 $mmol_c\ m^{-2}\ yr^{-1}$ for sites in south-western
677 and northern Sweden, respectively. The higher value for the northern site reflected higher Ca saturation in the
678 soil. The corresponding values for Asa and Flakaliden were larger, but of similar magnitude (34.5 and 40.5 $mmol_c$
679 $m^{-2}\ yr^{-1}$, respectively). Brandtberg and Olsson (2012) studied the same sites as Zetterberg et al. (2016) over a 10-
680 year period and found a general minor increase in extractable K soil stocks and a substantial decrease in the Ca
681 stocks, a result much similar to the findings of the present study. The results therefore suggest that other sources
682 of nutrient base cations exist in the soil, apart from weathering ($W_{depletion}$, $W_{profile}$) and depletion of ammonium-
683 chloride-extractable base cation stocks. Regarding K, fixed or structural K in clay minerals provides a dynamic
684 pool of K that is not included in modelled weathering or in NH_4Cl-extractable K (Simonsson et al., 2016).
685 Regarding Ca and Mg, dissolution from non-crystalline/amorphous compounds can be an important source in
686 soils depleted of these elements (Van der Heijden et al., 2017).

687 There are other possible explanations for the higher weathering rates with the base cation budget approach
688 compared to PROFILE for K, Mg and Ca. First, it is possible that the assumption made that no base cation uptake
689 takes place below 50 cm in the soil was wrong. If trees can take up base cations from deeper soil horizons (e.g.
690 Brantley et al., 2017), the discrepancy in weathering rates between the two methods would be reduced since
691 PROFILE predicted higher weathering rates with increasing depth. Second, PROFILE may produce conservative
692 estimates of present-day weathering because the model only captures steady-state chemical processes. It has been
693 postulated that e.g. mycorrhizae play an important role in nutrient uptake in forest trees through active foraging
694 by mycelia at mineral surfaces, but the nature and quantitative importance of biotic control or stimulation of
695 weathering has been much debated in recent decades (Finlay et al., 2009; Sverdrup, 2009; Smits and Wallander,
696 2017; Finlay et al., *this issue*). Thus, the results from the present study do not contradict the view that such
697 processes can be quantitatively important in field situations.

5. Conclusions

The release rate of important plant nutrients from the mineral soil has been previously shown to differ largely when estimated with different methods due to a lack of uniformity in method comparison and data collection, which has made it impossible to understand conceptual similarities and dissimilarities between methods. Three conceptually different methods were compared in a harmonized fashion for 8 soil profiles at two long-term experimental forest sites with the aim of quantifying variability in weathering rate estimates and making concrete suggestions for an improved future applicability of these methods.

The results indicated that historical weathering estimated by the depletion method was probably underestimated, particularly at Asa, or was reasonably accurate (Ca, Mg). Reasons for underestimated weathering rates at Asa was that all criteria for application of the method were not well fulfilled. The weakly developed and possibly erratic Zr gradients in the soil at Asa could have been caused by natural and anthropogenic disturbances. Future studies based on the depletion method should ensure that the Zr gradient with depth show a net enrichment of Zr towards the soil surface. This condition was not fulfilled for soil profiles at the Asa site. Another important outcome of the study was to show that within-site variations in Zr gradients can be large, as was the case at Flakaliden. At that site, two soil profiles showed obviously erratic Zr gradients for unknown reasons and were not included in estimates of site mean weathering rates. In sharp contrast to the depletion method, steady-state weathering by PROFILE increased with increasing soil depth, and weathering rates were also generally higher. PROFILE probably produced reasonably accurate estimates of present-day weathering rates, rather than underestimates, but likely overestimated weathering of Na and K. This conclusion was based on differences between historical and steady-state estimates in rank-order of elements, and that the back-calculation of current PROFILE weathering rates to simulate historic base cation losses suggested a rapid depletion of Na and K even at the lowest PROFILE weathering rates. A possible reason that K weathering rates were also overestimated by the PROFILE method were inappropriate dissolution rates for K-bearing minerals applied in the model, which should be accounted for in future PROFILE based weathering estimate.

In the second comparison including three methods, the base cation budget method produced much higher estimates of present-day weathering compared to estimates by the other methods, except for Na. This discrepancy was largely an effect of the large uptake rates of Ca, K and Mg in the biomass, in contrast to negligible accumulation of Na, and that this uptake was only partly balanced by measured depletion of extractable soil pools, particularly for Ca. The large discrepancy in weathering rates between the base cation budget method and the other methods suggest that there were additional sources available for uptake particularly of Ca and K by trees in the soil besides weathering and the measured depletion in extractable base cations.

6. Authors contribution

Authors contributed to the study as in the following: S. Casetou-Gustafson: study design, data treatment, analyses, interpretation and writing. Magnus Simonsson: study design, analysis, interpretation and writing. Johan Stendahl: study design, analysis, interpretation and writing B.A. Olsson: study design, data treatment, analysis,

interpretation and writing. S. Hillier: interpretation and writing. Sune Linder: Provided long-term experimental data, interpretation and writing. Harald Grip: Provided long-term experimental data, interpretation, and writing

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8. References

Akselsson, C., Westling, O., Sverdrup, H., Holmqvist, J., Thelin, G., Uggla, E., and Malm, G.: Impact of harvest intensity on long-term base cation budgets in Swedish forest soils, Water Air Soil Poll.: Focus, 7, 201-210, 2007.

Akselsson, C., Belyazid, S., Stendahl, J., Finlay, R., Olsson, B.A., Erlandsson Lampa, M., Wallander, H., Gustafsson, J.P., and Bishop, K. H.: Weathering rates in Swedish forest soils, In review in Biogeosciences (this issue).

Albaugh, T. J., Bergh, J., Lundmark, T., Nilsson, U., Stape, J. L., Allen, H. L., and Linder, S.: Do biological expansion factors adequately estimate stand-scale aboveground component biomass for Norway spruce?, Forest Ecol. Manag., 258, 2628-2637, 2009.

Albaugh, T. J., Bergh, J., Lundmark, T., Nilsson, U., Stape, J. L., Allen, H. L., and Linder, S.: Corrigendum to "Do biological expansion factors adequately estimate stand-scale aboveground component biomass for Norway spruce?", Forest Ecol. Manag., 270, 314, 2012.

Augustin, F., Houle, D., Gagnon, C., and Courchesne, F.: Evaluation of three methods for estimating the weathering rates of base cations in forested catchments, Catena, 144, 1-10, 2016.

Bailey, S. W., Buso, D. C., and Likens, G. E.: Implications of sodium mass balance for interpreting the calcium cycle of a forested ecosystem, Ecology, 84, 471-484, 2003.

Bain, D. C., Mellor, A., Robertson-Rintoul, M., and Buckland, S.: Variations in weathering processes and rates with time in a chronosequence of soils from Glen Feshie, Scotland, Geoderma, 57, 275-293, 1993.

Bain, D. C., Mellor, A., Wilson, M., and Duthie, D.: Chemical and mineralogical weathering rates and processes in an upland granitic till catchment in Scotland, Water Air Soil Poll., 73, 11-27, 1994.

Bergh, J., Linder, S., Lundmark, T., and Elfving, B.: The effect of water and nutrient availability on the productivity of Norway spruce in northern and southern Sweden, Forest Ecol. Manag., 119, 51-62, 1999.

Bergh, J., Linder, S., and Bergström, J.: Potential production of Norway spruce in Sweden, Forest Ecol. Manag., 204, 1-10, 2005.

Brandtberg, P.-O., Olsson, B.A.: Changes in the effects of whole-tree harvesting on soil chemistry during 10 years of stand development. For. Ecol. and Manage., 277, 150–162, 2012.

Brantley, S.L., Eissenstat, D.M., Marshall, J.A., Godsey, S.E., Balogh-Brunstad, Z., Karwan, D.L., Papuga, S.A., Roering, J., Dawson, T.E., Evaristo, J. (2017) Reviews and syntheses: on the roles trees play in building and plumbing the critical zone. Biogeosciences (Online) 14.

774 Brimhall, G. H., Ford, C., Bratt, J., Taylor, G., and Warin, O.: Quantitative geochemical approach to pedogenesis:
775 importance of parent material reduction, volumetric expansion, and eolian influx in lateritization, Geoderma, 51,
776 51-91, 1991.

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

780 Casetou-Gustafson, S., Akselsson, C., Hillier, S., and Olsson, B. A.: The importance of mineral composition
781 determinations to PROFILE base cation release rates: A case study, Biogeosciences (this issue), 1903–1920, 2019.

782 Chadwick, O. A., Brimhall, G. H., and Hendricks, D. M.: From a black to a gray box—a mass balance
783 interpretation of pedogenesis, Geomorphology, 3, 369-390, 1990.

784 Cosby, B., Hornberger, G., Galloway, J., and Wright, R.: Modeling the effects of acid deposition: Assessment of
785 a lumped parameter model of soil water and streamwater chemistry, Water Resour. Res., 21, 51-63, 1985.

786 Erlandsson Lampa, M., Sverdrup, H.U., Bishop, K.H., Belyazid, S., Ameli, A., and Köhler, S. J.: Catchment
787 export of base cations: Improved mineral dissolution kinetics influence the role of water transit time, In review in
788 Biogeosciences (this issue).

789 Finlay, R., Wallander, H., Smits, M., Holmström, S., Van Hees, P., Lian, B., and Rosling, A.: The role of fungi
790 in biogenic weathering in boreal forest soils, Fungal Biol. Rev., 23, 101-106, 2009.

791 Finlay, R.D., Mahmood, S., Rosenstock, N., Bolou-bi, E., Köhler, S.J., Fahad, Y., Rosling, Wallander, H.,
792 Belyazid, S., Bishop, K., Lian, B. Biological weathering and ist coseqeunce at different spatial levels – from
793 nanosclae to global sclae. Biogeosciences. In review in Biogeosciences (this issue).

794 Fredén, C.: The National Atlas of Sweden, Geology, Third Ed. SNA Publishing House, Stockholm, Sweden, 2009.

795 Fröberg, M., Berggren, D., Bergkvist, B., Bryant, C., & Mulder, J. (2006). Concentration and Fluxes of Dissolved
796 Organic Carbon (DOC) in Three Norway Spruce Stands along a Climatic Gradient in
797 Sweden. Biogeochemistry, 77(1), 1-23.

798 Fröberg, M., Grip, H., Tipping, E., Svensson, M., Strömgren, M., and Kleja, D. B.: Long-term effects of
799 experimental fertilization and soil warming on dissolved organic matter leaching from a spruce forest in Northern
800 Sweden, Geoderma, 200, 172-179, 2013.

801 Futter, M., Klaminder, J., Lucas, R., Laudon, H., and Köhler, S.: Uncertainty in silicate mineral weathering rate
802 estimates: source partitioning and policy implications, Environ Res. Lett., 7, 024025, 2012.

803 Greisman, A., and Gaillard, M. J.: The role of climate variability and fire in early and mid Holocene forest
804 dynamics of southern Sweden, J. Quartenary Sci., 24, 593-611, 2009.

805 Grennfelt, P., and Hov, Ø.: Regional air pollution at a turning point, Ambio, 2-10, 2005.

806 Harden, J. W.: Soils developed in granitic alluvium near Merced, California, Geological Survey Bulletin (USA)
807 1590-A, Soil Chronosequences in the Western United States, Government Printing Office, Washington DC, USA,
808 A1–A65, 1987.

809 Hedin, L. O., Granat, L., Likens, G. E., Buishand, T. A., Galloway, J. N., Butler, T. J., and Rodhe, H.: Steep
810 declines in atmospheric base cations in regions of Europe and North America, Nature, 367, 351-354, 1994.

811 Hedwall, P. O., Grip, H., Linder, S., Lövdahl, L., Nilsson, U., and Bergh, J.: Effects of clear-cutting and slash
812 removal on soil water chemistry and forest-floor vegetation in a nutrient optimised Norway spruce stand, Silva
813 Fenn**.**, 47, article id 933, 2013.

Hellsten, S., Helmisaari, H. S., Melin, Y., Skovsgaard, J. P., Kaakinen, S., Kukkola, M., Saarsalmi, A., Petersson, H., and Akselsson, C.: Nutrient concentrations in stumps and coarse roots of Norway spruce, Scots pine and silver birch in Sweden, Finland and Denmark, Forest Ecol. Manag., 290, 40-48, 2013.

Helmisaari, H.-S., Derome, J., Nöjd, P., and Kukkola, M.: Fine root biomass in relation to site and stand characteristics in Norway spruce and Scots pine stands, Tree Physiol., 27, 1493-1504, 2007.

Hillier, S.: Use of an air brush to spray dry samples for X-ray powder diffraction, Clay Miner., 34, 127-127, 1999.

Hillier, S.: Quantitative analysis of clay and other minerals in sandstones by X-ray powder diffraction (XRPD), in: Clay Mineral Cements in Sandstones, edited by: Worden, R., Morad, S.: International Association of Sedimentologist, Special Publication, John Wiley and Sons Ltd, Oxford, United Kingdom, 34, 213-251, 2003.

Hodson, M. E., Langan, S. J., and Wilson, M. J.: A sensitivity analysis of the PROFILE model in relation to the calculation of soil weathering rates, Appl. Geochem., 11, 835-844, 1996.

Hodson, M. E., and Langan, S. J.: The influence of soil age on calculated mineral weathering rates, Appl. Geochem., 14, 387-394, 1999.

Jansson, P.-E.: CoupModel: model use, calibration, and validation, Trans. Am. Soc. Agric. Eng., 55, 1337-1344, 2012.

Jauhiainen, E.: Age and degree of podzolization of sand soils on the coastal plain of northwest Finland, Comm. Biol., 68, 1-32, 1973.

Jönsson, C., Warfvinge, P., and Sverdrup, H.: Uncertainty in predicting weathering rate and environmental stress factors with the PROFILE model, Water Air Soil Poll., 81, 1-23, 1995.

Karlsson, P. E., Ferm, M., Hultberg, H., Hellsten, S., Akselsson, C., and Pihl Karlsson, G.: Totaldeposition av kväve till skog, IVL Swedish Environmental Research Institute, Stockholm, Sweden 37, 2012.

Karlsson, P. E., Ferm, M., Hultberg, H., Hellsten, S., Akselsson, C., and Pihl Karlsson, G.: Totaldeposition av baskatjoner till skog, IVL Swedish Environmental Research Institute, Stockholm, Sweden 65, 2013.

Kellner, O.: Effects of fertilization on forest flora and vegetation, Ph.D. thesis, Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science, Uppsala University, Sweden, 464, 32 pp., 1993.

Klaminder, J., Lucas, R., Futter, M., Bishop, K., Köhler, S., Egnell, G., and Laudon, H.: Silicate mineral weathering rate estimates: Are they precise enough to be useful when predicting the recovery of nutrient pools after harvesting?, Forest Ecol. Manag., 261, 1-9, 2011.

Kolka, R. K., Grigal, D., and Nater, E.: Forest soil mineral weathering rates: use of multiple approaches, Geoderma. Vol. 73 (1): 1-21.(1996), 73, 1996.

Langan, S. J., Sverdrup, H. U., and Coull, M.: The calculation of base cation release from the chemical weathering of Scottish soils using the PROFILE model, Water Air Soil Poll., 85, 2497-2502, 1995.

Likens, G. E., and Bormann, F. H.: Acid rain: a serious regional environmental problem, Science, 184, 1176-1179, 1974.

Likens, G. E., Driscoll, C. T., Buso, D. C., Siccama, T. G., Johnson, C. E., Lovett, G. M., Fahey, T. J., Reiners, W. A., Ryan, D. F., Martin, C. W., and Bailey, S. W.: The biogeochemistry of calcium at Hubbard Brook, Biogeochemistry, 41, 89-173, 1998.

Linder, S.: Foliar analysis for detecting and correcting nutrient imbalances in Norway spruce, Ecol. Bull. (Copenhagen), 178-190, 1995.

Lundström, U., Van Breemen, N., Bain, D., Van Hees, P., Giesler, R., Gustafsson, J. P., Ilvesniemi, H., Karltun, E., Melkerud, P.-A., and Olsson, M.: Advances in understanding the podzolization process resulting from a multidisciplinary study of three coniferous forest soils in the Nordic Countries, Geoderma, 94, 335-353, 2000.

Löfgren, S., Aastrup, M., Bringmark, L., Hultberg, H., Lewin-Pihlblad, L., Lundin, L., Karlsson, G. P., and Thunholm, B.: Recovery of soil water, groundwater, and streamwater from acidification at the Swedish Integrated Monitoring catchments, Ambio, 40, 836-856, 2011.

Marklund, L. G.: Biomass functions for pine, spruce and birch in Sweden, Department of Forest Survey, Swedish University of Agricultural Sciences, Umea, Sweden, Report 45, 1–73, 1988.

Marshall, C., and Haseman, J.: The quantitative evaluation of soil formation and development by heavy mineral studies: A grundy silt loam profile 1, Soil Sci. Soc. Am. J., 7, 448-453, 1943.

Nieves-Cordones, M., Alemán, F., Martínez, V., and Rubio, F.: K+ uptake in plant roots. The systems involved, their regulation and parallels in other organisms, Journal of plant physiology, 171, 688-695, 2014.

Nilsson, S. I., Miller, H. G., and Miller, J. D.: Forest growth as a possible cause of soil and water acidification - an examination of the concepts, Oikos, 39, 40-49, 1982.

Nykvist, N.: Effects of clearfelling, slash removal and prescribed burning on amounts of plant nutrients in biomass and soil, Swedish University of Agricultural Sciences, Department of Forest Ecology, Uppsala, Sweden, 210, 2000.

Ohlson, M., and Staaland, H.: Mineral diversity in wild plants: benefits and bane for moose, Oikos, 94, 442-454, 2001.

Olsson, B. A., Bengtsson, J., and Lundkvist, H.: Effects of different forest harvest intensities on the pools of exchangeable cations in coniferous forest soils, Forest Ecol. Manag., 84, 135-147, 1996.

Olsson, M., and Melkerud, P.-A.: Chemical and mineralogical changes during genesis of a Podzol from till in southern Sweden, Geoderma, 45, 267-287, 1989.

Olsson, M. T., and Melkerud, P.-A.: Weathering in three podzolized pedons on glacial deposits in northern Sweden and central Finland, Geoderma, 94, 149-161, 2000.

Olsson, M., Rosén, K., and Melkerud, P.-A.: Regional modelling of base cation losses from Swedish forest soils due to whole-tree harvesting, Appl Geochem, 8, 189-194, 1993.

Omotoso, O., McCarty, D. K., Hillier, S., and Kleeberg, R.: Some successful approaches to quantitative mineral analysis as revealed by the 3rd Reynolds Cup contest, Clay Clay Miner., 54, 748-760, 2006.

Petersson, H., and Ståhl, G.: Functions for below-ground biomass of *Pinus sylvestris*, *Picea abies*, *Betula pendula* and *Betula pubescens* in Sweden, Scand. J. Forest Res., 21, 84-93, 2006.

Reuss, J. O., and Johnson, D.W..: Acid Deposition and the Acidification of Soils and Waters, Ecol. Stud., 95, 1986.

Ryan, M. G.: Three decades of research at Flakaliden advancing whole-tree physiology, forest ecosystem and global change research, Tree Physiol., 33, 1123-1131, 2013.

Schaetzl, R. J., and Isard, S. A.: Regional-scale relationships between climate and strength of podzolization in the Great Lakes region, North America, Catena, 28, 47-69, 1996.

Schützel, H., Kutschke, D., and Wildner, G.: Zur Problematik der Genese der Grauen Gneise des sächsischen Erzgebirges (zirkonstatistische Untersuchungen), VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1963.

Sigurdsson, B. D., Medhurst, J. L., Wallin, G., Eggertsson, O., and Linder, S.: Growth of mature boreal Norway spruce was not affected by elevated [CO_2] and/or air temperature unless nutrient availability was improved, Tree Physiol., 33, 1192-1205, 2013.

Simonsson, M., and Berggren, D.: Aluminium solubility related to secondary solid phases in upper B horizons with spodic characteristics, Eur. J. Soil Sci., 49, 317-326, 1998.

Simonsson, M., Bergholm, J., Olsson, B. A., von Brömssen, C., and Öborn, I.: Estimating weathering rates using base cation budgets in a Norway spruce stand on podzolised soil: analysis of fluxes and uncertainties, Forest Ecol. Manag., 340, 135-152, 2015.

Simonsson, M., Bergholm, J., Lemarchand, D., and Hillier, S.: Mineralogy and biogeochemistry of potassium in the Skogaby experimental forest, southwest Sweden: pools, fluxes and K/Rb ratios in soil and biomass, Biogeochemistry, 131, 77-102, 2016.

Smits, M. M., and Wallander, H.: Role of mycorrhizal symbiosis in mineral weathering and nutrient mining from soil parent material, in: Mycorrhizal Mediation of Soil: Fertility, Structure, and Carbon Storage, edited by: Johnson, N. C., Gehring, C., and Jansa, J., Elsevier, United States, 35-46, 2017.

Starr, M., Lindroos, A.-J., and Ukonmaanaho, L.: Weathering release rates of base cations from soils within a boreal forested catchment: variation and comparison to deposition, litterfall and leaching fluxes, Environ. Earth Sci., 72, 5101-5111, 2014.

Stendahl, J., Lundin, L., and Nilsson, T.: The stone and boulder content of Swedish forest soils, Catena, 77, 285-291, 2009.

Stendahl, J., Akselsson, C., Melkerud, P.-A., and Belyazid, S.: Pedon-scale silicate weathering: comparison of the PROFILE model and the depletion method at 16 forest sites in Sweden, Geoderma, 211, 65-74, 2013.

Strengbom, J., Dahlberg, A., Larsson, A., Lindelow, A., Sandström, J., Widenfalk, O., and Gustafsson, L.: Introducing intensively managed spruce plantations in Swedish forest landscapes will impair biodiversity decline, Forests, 2, 610-630, 2011.

Sudom, M., and St. Arnaud, R.: Use of quartz, zirconium and titanium as indices in pedological studies, Can. J. Soil Sci., 51, 385-396, 1971.

Sverdrup, H.: Chemical weathering of soil minerals and the role of biological processes, Fungal Biol. Rev., 23, 94-100, 2009.

Sverdrup, H., and Rosen, K.: Long-term base cation mass balances for Swedish forests and the concept of sustainability, Forest Ecol. Manag., 110, 221-236, 1998.

Sverdrup, H., and Warfvinge, P.: Weathering of primary silicate minerals in the natural soil environment in relation to a chemical weathering model, Water Air Soil Poll., 38, 387-408, 1988.

Sverdrup, H., Warfvinge, P., and Wickman, T.: Estimating the weathering rate at Gårdsjon using different methods, in: Experimental Reversal of Rain Effects: Gardsjon Roof Project, edited by: Hultberg, H., and Skeffington, R., John Wiley & Sons Ltd, Chichester, United Kingdom, 231-249, 1998.

Tamm, C.-O.: Nitrogen in Terrestrial Ecosystems: Questions of Productivity, Vegetational Changes, and Ecosystem Stability. Ecological Studies 81, Springer-Verlag, Berlin, 115 p., 1991.

Tamm, O.: Studier över jordmånstyper och deras förhållande till markens hydrologi i nordsvenska skogsterränger barrskogsområdet, Reports of the Swedish Institute of Experimental Forestry, 26(2), 163-355, 1931. (In Swedish)

Taylor, A., and Blum, J. D.: Relation between soil age and silicate weathering rates determined from the chemical evolution of a glacial chronosequence, Geology, 23, 979-982, 1995.

Taylor, A., Lenoir, L., Vegerfors, B., and Persson, T.: Ant and earthworm bioturbation in cold-temperate ecosystems, Ecosystems, 1-14, 2019.

Thompson, M. L., and Ukrainczyk, L.: Micas, Soil mineralogy with environmental applications, in: Soil Mineralogy with Environmental Applications, edited by: Dixon, J. B., and Schulze, D. G., Soil Science Society of America Inc., Madison, 431-466 pp., 2002.

Van Der Heijden, G., Legout, A., Mareschal, L., Ranger, J., and Dambrine, E.: Filling the gap in Ca input-output budgets in base-poor forest ecosystems: The contribution of non-crystalline phases evidenced by stable isotopic dilution, Geochim. Cosmochim. Acta**,** 209, 135-148, 2017.

Van der Salm, C.: Assessment of the regional variation in weathering rates of loess and clay soils in the Netherlands, Water Air Soil Poll., 131, 217-243, 2001.

Velbel, M. A.: Geochemical mass balances and weathering rates in forested watersheds of the southern Blue Ridge, Am. J. Sci., 285, 904-930, 1985.

Viro, P.: Kivisyyden maarittamisesta, Summary: On the determination of stoniness. Commun. Inst. For. Fenn., 40, 8, 1952.

Warfvinge, P., and Sverdrup, H.: Critical Loads of Acidity to Swedish Forest Soils: Methods, Data and Results, Reports in Ecology and Environmental Engineering, Dpt. of Chemical Engineering II, Lund University, Lund, Sweden, 1995.

White, A. F., Blum, A. E., Schulz, M. S., Bullen, T. D., Harden, J. W., and Peterson, M. L.: Chemical weathering rates of a soil chronosequence on granitic alluvium: I. Quantification of mineralogical and surface area changes and calculation of primary silicate reaction rates, Geochim. Cosmochim. Acta, 60, 2533-2550, 1996.

Whitfield, C., Watmough, S., Aherne, J., Dillon, P.: A comparison of weathering rates for acid-sensitive catchments in Nova Scotia, Canada and their impact on critical load calculations, Geoderma 136, 899-911, 2006.

Whitfield, C. J., Watmough, S. A., and Aherne, J.: Evaluation of elemental depletion weathering rate estimation methods on acid-sensitive soils of north-eastern Alberta, Canada, Geoderma, 166, 189-197, 2011.

Wikström, P., Edenius, L., Elfving, B., Eriksson, L. O., Lämås, T., Sonesson, J., Öhman, K., Wallerman, J., Waller, C., and Klintebäck, F.: The Heureka forestry decision support system: an overview, Mathematical and Computational Forestry & Natural Resource Sciences, 3, 87, 2011.

Zetterberg, T., Olsson, B. A., Löfgren, S., von Brömssen, C., and Brandtberg, P. O.: The effect of harvest intensity on long-term calcium dynamics in soil and soil solution at three coniferous sites in Sweden, Forest Ecol. Manag., 302, 280-294, 2013.

Zetterberg, T., Olsson, B. A., Löfgren, S., Hyvönen, R., and Brandtberg, P. O.: Long-term soil calcium depletion after conventional and whole-tree harvest, Forest Ecol. Manag., 369, 102-115, 2016.

Table 1. Soil profile characteristics at 50 cm depth in the mineral soil at the Asa and Flakaliden sites

Site	Plot	Clay (%wt)	Silt (%wt)	Sand (%wt)	Coarse (%wt)	Density (g/cm^3)	Soil age (calendar years)
Asa	K1	9.49	25.04	45.30	20.18	1.10	14300
	K4	7.65	22.59	39.21	30.48	1.09	14300
	F3	4.95	25.26	40.54	29.25	0.99	14300
	F4	8.64	25.69	40.13	25.54	0.94	14300
Flakaliden	15A	1.92	9.21	68.98	19.68	1.89	10150
	14B	7.71	34.09	33.71	24.17	1.35	10150
	10B	7.75	45.17	37.23	8.90	1.36	10150
	11B	9.56	45.07	33.91	10.72	1.47	10150

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970 **Table 2.** A short description of characteristics of the three different approaches that are used in the study to
971 estimate base cation release rates at the pedon scale using a harmonized set of input data. The difference between
972 methods reflect expected differences due to different time scales, conceptual differences, assumptions about
973 weathering kinetics and pedogenesis.

Description	PROFILE	Depletion	Base cation budget
Time scale	Present-day	Long-term	Present-day
Concept	Steady-state	Historical	Dynamic
Weathering kinetics	Long-term kinetics	No assumption	No assumption
Pedogenesis	No assumption	Zr immobility, unweathered and homgeneous parent material	No assumption

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Table 3. Extractable concentrations of different elements at the reference depths used for calculating historical weathering rate at the Asa and Flakaliden sites.

Site	Plot	Ref. depth (cm)	Ca (%)	Mg(%)	K(%)	Na (%)	Zr (ppm)	Ti (%)
Asa	K1	80-90	1.41	0.51	0.93	1.06		0.34
	K4	80-90	1.29	0.44	0.88	1.00	288.1	-
	F3	60-70	1.41	0.55	0.87	1.04	282.6	-
	F4	80-90	1.26	0.49	0.85	0.98	293.3	-
Flakaliden	10B	60-70	1.09	0.57	0.88	0.87	243.8	-
	14B	60-70	1.59	0.70	0.81	1.03	336.1	-

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Table 4a. *Site parameters used in the PROFILE model*

Parameter	Source	Asa	Flakaliden
Temperature (°C)	Measurements at Asa and Flakaliden	6.1	2.3
Precipitation (m yr^{-1})	Measurements at Asa and Flakaliden	0.736	0.642
Total deposition ($mmol_c$ m^{-2} yr^{-1})	Measured data on open field and throughfall deposition available from nearby Swedish ICP Integrated Monitoring Sites	SO^{2-}_4: 27.0	SO^{2-}_4: 13.1
		Cl^-: 38.3	Cl^-: 5.6
		NO^-_3: 30.7	NO^-_3: 10.5
		NH^+_4: 21.6	NH^+_4: 9.9
		Ca^{2+}: 7.2	Ca^{2+}: 5.2
		Mg^{2+}: 6.8	Mg^{2+}: 1.9
		K^+: 1.9	K^+: 1.1
		Na^+: 31.5	Na^+: 5.6
Base cation net uptake ($mmol_c$ m^{-2} yr^{-1})	Previously measured data for Asa and Flakaliden: Concentrations in biomass from Linder (unpublished data). Biomass data from Heureka simulations.	Ca^{2+}: 46.2	Ca^{2+}: 26.7
		Mg^{2+}: 10.6	Mg^{2+}: 4.4
		K^+: 17.8	K^+: 6.7
Net nitrogen uptake ($mmol_c$ m^{-2} yr^{-1})	Previously measured data from Asa and Flakaliden: Concentrations in biomass from Linder (unpublished data). Biomass data from Heureka simulations.	81.0	32.4
Base cations in litterfall ($mmol_c$ m^{-2} yr^{-1})	Literature data from Hellsten et al. (2013)	Ca^{2+}: 116.8	Ca^{2+}: 40.6
		Mg^{2+}: 15.1	Mg^{2+}: 4.6
		K^+: 10.5	K^+: 3.2
Nitrogen in litterfall ($mmol_c$ m^{-2} yr^{-1})	Literature data from Hellsten et al. (2013)	179.8	47.5
Evapotranspiration (Fraction)	Precipitation data and runoff data. Runoff data calculated based on proportion of runoff to precipitation (R/P) at Gammtratten and Aneboda.	0.3	0.6

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***Table 4b**. Soil* parameters used in the PROFILE model.*

Parameter	Unit	Source
Exposed mineral surface area	$m^2\ m^{-3}$	Own measurements used together with Eq. 5.13 in Warfvinge and Sverdrup (1995)
Soil bulk density	$kg\ m^{-3}$	Own measurements
Soil moisture	$m^3\ m^{-3}$	Based on paragraph 5.9.5 in Warfvinge and Sverdrup (1995)
Mineral composition	Weight fraction	Own measurements
Dissolved organic carbon	$mg\ L^{-1}$	Previously measured data for Asa and Flakaliden: Measurements for B-horizon from Harald Grip and previously measured data from Fröberg et al. (2013)
Aluminium solubility coefficient	$kmol\ m^{-3}$	Own measurements for total organic carbon and oxalate-extractable Al together with function developed from previously published data (Simonsson and Berggren, 1998)
Soil solution CO_2 partial pressure	atm.	Based on paragraph 5.10.2 in Warfvinge and Sverdrup (1995)

*Physical and chemical soil layer specific input data are given in supplements (Table S3-S4)

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Table 5. Judgement of data quality for terms included in the base cation budget estimate of weathering

Term	Spatial scale	Temporal scale	Data source	Quality of term quantification
Deposition	Adjacent sites	Annual or monthly measurements	Svartberget experimental forest, and Integrated Monitoring site	Moderate: high quality of data, but estimates are not site-specific
Soil stock change	Site (initial) and plot (repeated)	Repeated samplings (2)	Unpublished data from J. Bergholm and H. Grip.	Moderate/low: repeated sampling biased by differences in methods of sampling and soil extraction.
Leaching	Plot	Sampling of soil water at 50 cm depth repeated 2 times per year. Water flux modelled (COUP).	H. Grip, unpublished data	High/moderate: High spatial and temporal resolution in soil chemistry, but uncertainty in separating lateral and vertical flow (Flakaliden).
Biomass accumulation	Site (control plots)	Growth increment measured from biomass studies at start and after 12 years.	Growth Albaugh et al. (2009) Nutrient content: S: Linder unpublished data	High/moderate: High quality in growth estimates and nutrient content at treatment scale, data lacking at plot scale

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Table 6: Standard errors and standard uncertainties ($mmol_c\ m^{-2}\ yr^{-1}$) for the terms in the base cation budget, Eq. (4). Combined standard uncertainty, plot average value and confidence interval for the weathering rate of base cation *i* derived from base cation budgets $W_{budget,\ i}$ ($mmol_c\ m^{-2}\ yr^{-1}$).

Site	Element	Deposition	Soil change	Biomass accum.	Leaching	Combined standard uncertainty	W_{budget}	Confidence interval (combined standard uncertainty × 3)
Asa	Ca	1.1	12.9	19.5	3.2	24	58	±71
	Mg	1.1	0.6	2.5	1.6	3	29	±10
	K	0.3	1.0	9.7	0.1	10	37	±29
	Na	4.0	0.9	0.0	5.1	7	7	±20
Flakaliden	Ca	0.8	10.5	13.3	0.7	17	28	±51
	Mg	0.3	1.1	1.5	0.3	2	12	±6
	K	0.2	0.6	6.7	0.2	7	19	±20
	Na	0.7	1.2	0.0	0.8	2	2	±5

Figure captions

Figure 1. Titanium (Ti) to zirconium (Zr) ratio (by concentration) used as an indicator of uniform parent material in all soil layers at Asa (F3, F4, K1, K4) and Flakaliden (10B, 11B, 14B, 15A).

Figure 2. Zirconium (Zr) gradient in the soil at Asa (KI, K4, F3, F4) and Flakaliden (10B, 11B, 14B, 15A)

Figure 3. (Left) Historical weathering rate of base cations ($mmol_c\ m^{-2}\ yr^{-1}$) estimated by the depletion method and (right) steady-state weathering rate estimated by the PROFILE model in different soil layers at Asa and Flakaliden.

Figure 4. Comparison of weathering rates ($mmol_c\ m^{-2}\ yr^{-1}$) for Ca, Mg, Na and K determined with the depletion method, the PROFILE model and the base cation budget method for the 0-50 cm layer at Asa and Flakaliden. For the weathering rates based on the depletion method and the PROFILE model, error bars represent the standard error calculated based on four soil profiles at each study site, except for Flakaliden, where the depletion method was only applied in two soil profiles. For weathering rates based on the base cation budget approach, error bars represent combined standard uncertainties, which are based on standard errors derived from plot-wise replicated data of the present experiments (for leaching and changes in exchangeable soil pools) and on standard uncertainties derived from Simonsson et al. 2015, where replicated data were missing in the present study (for accumulation in biomass and total deposition).

Figure 5. (Left) Sinks and (right) sources of base cations in ecosystem net fluxes at Asa and Flakaliden. The soil is a net source of soil base cation stocks decrease and a net sink if they increase. 'BC budget' = current base cation weathering rate (W_{budget}) estimated with the base cation budget method, including measured changes in soil extractable base cation stocks; 'PROFILE' = soil extractable pools estimated from base cation budget using PROFILE estimates of steady-state weathering rate; 'Historical' = soil extractable pools estimated from base cation budget using estimates of historical weathering rate by the depletion method. ‘Measured soil change’ and ‘Base cation budget estimated soil change’ indicates that equation 4 was used to estimate weathering rate or the soil change, respectively.

Figure 6. Time (years) required to achieve the measured historical element loss in different soil layers with maximum or minimum PROFILE weathering rates at (a) Flakaliden and (b) Asa.

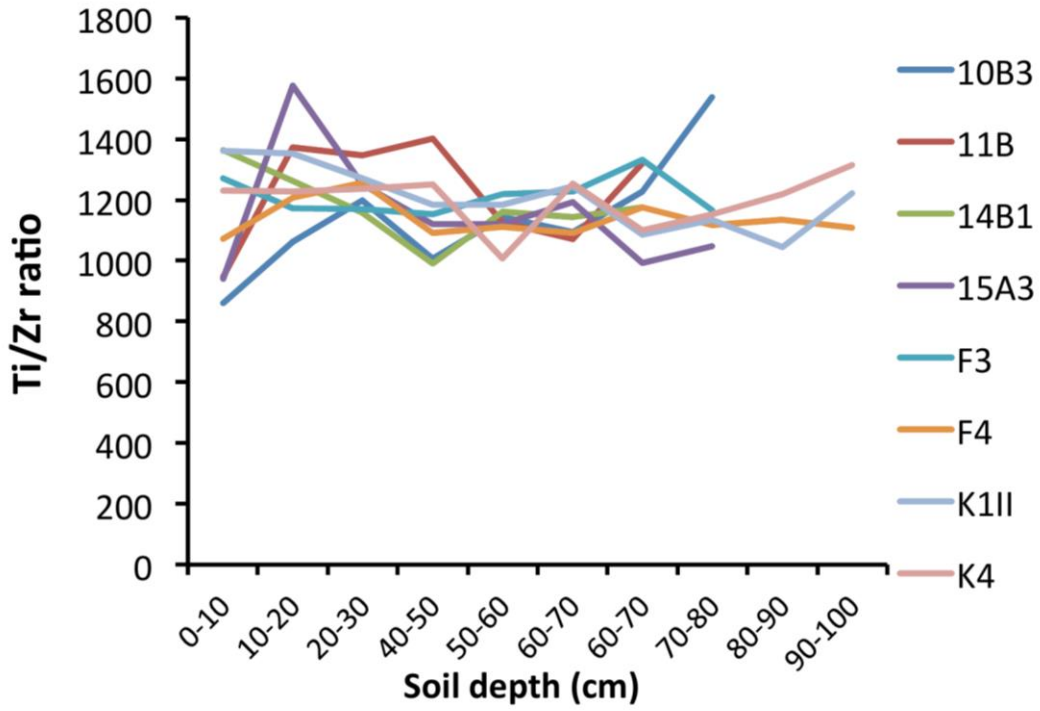
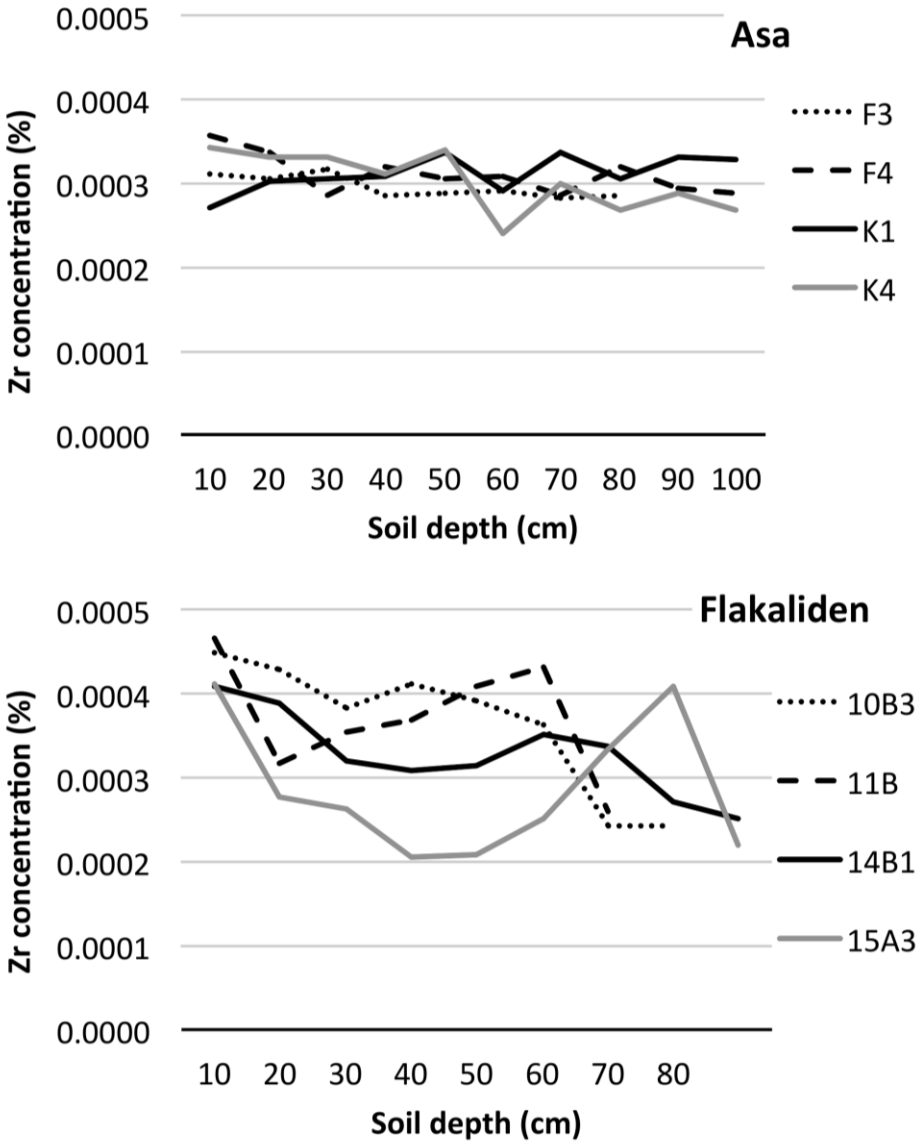

1800
1600
1400
1200
1000
800
600
400
200
0
Ti/Zr ratio
0-10
10-20
20-30
40-50
50-60
60-70
60-70
70-80
80-90
90-100
Soil depth (cm)
10B3
11B
14B1
15A3
F3
F4
K1II
K4

Figure 1.



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1080 **Figure 2**.

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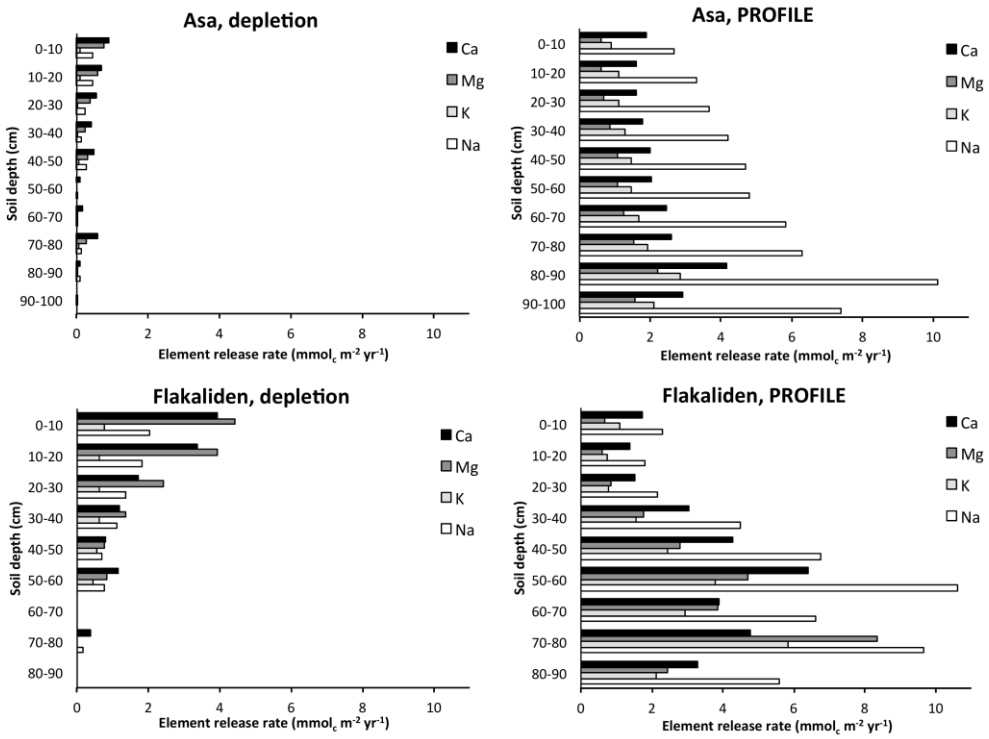

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1083 **Figure 3.**

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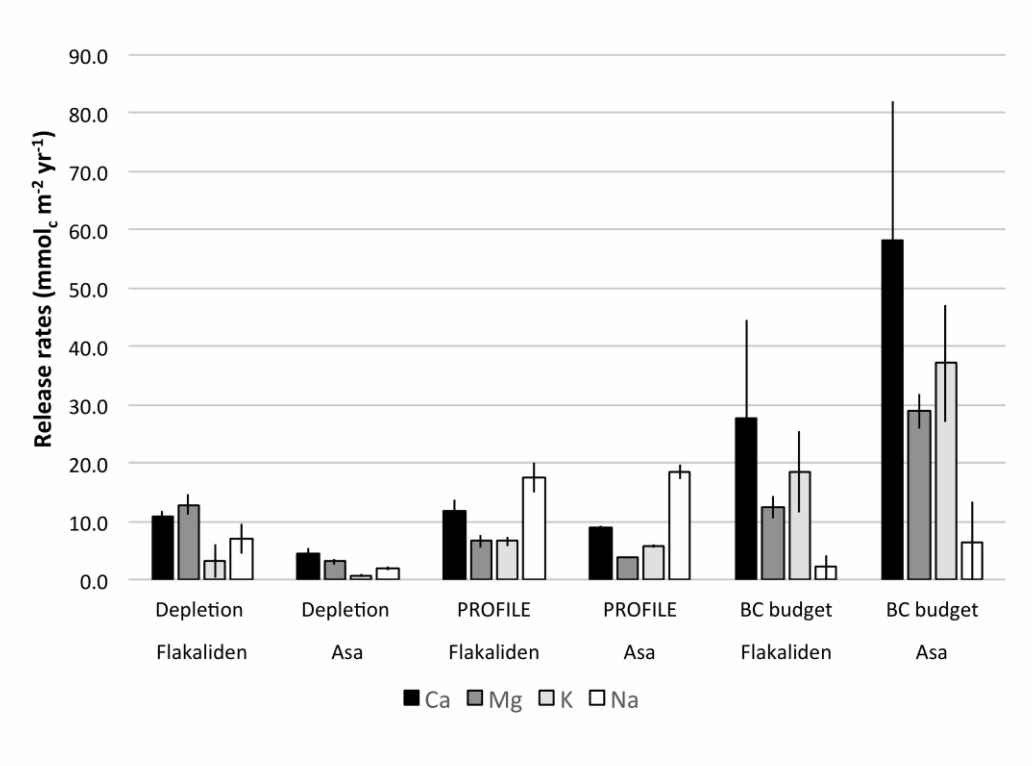

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1093 **Figure 4.**

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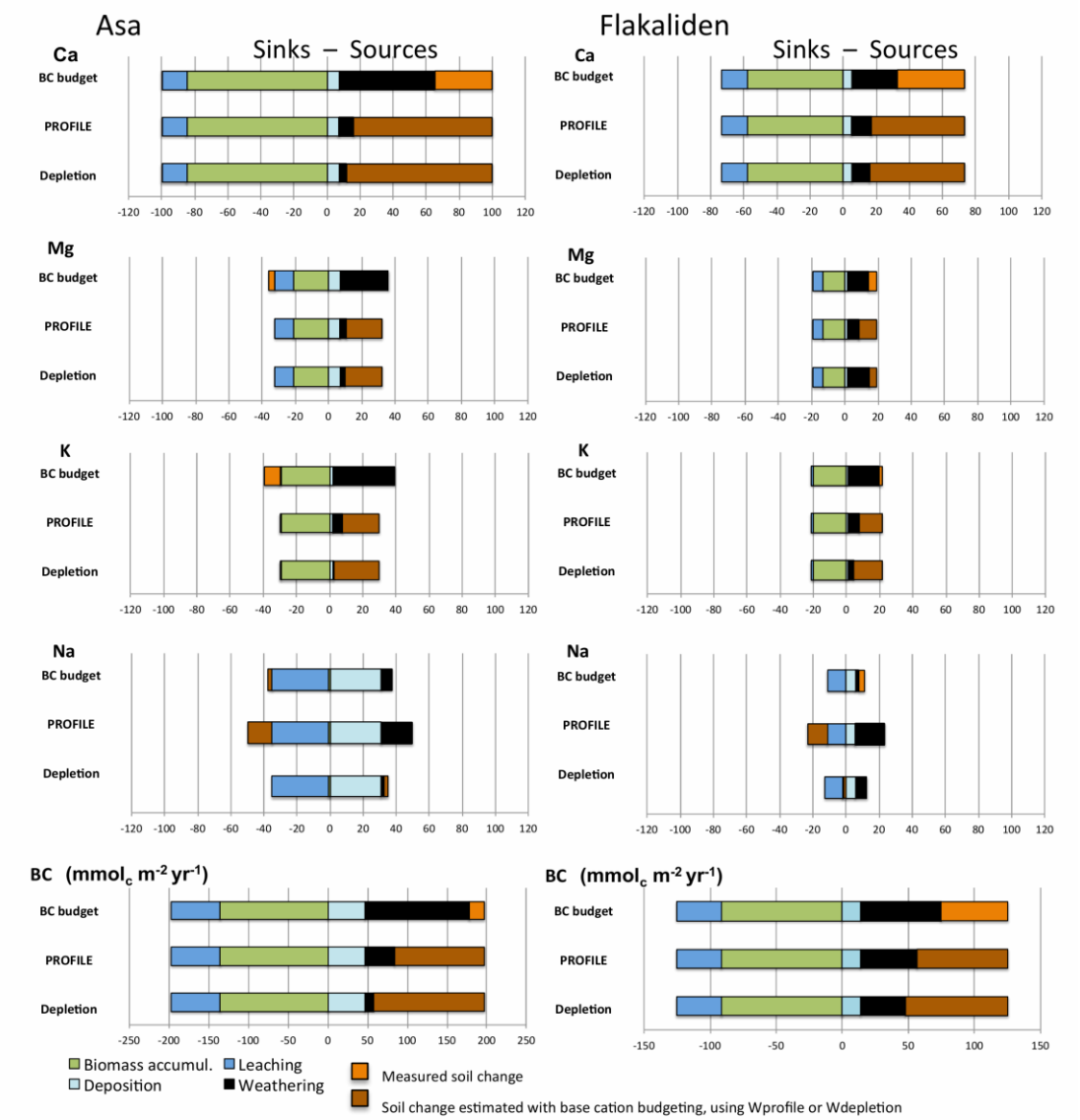
Asa
Flakaliden
Sinks – Sources
Ca
Mg
K
Na
BC budget
PROFILE
Depletion
BC (mmol$_c$ m^{-2} yr^{-1})
Biomass accumul.
Leaching
Deposition
Weathering
Measured soil change
Soil change estimated with base cation budgeting, using Wprofile or Wdepletion

Figure 5.

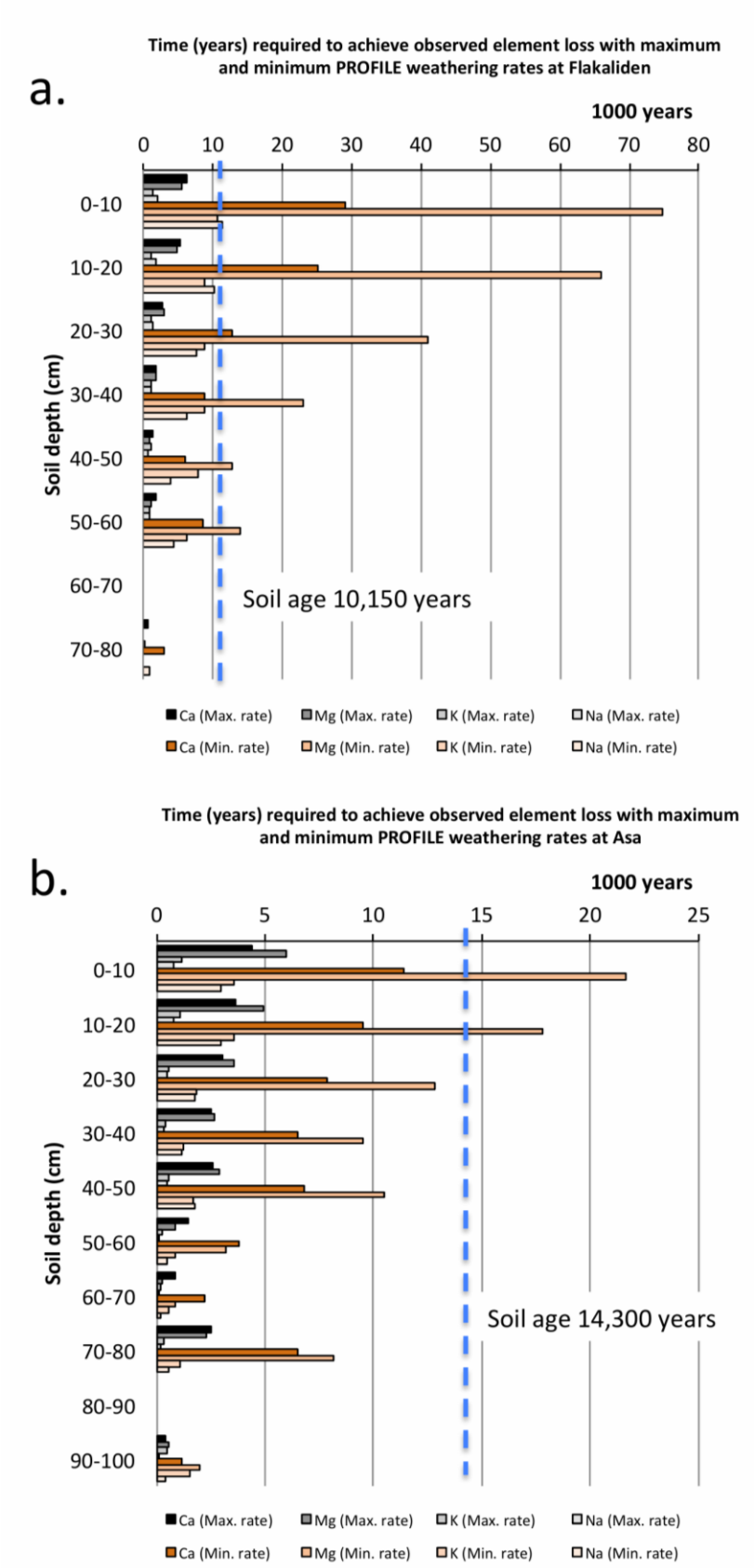
a.
Time (years) required to achieve observed element loss with maximum and minimum PROFILE weathering rates at Flakaliden
1000 years
0
10
20
30
40
50
60
70
80
Soil depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
70-80
Soil age 10,150 years
Ca (Max. rate)
Mg (Max. rate)
K (Max. rate)
Na (Max. rate)
Ca (Min. rate)
Mg (Min. rate)
K (Min. rate)
Na (Min. rate)
b.
Time (years) required to achieve observed element loss with maximum and minimum PROFILE weathering rates at Asa
1000 years
0
5
10
15
20
25
Soil depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
70-80
80-90
90-100
Soil age 14,300 years
Ca (Max. rate)
Mg (Max. rate)
K (Max. rate)
Na (Max. rate)
Ca (Min. rate)
Mg (Min. rate)
K (Min. rate)
Na (Min. rate)

Figure 6.