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 mass balance 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 m⁻² yr⁻¹, respectively. Corresponding values at Flakaliden were 11.0, 12.9, 3.2 and 7.0 mmol 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 m⁻² yr⁻¹, respectively, at Asa and 11.9, 6.7, 6.6 and 17.5 mmol 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 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 mass balance approach produced significantly higher weathering rates of Ca, Mg, and K (65, 23, 40 mmol m⁻² yr⁻¹ at Asa and 35, 14 and 22 mmol m⁻² yr⁻¹ at Flakaliden), but lower Na weathering rates similar to the depletion method (6.6 and 2.2 mmol 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 mass balance 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 cation per area per unit time.

Definitions Abbrebations:

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

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

$W_{mb}$ = Current weathering rate based on base cation budget mass balance 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; Hedlin et al., 1994; Likens et al., 1998; Bailey et al., 2003). These effects of weathering are important in areas where historical high sulphur (S) deposition has caused severe acidification of forest soils and waters (Reuss and Johnson, 1996), particularly in southern Scandinavia where acid-felicit 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 recovery from acidification began (Warfvinge and Bertills, 2000; Bertills et al., 2007). This recovery of the soil is mainly driven by silicate weathering (Evans et al., 2001; Shipley et al., 2001), but the process is slow (Futter et al., 2012; Akselsson et al., 2013; Futter et al., 2017). At the same time, forest growth has become a more important source of acidity, caused by the 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). The biomass extraction rate at harvesting determines the extent to which soil acidity produced by forest growth can be neutralised by decomposition of biomass left on-site. Whole-tree harvesting can thus result in more acid, base cation-depleted soils than stem-only harvesting (Olsson et al., 1996; Zetterberg et al., 2011), due to the smaller return of alkalinity. 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. The current Swedish environmental quality objective “Natural Acidification Only” targets a reduction in acid load due to forest growth and harvesting and to acid deposition (Bertills et al., 2007).

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 depletion-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). The methods used to determine base cation balance in that study included predicting weathering rates based on the PROFILE model and analysing regional data for deposition, leaching and base cation losses in harvested biomass. Negative balances, which indicate soil-base cation depletion in the soil (Olsen et al., 1996) found to be more frequent after whole-tree harvesting than stem-only harvesting, especially for Norway spruce compared with Scots pine, with the effect being more common in southern than in northern (boreal) Sweden. Among the elements studied, Ca was most frequently subject to base cation depletion. However, uncertainties in estimating the terms of the base cation balance can accumulate to produce large uncertainties in the overall balance, and therefore it is difficult to draw firm conclusions about the sustainability of different harvesting options based on base cation balance alone. There are also conflicting opinions about the consequences of long-term negative base cation balance in
soils for sustainable forest production (Binkley and Högberg, 1997, 2016). Experimental studies have demonstrated that growth of boreal forests is strongly limited by nitrogen (N), whereas co-limitation with phosphorus (P) may occur in hemiboreal and temperate forests (e.g. Tamm, 1991). Thus, concerns about base cation depletion in Swedish forest soils following increasing use of whole tree harvesting have so far been about soil acidification rather than tree nutrition, the latter expressed for example by the Swedish Forest Agency (2008) in their recommendation on nutrient compensation with wood ash.

In regional assessments of the sustainability of different harvesting regimes, the value of estimated weathering rate has a strong influence on the base cation balance. Klaminder et al. (2011b) 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. They concluded that the sources of uncertainties were as follows: input data > parameters > weathering concepts/assumptions. Differences in input data can be attributed to different time scales used when acquiring different input data, different time scales, challenges determining accurate mineralogical compositions and the use of field laboratory data compared with laboratory data (Vander Salm, 2001; Futter et al., 2012; Klaminder et al., 2011b). 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. Comparing weathering estimates based on these concepts requires that the methods are tested at the same spatial scale. 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. 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 m⁻² day⁻¹), 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).)

In society there is a pressing need to know if current forestry practices are sustainable, that is, if current/present-day weathering provides enough base cations (BC) to at least balance BC their export by forestry. Therefore, our goal should be to determine current/present-day mineral weathering rates in soil. All soils are, by definition, composed of biogeochemically altered material. The rates of extent/alteration that have occurred over the past as well as that the one that occurrences at present may differ (Klaminder et al., 2011; Stendahl et al., 2013; Klaminder et al., 2011), i.e. the average weathering potential under average long-term environmental change, i.e. ‘historical weathering’, is thus different from the, as well as the a one that occurs at present (i.e. 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) may differ (Stendahl et al., 2013; Klaminder et al., 2011). Moreover, present-day weathering rates estimated based on the steady-state concept, which lacks time the dimension of time, may differ from dynamic estimates of weathering rates derived from measured base cation balances. These three different concepts of estimating weathering cannot be covered by a single method (Klaminder et al., 2011; Futter et al., 2012), and so Weathering estimates based on these concepts have often differed largely from pedon to catchment scale, whereas truly. Thus, which is the reason why harmonized comparisons of methods require requiring it should be applied uniformly at the spatial scale of interest, i.e. the soil pedon. This spatial scale can be the pedon, which also contains the major part of the mineral nutrient sources in the soil available for, which is the source of mineral nutrients for forest growth. To our knowledge, Keiluweit et al. (1996) were the only ones that tried to previously revalued this approach. However, when comparing soil profile-based methods, it is important to understand variation with soil depth that exceeds 0.50 m, since the depletion method calculates weathering over the entire soil pedon.

Beside the PROFILE model, the depletion method is most widely used in Sweden to estimate weathering rates, specifically at the regional scale (Olsson et al., 1993). The depletion method makes use of soil profile-based mass balance estimates (Chadwick et al., 1990; Brumfield et al., 2001) to estimate total base cation losses since depletion in the soil above a reference soil depth, using an element in a weathering-resistant mineral as a standard, most commonly zirconium (Zr, e.g. present in zircon etc.) or titanium (Ti, e.g. present in rutile etc.) (Sudom and St.Arnaud, 1971; Harden et al., 1987; Chadwick et al., 1990; Bain et al., 1994), due to their stability.

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Methods may therefore reflect ‘true’ differences or conceptual differences between the methods.

The second approach commonly involves the mechanistic PROFILE model, by which estimates steady-state
release rates of base cations are estimated using steady-state mass balances 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 also still a need to improve
room for improvement in process descriptions of e.g. biological weathering and weathering brakes (e.g. Lampa
Erlandsson Lampa et al., this issue). The sensitivity of PROFILE to variations in soil physical parameters (e.g.
situation where the base cation
interaction of minerals. The third
approach to estimating weathering rate is the base cation budget approach mass balance
released cations, which are measured, within a system with defined boundaries. The missing source in the mass balance
equation is assumed to contain represent the weathering, but can also contain other unidentified sources. The base
cation budget mass balance approach is most reliable when based on long-term data from well-defined systems, although even then estimates of weathering rates tend to suffer from large uncertainties, as errors in the sinks
and sources can be expected to accumulate in the mass balance equation (Simonsson et al., 2015). The base
situation where the base cation uptake in biomass is high, it dominates the flux of the elements included in the
base cation budget. Nevertheless, the base cation budget approach has been mostly
been applied under non-steady-state conditions where accumulation in biomass were not directly measured but
estimated to be small, or base cation BC-stocks in the soil were assumed to be at steady-state (i.e. including
measures of soil exchangeable pools), due to lack of long-term data on base cation fluxes (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 rate.
comparing these two methods is that, taken together, they can provide complementary information about soil weathering potential (i.e. historical versus steady-state weathering) in individual soil layers.

In this study, we applied the aim was to apply three conceptually different methods of estimating weathering, the depletion method, the PROFILE model and the BC budget approach, to 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. Three optimum (tree) nutrition experimental sites were selected for the study to obtain a well-defined system with uniform spatial scale for observations, in line with the suggestion of by Futter et al. (2012). In addition, BCThe 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 and has been critically previously discussed in 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 structure and function, 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 had four replicates 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). For further details, see Linder (1995).
Flakaliden is located in the central boreal sub-zone with a harsh climate, with long cool days in summer and short cold days in winter. Mean annual temperature for the period 1990-2009 was 2.5 °C, and mean monthly temperature varied from -7.5 °C in February to 14.5 °C in July. Mean annual precipitation in the period was ~650 mm, with approximately one-third falling as snow, which usually covers the frozen ground from mid-October to early May. Mean length of the growing season (daily mean temperature ≥ 5 °C) was 148 days, but with large between-year variations (Table 1) (cf. Sigurdsson et al., 2013).

Asa is located in the hemi-boreal zone, where the climate is milder than at Flakaliden, which is reflected in a longer growing season (193 days). Mean annual temperature (1990-2009) was 6.3 °C, mean monthly temperature varied from -1.9 °C in February to 16.0 °C in July and mean annual precipitation was ~750 mm. The soil is periodically frozen in winter. The difference in climate is reflected in differences in site productivity, which broadly follows climate gradients in Sweden (Bergh et al., 2005).

The soils at Asa and Flakaliden differ in age due to differences in the time since deglaciation (Table 1). Soil age is from approximately 14,500 thousand years at Asa and 10,150 thousand years at Flakaliden (based on National Atlas of Sweden; estimated from Fredén, 2009). The soil type at both sites is Udic Spodosol, with a mor humus layer overlying glacial till derived from felsic igneous rocks bedrock. The soil texture is classified as sandy loam. The transition between the B- and C-horizon transitions to C horizon is mostly located at 25-50 cm depth at Flakaliden and 50-60 cm depth at Asa. The natural ground vegetation at Flakaliden is dominated by Vaccinium myrtillus (L.) and V. vitis-idaea (L.) dwarf-shrubs, lichens and mosses (Kellner, 1993; Strengbom et al., 2011). The ground vegetation at Asa is dominated by Deschampsia flexuosa, (L.) and mosses (Strengbom et al., 2011; Hedwall et al., 2013).

2.2 Soil sampling and analyses of geochemistry and mineralogy

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

Soil sampling was performed in October 2013 (Flakaliden) and March 2014 (Asa), in the border zone of four plots at each site. Plots selected for sampling were performed in an untreated control plots (K1 and K4 at Asa) and 10B and 14B at Flakaliden) and fertilised (F) plots (F3, F4 at Asa and 15A and 11B at Flakaliden) in October 2013 (Flakaliden) and March 2014 (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 was extracted using a A rotary drill (17 cm inner diameter) was used to extract one intact soil core per plot at Flakaliden and in plot K1 at Asa. In plots K4, F3 and F4 at Asa, soil samples were instead taken from the wall of 1 m deep manually dug soil pits, due to inaccessible terrain for the rotary drill machinery. Maximum soil depth was shallower at Flakaliden (70-90 cm) than at Asa (90-100 cm). The volume of stones and boulders was determined for each plot at the two study sites using the penetration method described by Viro (1952) to a maximum depth of 30 cm and by applying the fitted function described by Stendahl et al. (2009). Mean stone and bolder content was higher at Flakaliden (39%) than at Asa (28%).
Soil samples were taken from each 10-cm soil layer. Prior to chemical analysis, these samples were dried at 30-40 °C and sieved to <2 mm (Table 2). 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 HNO₃ extracts of fused samples that were milled and ignited (1000 °C) prior to fusion with LiBO₂.

Quantitative soil mineralogy was determined with the X-ray powder diffraction (XRD) technique (XRPD). Soil samples were prepared by spraying and drying slurries of micronised soil samples (<2 mm) micronised in ethanol. A full pattern fitting approach was used for Quantitative mineralogical analysis of the diffraction data was performed using a full pattern fitting approach (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 mineral identified mineral components. The determination of chemical composition of the various minerals present in the soils was conducted by electron microprobe analysis (EMPA) of mineral grains subsampled from the silted (<2 mm) soil samples.

2.3 Historical weathering determined with the depletion method

2.3.1 Method description

The depletion method, 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):

\[ W_{\text{depletion},i} = \frac{\rho_i \times (X_{\text{w,i}} - X_{\text{r,i}})}{Zr} \]

where \( W \) denotes loss of the \( i \)th element (g m⁻²), \( X \) denotes mobile element concentrations (%), \( Zr \) denotes immobile element concentrations (%), \( \rho \) and \( Zr \) denote a weathered soil layer and the assumed unweathered reference layer, respectively, \( d \) is layer depth (m), and \( \rho \) is bulk density (g m⁻³). Zirconium is commonly used as the immobile element due to the inert nature of the mineral zircon (ZrSiO₄), although Ti is sometimes used due to the resistance of the Ti-containing minerals anatase and rutile (TiO₂) to weathering (Olsson and Melkerud, 1989). The unweathered reference layer is defined by a reference layer that is located in the soil 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 the reference layer. Zr is enriched compared with the mobile element (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 the Zr concentration of Zr and Zr/zr base cation ratios are constant below the reference layer.
Table 2.3 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 defining 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. Assumption testing Application

Prior to calculating base cation weathering rates with the depletion method, fractional volume change ($V_p$) 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 Asa and Flakaliden (both sites (Table S5). The homogeneity of the parent material was also evaluated (Fig. 1) using the criterion that, since zircon and anastase are weathering resistant minerals, it was assumed that the ratio of Ti to Zr should be more or less stable with soil depth in an originally homogeneous material and, as such, any uniformity of the parent material could be assumed ensured. Use of the ratio of two immobile elements resistant minerals to establish uniformity of parent material has been suggested previously (Sudom and St.Arnaud, 1971; Starr et al., 2014). This was the case for plots F3, K1 and F4 at Asa, but not in plot K1 where there was somewhat more variability in plot K1 (i.e. the Zr concentrations decreased towards the soil surface, Fig. 2). Consequently, Ti was used as the immobile element instead of Zr for this profile. At Flakaliden, variability in both the Zr and Ti gradients was observed, but the parent material was considered sufficiently uniform for all plots except 15A, eliminated consideration. 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 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.

2.3.3. Input data

Bulk density was estimated for each soil layer except in some plots where density measurements could not be made below a certain soil depth or where a large and sudden decrease in bulk density with increasing soil depth was observed. 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: soil layer 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:

\[ \rho_{BD} = 1.3 \ e^{-0.1x_{BD}} = 1.3 + 0.1x \]

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

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

\[ \rho_{BD} = 1.8 \ e^{-0.2x_{BD}} = 1.8 + 0.2x \]

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 2X) can be used to estimate the steady state weathering of soil profiles, whereas weathering of the 4th base cation (\( W_{cat, 4} \)) is described by long-term mineral dissolution kinetics at is known to be primarily determined by soil physical properties 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 42.

Exposed mineral surface areas were estimated from soil bulk density and texture data using the algorithm specified in Warfvinge and Sverdrup (1995). Volumetric field 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).

Aluminum (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 Gammmratten (for Flakaliden) (Löfgren et al., 2011). Na was used as a tracer in order to distinguish canopy exchange from dry deposition for Ca, Mg and K. Na was used as a tracer ion.

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. Finally, total deposition for all elements was estimated by summing up dry deposition and wet deposition. The canopy budget method of Staelens et al. (2008) was applied as in Zetterberg et al. (2016). The canopy budget model is commonly used for elements that are prone to canopy leaching (Ca²⁺, Mg²⁺, K⁺, Na⁺, SO₄²⁻) for canopy uptake (NH₄⁺, NO₃⁻) and it calculates total deposition as the sum of dry deposition and wet deposition. 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). Finally, total deposition for all elements was calculated as the difference between 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 weathering rate changes in soil physical and mineralogical input were affected primarily by soil physical and mineralogical 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 (‘homogeneous mineralogy’), or (2) soil mineral percentages (‘homogeneous soil physics’), or (3) both (‘homogeneous soil physics and mineralogy’) for each of the following three test scenarios: (1) homogeneous soil physical properties (soil bulk density and specific exposed mineral surface area), (2) homogeneous mineralogy, and (3) homogeneous soil (i.e., soil physics and mineralogy). For homogeneous soil, all soil layers (0-100 cm) were given the same value of the test variable, which was e.g., the average value for the actual soil profile (0-100 cm). 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 ‘homogeneous’ input data. The ratios of sum of
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, \( W_{\text{BC}}(i) \), 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 \( (TD_{\text{BC}}) \) and weathering are the major sources of mobile and plant-available base cations in the soil, and that leaching \( (L_{\text{BC}}) \) and accumulation of base cations in biomass \( (\Delta B_{\text{BC}}) \) are the major sinks. A change in the extractable soil stocks of base cations over time \( (\Delta S_{\text{BC}}) \) can be 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,

\[
W_{\text{BC}}(i) = L_{i} + \Delta B_{i} + \Delta S_{i} - TD_{i} \tag{4}
\]

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 mass balance budget, Eq. (4). 

2.5.3. Changes in exchangeable soil pools, \( \Delta S_{\text{BC}} \)

Changes in extractable base cation stocks in the soil were calculated from the difference between two soil sampling linear regressions of stocks measured at repeated 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. The organic layer and the mineral soil were sampled to 40 cm or deeper in 1986 and 1998 at Flakaliden, and in 1988 and 2004 at Asa.

At Flakaliden, soil sampling for chemical analyses was carried out in September 1986 in the border zone of the four control plots, using a 5.6 cm diameter corer for the organic layer and a 2.5 cm diameter corer for the mineral soil. In each plot, 25 samples were taken and lumped together to make one sample for each soil layer, i.e., the humus layer, and 10 cm layers down to at most 40 cm in the mineral soil. The plots were re-sampled in 1998 for chemical analyses, in the same way as in 1986. Soil sampling at Asa was conducted in 1988, prior to the start of the experimental treatments, using the same method as at Flakaliden. The transition from the humus layer to the mineral soil was less clear at Asa than at Flakaliden.
Accumulation of base cations in tree biomass, \textit{A. P. L. B. C. (1987-2003)}

The calculations were based on increments in aboveground biomass at Asa and Flakaliden for this period (Albaugh et al., 2009, 2012) 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 Asa and Flakaliden (the sites (Albaugh et al., 2009, 2012). The allometric functions were based on destructive sampling (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 HNO₃ and HClO₃, 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, \( L_i \), Le

Base cation leaching was quantified in 6-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 on 2-3 occasions per year 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 were 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 current 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 late 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.

An additional illustration of the variation in water chemistry with time of the year could be given as Fig. S4 to show base cation fluxes for this period and to compare with the drainage flux (Fig. S5). Base cation leaching was quantified in 6-month intervals from modelled runoff multiplied by average element concentrations in soil water collected with tension lysimeters at 50 cm soil depth. Runoff was calculated using CoupModel (Jansson, 2012). 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 biomass. 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.

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).
CoupModel was parameterised based on measured hydraulic soil properties. The model was run with hourly mean values of local measured climate variables (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 the best agreement between measured and calculated soil water content. Annual evapotranspiration increased by about 50 mm at both sites during the period 1987–2003 at Flakaliden and 1990–2007 at Asa due to the increment in tree biomass. Soil water was collected from five automatic tension lysimeters (TD5) installed at 50 cm depth in each experimental plot. Soil water was collected on 2–3 occasions per year during frost-free seasons, applying an initial tension of 70 kPa in 250 mL sampling bottles, and left overnight. Three soil water samples were pooled per plot. The base cation concentration in the soil solution was determined with ICP AES.

2.5.6. Assessment Judgement of data quality in base cation budget

The precision and accuracy of a base cation budget estimate of BCmass 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 BCmass. 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 54). 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 1998/2003 and base in methods in repeated samplings, 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 of W\text{BCmass} obtained by the PROFILE (W\text{PROFILE}, W\text{PROFILE}) and depletion method (W\text{depletion}, W\text{depletion}) 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 Åkesson et al. (2007), were also used to place the PROFILE and depletion method estimates of W\text{BCmass} in the context of other base cation fluxes at the ecosystem scale.

2.6 Statistical analyses

Site mean values and standard error (SE) of W\text{depletion}, W\text{PROFILE} were calculated based on the four (or two) soil profiles studied at each site. For W\text{depletion}, an average based on the four control plots at each site was calculated as well as a combined standard uncertainty. The latter was partly based on standard errors derived from plot-wise replicated data of the present experiments (for leaching and changes in exchangeable soil pools, SE(L) and SE(AS), respectively), partly on standard uncertainties (u) derived from Simonsson et al. 2015, where replicated data were missing in the present study (for accumulation in biomass and total deposition, u(AR) and u(TD), respectively). Because total deposition and bioaccumulation differed substantially from those in the study of Simonsson et al.
2015, relative standard uncertainties were derived from that study, and multiplied with the average deposition and bioaccumulation rates at Asa and Flakaliden, respectively, to yield realistic standard uncertainties for the present sites. For the weathering rate of the ith base cation according to Eq. (4), a combined standard uncertainty (\(u_i\)) was calculated as:

\[
u_i(W_{\text{budget},i}) = \sqrt{(SE(L_i))^2 + (u(\Delta B_i))^2 + (SE(\Delta S_i))^2 + (u(TD_i))^2}
\]  

(5)

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

Site mean values and standard error (SE) of weathering rates were calculated based on the four (or two) soil profiles studied at each site (\(W_{\text{control},i}\)) and on the \(W_{\text{budget},i}\) estimates for the four control plots at each site. The combined standard uncertainty of \(W_{\text{budget},i}\) was estimated as the square root of the sum of squared standard errors of the four replicate samples. Standard errors were calculated as the standard deviation of the four replicate samples divided by the square root of their number. Standard errors were derived from that study, and multiplied with the average deposition and base cation biomass accumulation in biomass and deposition rate experiments based on calculations from Simonsson et al. (2015). Table 1-8 in that paper of an experimental study site in southern Sweden (Skogaby), since \(W_{\text{control},i}\) and \(W_{\text{budget},i}\) data were not available for individual plots. A coverage factor of 3 was then used.

3. Results

3.1 Depletion method estimates of historical weathering rates

At both Asa and Flakaliden, historical weathering rates estimated with the depletion method (\(W_{\text{depletion}}\)) were highest in the upper soil layers and showed a gradual decrease down to the reference depth, which was defined as the 20 cm soil at Flakaliden and for most plots at 80-90 cm at Asa (Fig. 3). Weathering had also taken place below the reference depth. In line with the younger age of the soils at Flakaliden (indicated also by higher abundance of the rock, a higher content of more easily weatherable minerals, more easily weatherable minerals, amphibole, and calcite plagioclase), and also rock, higher historical annual weathering rate to 90 cm soil depth was higher at Flakaliden, 37.8 mmol m⁻²yr⁻¹, compared to Asa, 17.8 mmol m⁻²yr⁻¹. The base cation weathering down to 90 cm soil depth amounted to 12.3 mmol m⁻²yr⁻¹ at Asa and 32.825.1 mmol m⁻²yr⁻¹ at Flakaliden. The corresponding value for the 0-50 cm horizon depth was 14.1 mmol m⁻²yr⁻¹ at Flakaliden and 10.5 mmol m⁻²yr⁻¹ at Asa and 11.122.4 mmol m⁻²yr⁻¹ at Flakaliden. The gradients with depth showed that \(W_{\text{depletion}}\) increased towards the surface, although this trend was more pronounced at Flakaliden than at Asa. Furthermore, at Flakaliden, \(W_{\text{depletion}}\) was highest for Mg, followed by Ca, Na and K (Figs. 2 and 3). At Asa, the largest average mass loss was observed was highest for Ca, closely followed by Mg, Na and K (Figs. 2 and 4).
The steady state weathering rate estimated by the PROFILE model (W_{profile}) differed from the historical rate with respect to all aspects covered by the three starting hypothesis test criteria, i.e. (1) total weathering rate in the 0-50 cm soil layer, (2) variation in weathering with depth and (3) ranking order of base cations (Figs. 3 and 4). Firstly, regarding base cation weathering rate in the upper 50 cm of the mineral soil, W_{profile} estimates for Asa and Flakaliden (Asa: 37.1 mmol m^{-2} yr^{-1}, Flakaliden: 42.7 mmol 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 m^{-2} yr^{-1}) and almost 3.45-fold higher at Flakaliden (127.6 mmol 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 (Asa (down to 90 cm) and Flakaliden (down to 60 cm). At Flakaliden, anomalously high contents of K and Mg-bearing tri-octahedral mica (Casentou-Gustafson et al., 2018) gave rise to increased particularly high weathering rates at 70-80 cm. Thirdly, as opposed to W_{depletion}, Asa had more high specific soil layer at both sites 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.

In general, PROFILE also predicted much higher weathering rates than the depletion method (Fig. 2). However, both methods estimated consistently higher weathering rates at Flakaliden than Asa. 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 (83.4 mmol m^{-2} yr^{-1}) and almost 5-fold higher at Flakaliden (127.6 mmol m^{-2} yr^{-1}). Weathering rates are often reported for the upper 50 cm soil layer, as an approximation of the root zone. On.According to the base cation weathering rate in the upper 50 cm of the mineral soil, W_{profile} estimates for Asa and Flakaliden were more similar (Asa: 37.1 mmol m^{-2} yr^{-1}, Flakaliden: 42.7 mmol m^{-2} yr^{-1}). This was not the case for W_{depletion} or shown above, as the estimate for Flakaliden was more than twice that obtained for Asa. However, W_{depletion} was higher than W_{profile} for Mg. In relative terms, the difference between sites in W_{profile} in the 0-50 cm layer was similar to the difference observed for the whole soil profile.

The sensitivity analysis of the PROFILE model using homogeneous soil physical and/or mineralogical properties demonstrated that the variation in soil physical parameters (i.e., soil bulk density and specific exposed mineral surface area, soil texture and density) with depth had a greater influence rather than mineralogy was the most important input data explaining the observed change in W_{profile} with soil depth. Applying homogeneous mineralogy had little effect, with the original gradient of W_{profile} (Fig. 2) being similarly reproduced with depth. However, when homogeneous soil physical conditions were applied (i.e., a combination of homogeneity in soil physics and soil mineralogy), there were some small variations in W_{profile} between soil layers (Tables S1 and S2). In terms of the ratio of sums of squared errors, the "homogenised" calculated from the difference in W_{profile} between actual and homogenous soil, 75-85% of the total error at Flakaliden was due to homogeneity in soil physics only, while the error due to homogeneous mineralogy was 2-12%. Soil physics of scenario (1) produced 75% or more of the error obtained with "homogenised" soil physics and mineralogy (scenario (3)), leaving a mere 25% or less to the "homogenised" mineralogy of scenario (2). The corresponding error values for Asa...
were 76.94% and 1.4%, respectively. Also see Tables S1 and S2. One exception to these findings was plot 10B at Flakaliden, which showed somewhat higher error (17%) resulting from homogenous mineralogy. This was due to the anomalously high content of triocahedral mica at 70-80 cm depth, as previously reported by Caseton-Gustafson et al. (2018). At Asa, an outlier to the results was plot F1, whose homogenous soil physical properties produced 100% of the error resulting from homogenous soil. This was because, by coincidence, soil profile F1 had relatively high bulk density and exposed mineral surface area in the uppermost soil layer, compared with the average soil physical input data, and therefore the homogenous soil test produced lower weathering rates. The soil physical input parameters 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\text{profile} for all elements at both sites, with R² values ranging from 0.65 to 0.89 (Fig. S1). The relationship between bulk density and W\text{profile} was also strong and showed the same linear response, although R² 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 the \textit{base cation budget mass balance} (W\text{mb}), W\text{profile}, and W\text{depletion} made for the 0-50 cm soil layer. The physical boundary for the \textit{base cation budget mass balance} was defined by the depth of soil solution sampling (50 cm). It was found that, for most elements, W\text{mb} > W\text{profile} in the 0-50 cm layer was higher, or much higher, than W\text{depletion} (Fig. S4). Compared with the PROFILE model, estimates, the base cation budget mass balance 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\text{depletion} average annual long-term weathering rates based on the depletion method and W\text{profile} PROFILE method, respectively. The closest resemblance between methods was found between W\text{depletion} and W\text{profile} 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).

### 3.4 Base cation fluxes in measured base cation budgets mass balances

As to the general pattern in base cation fluxes (terms) of in the \textit{base cation budget mass balance} was the difference between Na showed patterns different from those of Ca on the one hand, and K, Mg and Ca on the other (Fig. S4). For Na, uptake in biomass was negligible and leaching was the dominant sink. For the latter three elements, this difference was largely due to accumulation in biomass being the dominant sink for the latter elements, whereas Na uptake in biomass was negligible and leaching was the dominant sink. Compared with biomass uptake, loss by leaching was a negligible sink for K, but significant for Mg and Na. Deposition generally represents only as a minor small source of base cation inputs, 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.
In summary, the base cation budget mass balance calculations indicated that weathering was a particularly dominant source of K and Mg, but weathering contributed a relatively smaller proportion of the total Ca sources than for K and Mg (61% at Asa and 43% at Flakaliden).

The combined uncertainty of $W_{\text{combined}}$ 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 $W_{\text{combined}}$, the combined uncertainty was the same order of magnitude for Na, about the half for Ca, one-third for K, and lower for Mg. In relation to the mean $W_{\text{combined}}$, the combined uncertainty was about 3 times higher for Na, 2 times higher for Ca and of the same order of lower for K and Mg. The contribution of the combined uncertainty from the different terms in equation (4) reflected their quantitative importance in the budget for each element. For example, uncertainty in biomass accumulation dominated in the combined uncertainty for Ca and K, but was negligible for Na.

By using the weathering estimates obtained using with PROFILE and the depletion method in the base cation mass balance equation (Eq. (4)), in combination with measured estimates of deposition, leaching and uptake in biomass, alternative soil balances were estimated (Fig. 54). Since the base cation mass balance 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 was used. Furthermore, as a consequence of the substantially higher $W_{\text{profile}}$ for Na, the PROFILE based base cation mass balance 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, the approaches are not only complicated to interpret due to the fact that the comparisons are not carried out in a harmonized way, i.e. at the same scale (pedon/catchment), using exactly identical the same sampling locations and methods for common input data, and whenever methods are compared, the consistent assumptions about the same weathering zone (i.e. 0-50 cm or 0-100 cm), or that the comparisons do not deal with similar quantities at spatial or temporal scales. Concerning the spatial scale, to our knowledge, the base cation mass balance approach has most often been applied at the catchment and forest stand scale, whereas the depletion method and the PROFILE model are normally applied at the smaller pedon scale. In the present study, the base cation mass balance approach included data at stand level over a period when the stand showed 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 a safe reference value of the "true" weathering rate at the study sites. However, for the purposes of the following discussion, we are of the view that the conceptual differences between these 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 a particular element.

4.2 Depletion method estimates versus PROFILE model estimates

Pedon scale weathering rates—a comparison with other studies

Modelled (\(W_{\text{profile}}\)) and historical (\(W_{\text{depletion}}\)) 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 to see if there are similarities in weathering estimates for the 0-50 cm depth in the soil profile. A major finding of this study was that, in the 0-50 cm soil profile, \(W_{\text{profile}}\) was higher than \(W_{\text{depletion}}\) for Na and K, and the methods generally failed to fulfill our first test criterion concerning weathering at the soil profile as a whole. Similarly, high ratios of \(W_{\text{profile}}/W_{\text{depletion}}\) of 4 were found at catchment scale by Augustin et al. (2016). At the pedon scale, Stendahl et al. (2013) found \(W_{\text{profile}}/W_{\text{depletion}}\) ratios of on average 2.7 for 16 Swedish study sites (with average max. and min. ratios of 7.9 and 0.3, respectively)2.3 and 2.2 at Vindeln and Sverdaberg close to Flakaliden; this ratio was larger than the one found for Asa even larger than obtained for Flakaliden in our study (1.5) and lower than the one found for Asa (5.1). By contrast, the geographically closest site to Asa (Lammhult, approx. 10 km) had a much lower ratio (1.1, compared with 3.5 in our study). 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), while the high ratio we obtained for Asa was close to that (4.6) reported by Stendahl et al. (2013) for Skånes Värsjö, another site located in south-western Sweden (in the county of Skåne). 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 \(W_{\text{depletion}}\) was 1.9-fold greater than \(W_{\text{profile}}\) 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 estimated by the depletion method and the PROFILE model can be expected to differ due to differences in 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 the end of the 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

Further, the comparison of results from testing our first criterion with results from other studies can be done by estimates from the magnitude of weathering for soils of similar pedogenesis, but also from the proportions of the estimates of depletion versus PROFILE. In terms of the magnitude of the estimates, a general finding of this study concerning weathering at the pedon scale was that total modelled (W_{model}) and historical (W_{historical}) base cation weathering rates were low within the range of in good agreement with recent published data for similar forest sites on pedolic till soils (Stendahl et al., 2013). However, the historical weathering rates at Asa were of similar magnitude to the lowest historical weathering rate observed by Stendahl et al. (2013) and the historical weathering rates for Flakaliden were of similar magnitude to their lowest, at least with regard to Ca and Mg.

Most Nordic studies on historical weathering rates have been conducted in the boreal region (Tamm, 1920, 1931; Land et al., 1999; Olsson and Melkerud, 2000; Stendahl et al., 2013; Starr et al., 2014). Even though soil profile depth and soil age in these weathering studies differ from those in ours, they obtained higher rates (Land et al., 1999; Olsson and Melkerud, 2000; Stendahl et al., 2013), similar rates (Stendahl et al., 2012) or lower rates (Starr et al., 2014) for soils developed on glacial tills.

4.2.1 Depletion method estimates versus PROFILE model estimates

A major finding of this study was that, in the 0-50 cm soil profile, W_{historical} were higher than W_{model} for all elements except Na, and the methods generally failed to fulfill our first test criterion concerning weathering in the soil profile as a whole. However, weathering rates estimated by the depletion method and the PROFILE model can be expected to differ due to differences in temporal scale. 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 the end of the glaciation 12,000 years B.P., towards a peak at 9000 years B.P., followed by a gradual decrease below initial levels.

In terms of the proportion of the estimates of depletion versus PROFILE. However, in the present study, PROFILE generally yielded higher weathering rates than the depletion method at both study sites. Similar results have been found in other studies, as indicated by high modelled to historic weathering rate ratio (W_{model}/W_{historical}). At catchment scale, Augustin et al. (2016) found that weathering estimated by PROFILE was on average 4-fold greater than weathering based on the depletion method. At the pedon scale, Stendahl et al. (2013) found W_{model}/W_{historical} ratios of 2.8 and 2.2 for two sites near Flakaliden, namely Vindeln and Svartberget, which are similar larger than values compared to that found for Flakaliden in our study (12.30). However, the geographically
The intense weathering at depth simulated by PROFILE is obviously in contrast with the
historical 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
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 \( W_{\text{profile}} \) and
exposed mineral surface area and bulk density (Figs. S1-S2) and by the findings of Jönsson et al. (1995).

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
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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
\( W_{\text{profile}} \) values were possible to reconcile with the observed historical weathering, because the PROFILE model
predicted increasing weathering rates with increasing soil depth, which was contrary to the depletion method.
Since soil forming processes and ageing of minerals suggest that the present weathering rate might differ from
the average historical value, we calculated the hypothetical time needed for the simulated current PROFILE
weathering rates to accomplish the element losses determined with the depletion method was calculated.
Specifically, one can imagine this approach corresponds to a situation where there is a front of intense weathering
moving down through the soil profile, during which a pristine horizon would undergo an episode, limited in time,
of intense weathering followed by slower weathering in the ageing material. In concert with this notion, 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 with PROFILE than observed by the depletion method ("min rates" in Fig. 6), particularly at Flakaliden, and for K and Na also at Asa. Hence, the current minimum weathering rates according to PROFILE are not generally sustainable within the limits set
by the depletion method. Provided that the current weathering rate did not substantially exceed the historical
average, this suggests a positive bias in \( W_{\text{profile}} \) at the investigated sites, indicating either bias in either of the
methods, or a current weathering pressure that is correctly modelled but exceeds the historical average.

closest site to Asa (Lammhult, approx. 10 km) had a much lower ratio (1.1 compared with 3.5 in our study).
Similarly low ratios have been reported for the Gårdsjön site situated in south-western Sweden (i.e. county of
Västra Götaland) (Sverdrup et al., 1998; Stendahl et al., 2013), while the high ratio we obtained for Asa was close
to that (4.6) reported by Stendahl et al. (2013) for Skånes Värsjö, another site located in south-western Sweden
(i.e. the county of Skåne). 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
\( W_{\text{profile}} \) was 1.9-fold greater than \( W_{\text{hist}} \) 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.

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
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the present minimum weathering rate, presently simulated for the topmost 1-3 layers (Fig. 2), would often result
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by the depletion method ("min rates" in Fig. 6), particularly at Flakaliden, and for K and Na also at Asa. Hence, the current minimum weathering rates according to PROFILE are not generally sustainable within the limits set
by the depletion method. Provided that the current weathering rate did not substantially exceed the historical
average, this suggests a positive bias in \( W_{\text{profile}} \) at the investigated sites, indicating either bias in either of the
methods, or a current weathering pressure that is correctly modelled but exceeds the historical average.
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) could demonstrate 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, was the dominant K in the soil, 25-50% of the weathering of K had occurred in bearing mineral in a till soil in south western Sweden, a large proportion of the K loss was explained by 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 generate overestimates rather than underestimates for base cation weathering rates. 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. As to possible errors in weathering rates according to PROFILE, the sensitivity test indicated that the within-profile variability of soil physical properties had a much greater effect on simulated weathering rates than the differences in mineralogy between different horizons. Therefore, the notion of a weathering front, significantly changing the mineralogical composition of the soil, does not appear to be able to result in any episodic modelled weathering for the studied soils; the decline in weathering rate with time is more likely to be attributable to disappearance of fine particles, or also indicated by the positive correlation between W$_{\text{profile}}$ and exposed mineral surface area and bulk density (Figs. S1-S2). Moreover, given the variability of physical and mineralogical properties in the investigated soils, fine tuning parameters related to the exposed mineral surface area is most likely to affect the model output, similarly to the findings of Jönsson et al. (1995). Furthermore, the discrepancy between W$_{\text{profile}}$ and W$_{\text{depletion}}$ with respect to soil depth gradient implies that the PROFILE model produces weathering rate patterns that are not in line with the classic notion of weathering rates being highest in the A or E horizon (Tamm, 1931). However, it is consistent with the more recent notion that mineral dissolution decreases with increasing time/exposure to weathering (White et al., 1996; Parry et al., 2015). In line with this, the results support the view that historical weathering rates do not show identical depth gradients to steady-state weathering.
rates, and that $W_{\text{Na}}$ and $W_{\text{K}}$ could both be accurate estimates of steady-state and historical weathering rates, respectively.

As to possible bias in the historical weathering rates, underestimates are possible at Asa, where the low values of $W_{\text{Na}}$ 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 complicated and erratic disturbance Zr gradient (Fig. 5 and Table S3) 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 indeed dominated at Asa until only 1000-2000 years BP, with species such as *Scots pine* (*Pinus sylvestris*), *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 complicated and heterogeneous Zr gradients (Fig. S3) and Zr/base cation ratios (Fig. S5) 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 argumentation 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 the B/C-horizon at Flakaliden, such as local heterogeneities of the deposited till, which was suggested by the unstable Ti/Zr ratio in soil profile 15A and 11B. However, the observed peaks in the Ti/Zr gradients were only explained by irregularities in Ti gradients (i.e. increases in the Ti/Zr ratio indicate that Ti concentrations are increasing) the latter has to be treated carefully since in cases where both Zr and Ti show inconsistent patterns with soil depth, the Ti/Zr ratio will still be stable and hereby overshadows heterogeneous trends observed with soil depth for both elements (Fig. S3 and Fig. S5). Thus, heterogeneous heterogeneities in Zr gradients observed in the B/C-horizon could be attributed to local heterogeneities of the parent material irrespective of whether the Ti/Zr gradients are stable at these depths. At Flakaliden, the small-scale variation in Zr mobility might be one of the driving forces behind the large within-site variation in Zr gradient (Fig. S5). The latter is exemplified in different patterns of Zr enrichment for different soil profiles (Fig. S5). An increase with depth could indicate Zr transport from shallower to deeper soil layers, most significantly reflected in the Zr/base cation ratio for K (Fig. S3). In relation to this, in a column experiment Hodson et al. (2002) found that K was the most sensitive element to Zr mobility and that redistribution of Zr led to insignificant underestimations of base cation weathering. An alternative explanation for the increased subsoil Zr content could be related to the distinct peaks of rare earth metals in the B-horizons of Swedish podzolic soils reported by Tyler.
et al. (2004), who related them to increased solubility. Increasing Zr concentration in the B-horizon of forest soils in northern Sweden has also been reported by Melkerud et al. (2000) and, in particular, in a study by Olsson and Melkerud (2000).

Regardless of errors in the Zr gradients, both $W_{\text{yaksol}}$ and $W_{\text{profile}}$ showed more marked gradients with soil depth at Flakaliden compared to Asa. This could be expected based on the more well-developed podzol profile at Flakaliden. It has been postulated that the formation of podzols is enhanced by long duration and great depth of snow cover (Jauhiainen, 1973; Schaezel and Isard, 1996), which would imply that podzol formation had progressed further at Flakaliden than at Asa (Lundström et al., 2000). At Flakaliden, the average mass loss of Ca and Mg was 4.0-fold larger in the E-horizon than in the B-horizon, which is similar to findings by Olsson and Melkerud (2000) of a 5-fold higher ratio between losses of base cations in the E- compared with the B-horizon.

The weathering rates of PROFILE may 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.

### 4.3 Weathering in a base cation budget/mass balance perspective

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

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

Despite the considerable uncertainties in $W_{\text{yaksol}}$, $W_{\text{profile}}$ estimates, the mass balance approach illustrated that accumulation in biomass was a dominant sink for all base cation elements except Na. This is in line with findings by Nykvist (2000) for two Norway spruce sites in Sweden and by Simonsson et al. (2015) for an aggrading...
The Na fluxes differed from those of the other base cations, probably because Ca, Mg and K are important plant nutrients whereas Na is not. Calcium and Mg uptake in forest trees is considered to be more or less passive flow driven by transpiration fluxes, whereas K uptake is an energy-demanding active process (Nieves-Cordones et al., 2014). Considering that Na was the dominant base cation in the soil solution at 50 cm soil depth (Fig. 3), the negligible accumulation of Na in tree biomass suggests that Na uptake in trees is physiologically blocked. Low concentrations of Na seem to be a general feature of terrestrial plants in boreal forests (e.g. Sverdrup et al., 1998). Thus, the negligible Na accumulation in tree biomass and the particularly low deposition at Flakaliden simplify the Na budget mass balance to only three major counterbalancing fluxes: weathering, deposition and leaching. Since $W_{\text{dep,Na}}$ and $W_{\text{leach,Na}}$ of Na were fairly similar, and were much lower than $W_{\text{depl,Na}}$, our results provide additional support for the claim that the PROFILE model produced consistently too high Na weathering.

Accumulation of Ca, Mg and K in biomass made up the dominant sink. Since deposition and measured depletion of extractable Ca, K and Mg in the soil did not balance this sink, substantial missing sources, where estimated as an apparent weathering rate, were needed to reach a balance. Using the alternative weathering estimates by PROFILE and the depletion method in the base cation budget mass balance resulted in even larger estimated depletion in the soil to balance the sinks than was actually measured. Assuming that the measurements of accumulation in biomass, deposition and leaching were reasonably accurate, the results either indicate large uncertainties in measurement of soil changes and/or that additional sources of base cations in the soil balanced the sinks. Uncertainties in estimating soil changes were probably significant, since the estimates of soil depletion were based on two single measurements over 12 years and the extraction procedures were not identical over time. Nevertheless, the changes observed in extractable Ca stocks in the soil are in line with observations over 22 years of aggrading Norway spruce forests by Zetterberg et al. (2016), who reported exchangeable Ca depletion rates of 5-11 and 23-39 mmol m$^{-2}$ yr$^{-1}$ for sites in south-western and northern Sweden, respectively. The higher value for the northern site reflected higher Ca saturation in the soil. The corresponding values for Asa and Flakaliden were larger, but of similar magnitude (34.5 and 40.5 mmol m$^{-2}$ yr$^{-1}$, respectively). Brandberg and Olsson (2012) studied the same sites as Zetterberg et al. (2016) over a 10-year period and found a general minor increase in extractable K soil stocks and a substantial decrease in the Ca stocks, a result much similar to the findings of the present study. Moreover, exchangeable K stocks in the soil normally show little variation over time (B.A. Olsson, unpublished data). Great depletion in exchangeable K stocks in the soil is therefore unlikely. The results therefore suggest that other sources of nutrient base cations exist in the soil, apart from weathering ($W_{\text{depl,K}}$, $W_{\text{depl,Mg}}$, $W_{\text{depl,Ca}}$) and depletion of ammonium-chloride-extractable base cation stocks. It is well-known that the exchangeable...
extractable nutrient stock in the soil is defined by the extraction medium and procedure. A test of different extractants used on the soils in the present study revealed that using \( \text{NH}_4\text{OAc} \) posed a risk of underestimating the amount of base cations in the soil and that the yield of exchangeable extractable base cations decreased in the order \( \text{aq} \text{H}_2\text{O} > \text{HCl} > \text{EDTA} > \text{BaCl}_2 > \text{NH}_4\text{OAc} \) (Olofsson, 2016). Using a more potent extractant than \( 1\text{M NH}_4\text{Cl} \) would probably have resulted in different findings on the change in extractable and plant-available base cations in the soil. Regarding K, fixed or structural K in clay minerals provides a dynamic pool of K that is not included in modelled weathering or in NH-Cl-extractable K (Simonsson et al., 2016). Regarding Ca and Mg, dissolution from non-crystalline/amorphous compounds can be an important source in soils depleted of these elements (Van der Heijden et al., 2017).

There are another possible explanations for the higher weathering rates with the base cation budgetmass balance approach compared to the PROFILE for K, Mg and Ca. First, it is possible that the assumption made that no base cationBC uptake takes place below 50 cm in the soil was wrong. If trees can take up base cationsBC from deeper soil horizons (e.g. Brantley et al., 2017), the discrepancy in weathering rates between the two methods would be reduced since PROFILE predicted higher weathering rates with increasing depth. Second, PROFILE may produce conservative estimates of present-day weathering because the model only captures steady-state chemical processes. It has been postulated that e.g. mycorrhizae play an important role in nutrient uptake in forest trees through active foraging by mycelia at mineral surfaces, but the nature and potential quantitative importance of biotic control or stimulation of weathering has been much debated in recent decades (Finlay et al., 2002; Sverdrup, 2009; Smits and Wallander, 2017; Finlay et al., this issue). Based on the results of the present study, the hypothesis of significant biological control of weathering was not rejected. Thus, the results from the present study do not contradict the view that such 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. We compared in a first step weathering rate estimates by the PROFILE model and the depletion method in the 0-100 cm horizon, since a detailed assessment of the latter method can only be made by consideration of the whole soil profile where a reference depth is defined. In a second step, weathering rate estimates of the three methods where compared for the upper 0-50 cm soil horizon.

In the first comparison, 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 BC losses suggested a rapid depletion of Na and K even at the lowest PROFILE weathering rates. A possible reason for that also K weathering rates were also overestimated by the PROFILE method was that 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, Ca in particular 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 of particularly Ca and K by trees in the soil besides weathering and the measured depletion in extractable base cations.

5. Conclusion

The depletion method, PROFILE model and mass balance approach was used to estimate weathering rates at two coniferous forest sites in Sweden. The methods estimated weathering rates at different spatial and temporal scale, and no estimate was taken as a reference value of the true (current) weathering rate. There was no similarity in weathering estimates between the depletion method and the PROFILE model with respect to BC weathering in the 0–50 cm soil layer and the soil depth gradient in weathering rates except that both methods indicated higher weathering rates and more marked depth gradients at Flakaliden compared to Asa. The PROFILE model produced consistently higher weathering rates than the depletion method except for Mg, and while the depletion method estimated decreasing weathering rates with increasing soil depth, the PROFILE model predicted the opposite. The mass balance method produced significantly higher weathering rates for all elements except Na. A cross-examination of the estimates stressed the importance of that all criteria for application of the depletion method must be satisfied. Erratic or weakly developed Zr gradients in the soil, possibly caused by natural and...
anthropogenic disturbances can be a cause to why the depletion method underestimates weathering rates. The higher weathering rates of K by PROFILE compared to the depletion method could be an indication of that inaccurate dissolution rates of K-bearing minerals was used in the model. On the other hand, high mass balance estimates for K, Ca and Mg weathering suggests that there were additional sources of base cations for tree uptake in the soil besides weathering and measured depletion in exchangeable base cations, and that PROFILE produced conservative estimates of base cation supply to forest trees.

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. Hårald 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., Hultberg, H., Karlsson, P. E., Karlsson, G. P., and Hellsten, S.: Acidification trends in south Swedish forest soils 1986–2008—Slow recovery and high sensitivity to seafood episodes, Sci. Total Environ., 444, 271–287, 2013.

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.

References
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 granite till catchment in Scotland, Water Air Soil Poll., 73, 11-27, 1994.

Bergh, J., Linder, S., Lundmark, T., and Elving, 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.

Bertill, U., Fölster, J., and Lager, H.: Only natural acidification—in depth assessment of the environmental objective, Swedish Environmental Protection Agency Report, 5766, 116, 2007.

Binkley, D., and Högberg, P.: Does atmospheric deposition of nitrogen threaten Swedish forests?, Forest Ecol. Manag., 92, 219-232, 1999.

Binkley, D., and Högberg, P.: Tarum review: revisiting the influence of nitrogen deposition on Swedish forests, Forest Ecol. Manag., 368, 222-230, 2016.

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.

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

Cosby, B., Hornberger, G., Galloway, J., and Wright, R.: Modeling the effects of acid deposition: Assessment of a lumped parameter model of soil water and streamwater chemistry, Water Resour. Res., 21, 51-63, 1985.
Erlandsson Lampa, M., Sverdrup, H.U., Bishop, K.H., Belzazid, S., Ameli, A., and Köhler, S. J.: Catchment export of base cations: Improved mineral dissolution kinetics influence the role of water transit time, In review in Biogeosciences (this issue).

Evans, C., Cullen, J., Atewell, C., Kopicka, J., Marchetto, A., Moldan, P., Prechtel, A., Rogora, M., Veselý, J., and Wright, R.: Recovery from acidification in European surface waters, Hydrol. Earth Syst. Sci., 5, 283-298, 2001.

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

Finlay, R.D., Mahmood, S., Rosenstock, N., Bolouibi, E., Köhler, S.J., Fahad, Y., Rosling, Wallander, H., Belzazid, S., Bishop, K., Lian, B. Biological weathering and its consequence at different spatial levels – from nanoscale to global scale. Biogeosciences. In review in Biogeosciences (this issue).

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

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

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

Futter, M., Ring, E., Högbom, L., Entenmann, S., and Bishop, K.: Consequences of nitrate leaching following stem-only harvesting of Swedish forests are dependent on spatial scale, Environ. Pollut., 158, 3552-3559, 2010.

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

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

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

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

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

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

Hellsten, S., Helmisaaari, H. S., Melin, Y., Skovsgaard, J. P., Kaakinen, S., Kukkola, M., Saarssalmi, 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.

Helmisaaari, H.-S., Derome, N., Nojd, 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 Sedimentologists, 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.

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, 2011b.

Land, M., Ingri, J., and Ohlander, B.: Past and present weathering rates in northern Sweden, Appl. Geochem., 14, 761-774, 1999.
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.

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

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, Umeå, 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 I, Soil Sci. Soc. Am. J., 7, 448-453, 1943.

Melkerud, P.-A., Bain, D., Jungman, A., and Tarvainen, T.: Chemical, mineralogical and morphological characterization of three podzols developed on glacial deposits in Northern Europe, Geoderma, 94, 335-353, 2000.

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.

Olofsson, J.: Base cations in forest soils: A pilot project to evaluate different extraction methods, Swedish University of Agricultural Sciences, Uppsala, 2016.

Olsson, B. A.: Effects of biomass removal in thinnings and compensatory fertilization on exchangeable base cation pools in acid forest soils, Forest Ecol. Manag., 122, 20-39, 1999.

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.

Perry, S. A., Hodson, M. E., Kemp, S. J., and Oelkers, E. H.: The surface area and reactivity of granitic soils: I. Dissolution rates of primary minerals as a function of depth and age deduced from field observations, Geoderma, 237, 21-35, 2015.

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.

Schatzel, 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 (zurkonstatistische 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 [CO₂] 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.

Skjelkvåle, B., Mannio, J., Wilander, A., and Andersen, T.: Recovery from acidification of lakes in Finland, Norway and Sweden 1990? 1999, Hydrol. Earth Syst. Sci., 5, 327-338, 2001.

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.

Staelens, J., Houle, D., De Schrijver, A., Neirynck, J., and Verheyen, K.: Calculating dry deposition and canopy exchange with the canopy budget model: review of assumptions and application to two deciduous forests, Water Air Soil Poll., 191, 149-169, 2008.

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.

Stenberg, 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., and Warfvinge, P.: Calculating Field Weathering Rates Using a Mechanistic Geochemical Model Profile, Appl. Geochem., 8, 271-283, 1993.

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

Swedish Forest Agency: Rekommendationer vid uttag av avverkningsrester och askåterföring [Recommendations for harvesting of logging residues and ash return]. Meddelande 2 – 2008. Swedish Forest Agency, Jönköping, 2008.
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.: Markstudier i det nordsvenska barrskogsområdet. Reports of the Swedish Institute of Experimental Forestry, 17(3), 190-276, 1920.

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.

Tyler, G.: Vertical distribution of major, minor, and rare elements in a Haplic Podzol. Geoderma, 119, 277-290, 2004.

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 Bartille, U.: Naturens återhämtning från försurning – aktuellt kunskap och framtidsscenarier. Swedish Environmental Protection Agency Report, 5028, 98, 2000.

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., Aberne, 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 et al. 2006.
Table X: Shown is a short description of characteristics of three different approaches that are used in this study to estimate base cation release rates at the pedon scale using a harmonized set of input data. The differences between methods reflect differences expected due to different time scales, conceptual differences, assumptions about weathering kinetics, and pedogenesis.

| Description | PROFILE | Depletion | Base-cation budget |
|-------------|---------|-----------|--------------------|
| Time scale  | Present-day | Long-term | Present-day |
| Concept     | Steady-state | Historical | Dynamic/Current |
| Weathering kinetics | Long-term kinetics | No assumption | No assumption |
| Pedogenesi  | No assumption | Zr immobility, unweathered and homogenous parent material | No assumption |
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/cm³) | 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                   |

Table 2. A short description of characteristics of the three different approaches that are used in the study to estimate base cation release rates at the pedon scale using a harmonized set of input data. The difference between methods reflect expected differences due to different time scales, conceptual differences, assumptions about 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 homogenous parent material | No assumption |
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   | 738.10   | 0.00028 |
|        | F3   | 60-70           | 1.41   | 0.55   | 0.87  | 1.04   | 732.64   | 0.00026 |
|        | F4   | 80-90           | 1.26   | 0.49   | 0.85  | 0.98   | 793.74   | 0.00029 |
| Flakaliden | 10B  | 60-70           | 1.09   | 0.57   | 0.88  | 0.87   | 743.94   | 0.00024 |
|        | 14B  | 60-70           | 1.59   | 1.63   | 0.70  | 0.81   | 1.03     | 1.03   |
|        | 15A  | 60-70           | 1.46   | 0.59   | 0.84  | 1.15   | 0.00025  | -      |
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, m\(^2\) yr\(^{-1}\)) | Measured data on open field and throughfall deposition available from nearby Swedish ICP Integrated Monitoring Sites | SO\(_4\)\(^2-\): 27.0 | SO\(_4\)\(^2-\): 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, 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, 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, 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, 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        |
Table 4b. Soil* parameters used in the PROFILE model.

| Parameter                           | Unit       | Source                                                                 |
|-------------------------------------|------------|------------------------------------------------------------------------|
| Exposed mineral surface area        | m² 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                       | m³ 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 CO₂ 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)
Table 3. Description of parameters used in the PROFILE model

| Parameter                        | Description | Unit          | Source                                                                 |
|----------------------------------|-------------|---------------|------------------------------------------------------------------------|
| Temperature                      | Site        | °C            | Measurements at Asa and Flakaliden                                     |
| Precipitation                    | Site        | mm yr⁻¹       | Measurements at Asa and Flakaliden                                     |
| Total deposition                 | Site        | mmol m⁻² yr⁻¹| Measured data on open field and throughfall deposition available from nearby Swedish ICP Integrated Monitoring Sites |
| Base cation net uptake           | Site        | mmol m⁻² yr⁻¹| Previously measured data for Asa and Flakaliden; Concentrations in biomass from Linder (unpublished data); Biomass data from Heureka simulations |
| Net nitrogen uptake              | Site        | mmol m⁻² yr⁻¹| Previously measured data for Asa and Flakaliden; Concentrations in biomass from Linder (unpublished data); Biomass data from Heureka simulations |
| Base cations in litterfall       | Site        | mmol m⁻² yr⁻¹| Literature data from Hellsten et al. (2013)                             |
| Nitrogen in litterfall           | Site        | mmol m⁻² yr⁻¹| Literature data from Hellsten et al. (2013)                             |
| Evaporation fraction             | Site        | Fraction      | Precipitation data and runoff data. Runoff data been calculated based on proportion of runoff to precipitation (R/P) at Gamttratten and Anneboda |
| Exposed mineral surface area     | Soil        | m² m⁻³        | Grain measurements used together with Eq. 5.13 in Warfvinge and Sverdrup (1995) |
| Soil bulk density                | Soil        | kg m⁻³        | Grain measurements                                                     |
| Soil moisture                    | Soil        | m² m⁻³        | Based on paragraph 5.9.5 in Warfvinge and Sverdrup (1995)               |
| Mineral composition              | Soil        | Weight fraction| Grain measurements                                                   |
| Dissolved organic carbon         | Soil        | mg L⁻¹        | Grain measurements for B horizon from Harald Grip and previously measured data from Fröberg et al. (2013) |
| Aluminium solubility coefficient | Soil        | kmol m⁻²      | Grain measurements for total organic carbon and oxide-extractable Al together with function developed from previously published data (Simonsson and Berggren, 1998) |
| Soil solution CO₂ partial pressure| Soil        | atm.          | Based on paragraph 5.10.2 in Warfvinge and Sverdrup (1995)             |
Table S4. Assessment of data quality for terms included in the mass balance 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 (4) | Unpublished data from J. Bergholm and H. Grip. Olofsson (2016) | Moderate/lower; repeated sampling biased by differences in methods of sampling and soil extraction |
| Leaching           | Plot                   | Sampling of soil water at 50 cm-depth repeated 3 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 | Linder unpublished data | High/moderate: high quality in growth estimates and nutrient content at treatment scale, data lacking at plot scale |
### 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 |
Table 6: Standard errors and standard uncertainties (mmol, 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 $W_{\text{budget},i}$ (mmol, m$^{-2}$ yr$^{-1}$). Estimated combined uncertainty (mmol, m$^{-2}$ yr$^{-1}$) of weathering rates calculated by the BC budget approach. The combined uncertainty is the sum of 95% confidence intervals of each term in the BC budget (Eq. 4).

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

| Site   | Element | Deposition | Soil-change | Biomass-accum | Leaching | Combined-uncertainty |
|-------|---------|------------|-------------|---------------|----------|---------------------|
| Asa   | Ca      | 1.1        | 23.4        | 16.3          | 6.2      | 92.8                |
|       | Mg      | 3.9        | 10.4        | 7.5           | 3.0      | 44.8                |
|       | K       | 11.0       | 1.7         | 0.0           | 10.0     | 33.6                |
|       | Na      | 0.5        | 1.3         | 0.0           | 0.5      | 33.3                |
| Flakaliden | Ca  | 2.5        | 20.6        | 40.0          | 1.4      | 64.4                |
|       | Mg      | 0.0        | 2.4         | 4.4           | 0.6      | 8.3                 |
|       | K       | 1.5        | 1.7         | 20.0          | 0.4      | 22.3                |
|       | Na      | 2.3        | 2.1         | 0.0           | 1.6      | 6.1                 |
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 (K1, K4, F3, F4) and Flakaliden (10B, 11B, 14B, 15A).

**Figure 3.** (Left) Historical weathering rate of base cations (mmol, m² 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, m² yr⁻¹) for Ca, Mg, Na and K determined with the depletion method, the PROFILE model and the base cation budget mass balance 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 mass balance' = current base cation weathering rate (W_{BC}) estimated with the base cation budget mass balance method, including measured changes in soil extractable base cation stocks; 'PROFILE' = soil extractable pools estimated from base cation budget mass balance using PROFILE estimates of steady-state weathering rate; 'Historical' = soil extractable pools estimated from base cation budget mass balance using estimates of historical weathering rate by the depletion method. ‘Measured soil change’ and ‘Base cation budget mass balance estimated soil change’ indicates that equation 4 was used to estimate weathering rate or the soil change, respectively.

**Figure 6.** Zirconium (Zr) gradient in the soil at Asa (K1, K4, F3, F4) and Flakaliden (10B, 11B, 14B, 15A).

**Figure 7.** 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.
Figure 1.
Figure 2.
Figure 32.
Figure 4.

Release rates (mmol m$^{-2}$ y$^{-1}$)

- Depletion
- PROFILE
- BC budget

Species:
- Ca
- Mg
- K
- Na
b. Time (years) required to achieve observed element loss with maximum and minimum PROFILE weathering rates at Aria

Soil depth (cm)

- Ca (Max. rate)
- Mg (Max. rate)
- K (Max. rate)
- Na (Max. rate)
- Ca (Min. rate)
- Mg (Min. rate)
- K (Min. rate)
- Na (Min. rate)

Soil age 14,300 years
Figure 6.

a. Time (years) required to achieve observed element loss with maximum and minimum PROFILE weathering rates at Flakuliden

b. Time (years) required to achieve observed element loss with maximum and minimum PROFILE weathering rates at Asa
Resubmission letter

Dear Prof. Andersson,

Thank you for providing the reviews and for your editorial comments on our manuscript and the opportunity to submit a revised version. Your suggestions (marked in grey color) were:

Original comments:

Associate Editor Decision: Publish subject to minor revisions (review by editor) (12 Apr 2019) changed to major revision (review by editor) (15 Apr 2019) by Suzanne Anderson Comments to the Author:

I have received three reviews of the manuscript, of which two were quite positive and one was extremely negative. My own reading lies somewhere between these poles. I think with attention to the comments of the reviewers the authors will be able to produce an acceptable contribution.

The goal of the manuscript is to assess different methods to determine current mineral weathering rates in soils. The question is of more than academic importance, as mineral weathering must in the long run replace cation loss resulting from forest harvesting and consequent soil acidification. The work is conducted in the context of a Swedish environmental goal of managing sustainable forestry. Three established methods of assessing weathering rates are tested in two well-characterized forest soils in Sweden. While the work is clearly important from this perspective, the question and the methods used are not an approach that is likely to bring about a paradigm shift or blinding insight.

Reviewer #1 offered the very negative appraisal, based mostly on two points—first that the methods and models used have been compared in other sites before, and therefore there is nothing new. The second complaint was that little data was used from the two study sites. I sympathize with the authors response that this study is distinguished from others by the quality of the data available for the method comparison (a key being uniformity of collection and analysis methods). Both negative points can be addressed with nearly the same antidote: providing a much clearer description of how the data used is generated. I suggest the authors come up with a way to highlight responses to this reviewer very early and with some panache in the text. The text is rather long overall, and while methodical in its presentation, it is easy to miss the point amidst some of the details.

General points to attend from Reviewers 2 & 3:

1) Terminology: Reviewer #2 found the manuscript very interesting, but also offers some helpful guidance on improving clarity. I concur with this reviewer that the terminology naming the methods was hard to keep straight. In short, these are “depletion method”, the “steady-state method”, and the “mass balance method”. For instance, the depletion method (based on the assumption of Zr immobility) is in essence a mass balance calculation. I wonder if the authors could come up with a small table that would summarize the 3 methods? It would be
helpful to have these briefly outlined and set apart from the text in a way that the reader can
circle back quickly when confusion sets in.

I believe some terminological confusion arises because the goals of this study are narrowly
focused on determining the weathering rate going on in Swedish forests now, to address the
needs of forest management now. Some of the methods employed (depletion method in
particular) are averaged over much longer timescale than the present (more on this below).
Moreover, choices such as focusing only on the top 50 cm are driven by interest in weathering
in the rooting zone. I think the authors might rewrite the introduction and parts of the discussion
to highlight how their motivations might differ from those of a pedologist, interested in the full
history and depth of soil development, or from a geochemist interested in weathering rates
over long time scales.

2) Soil age: I disagree with Reviewer #2 on soil age changing with depth in the soil profile. It
is standard soil science to use soil age in the manner used by the authors. However, the
authors need to correct an error in their reporting of soil ages. Asa is reported to be 143 000
thousand years old (or 1.43 x 10^8 years…. Cretaceous!), while Flakaliden is reported as 10
150 thousand (1.015 x 10^7 years). I'm pretty sure the authors mean 143 ka and 10.15 ka,
respectively. These ages are significantly different. Asa has been exposed and weathering
since the last interglacial, while Flakaliden is only Holocene. The significant difference in
weathering (disintegration of boulders, accumulations of clay and organic matter, etc) in till
from different glaciations is an important tool in determining relative ages. I am surprised that
the influence of the much longer pedogenesis at the Asa site is not addressed in the
manuscript. Since Asa was apparently not glaciated in the last glaciation, I would guess it was
instead subjected to periglacial processes for ~100 ka of its age. I also wonder about any
eolian (e.g. loess) deposition during the last glaciation? In any case, I would like the authors
to address the very different history of weathering at these sites and how this impacts the
weathering rates they assess. (In line 218-219, the soils are described as similar in B horizon
thickness-- quite surprising given the 1000 fold difference in age of these soils that the B
horizons are similar in thickness. You will need to explain why-- it's striking that the very old
soil in the warmer climate seems to be quite similar to the very young soil in the colder climate.)

3) Table 4 “quality of term quantification”. Several reviewers were unimpressed with a vague
and subjective description of the quality of quantification of different terms in the mass balance
method. Is there a better way to do this?

Reviewer #2 offers a number of useful comments on minor points in the manuscript, please
address these.

4) I found the Conclusions section to be unsatisfying. As the 11th group to compare different
weathering rate computation methods, is our knowledge of weathering rates improved? Did
using more carefully collected data and uniform sampling methods improve these numbers? I
am not sure from reading the conclusions. Nor am I sure what recommendation would be
made to land managers on the basis of this work for how to measure weathering rates. I
suggest pulling back out to the big picture, and addressing the reader who has skipped from
introduction straight to conclusions in rewriting this section.

My own minor comments:

Line 65: The definition of “weathering rate” given does not define a rate (dimensionally).
Line 182: I’m surprised at lack of attention to till mineralogy: does this differ between sites?
Line 200: Describe the solid fertilizer used.
Line 218: “sandy loam till” is not a texture. “sandy loam” is.
Pinus is conifer, not deciduous. What was the vegetation at Asa during the last glaciation?

Response:

We have carefully read through all the comments and have critically discussed possible changes. We hope that you will find all major points sufficiently addressed and that the manuscript is acceptable to you in revised form.

In terms of changes we have focused mainly on your principal suggestions, i.e. to “describe very early and with panache” that three methods are required to cover three very different conceptual views on weathering (i.e. steady-state, historical and dynamic weathering). To our knowledge this has not been done to the same extent previously based on harmonized implementation of all methods for the same sites. Kolka et al. (1996) is the only group that used a similar approach, however, that study was based on less detailed data. We hope that our discussion of these different estimates in a mass balance perspective adds further novel insights into how these methods relate to other ecosystem sources and sinks of base cations in an aggrading forest ecosystem.

Details of the changes in the manuscript are as follows:

1. Terminology:
   - Throughout the manuscript: We have changed the name of the third method used to estimate weathering from “mass balance approach” to “base cation budget”. We have also added a new table (Table 2) that summarizes major differences (conceptual, scales etc.) between the methods.
   - Additionally, we have rewritten parts of the introduction and discussion to highlight our rationale behind the use of the perspective of historical versus present-day weathering estimates.

2. Soil age (Line 284): The soil age at Asa should be 14,300 years, not 143,000 years. This was an unfortunate typo in the text (but the correct age was given in Figure 6). The soil age at Flakliden is younger, but both soils were formed during the end of the latest (Wechselian) ice age, and there is no eolian loess deposition at either site (Fréden 2009).
3. Former Table 4 (Now table 5): We have now attempted to give an additional description of the quality and uncertainty of different terms in the base cation budget (former "mass balance method") by estimating combined uncertainty, which is given in a separate Table (Table 6). The combined uncertainty provides a better picture of the uncertainty of weathering estimates by the base cation budget approach. New text describing the method of calculation, material and methods, results and discussion is now inserted at appropriate places in the manuscript, i.e., at Lines 582-595, 700-706 and 945-946.

4. Conclusions: We have made a new improved version of the conclusions that we hope is clear and informative with respect to the novelty of our study, and has more obvious links with the context and rational given in the Introduction. We stress that a contribution of new knowledge is gained from using a harmonized study design, i.e. (1) where similarities and dissimilarities of methods occur with regard to different test criteria, and (2) in terms of the similarities and dissimilarities of different methods with regard to their relative importance in the overall base cation budgets. All of which enable us to identify some important issues for future research.

5. Minor comments:

- Line 66: We have changed the definition of weathering rate so that dimensions are evident.
- Line 247-249: We have cited Casetou-Gustafson (2018) where all details can be found about soil mineralogy at Asa and Flakaliden.
- Line 267-268: We have added the information about which base cations were contained in the solid fertilizer mix.
- Line 287: We changed soil texture to sandy loam.
- Lines 899-900: We improved this sentence. Furthermore, we would like to clarify that there was no vegetation during the last glaciation as Asa was glaciated.

Additional changes:

- We found an unfortunate error in the calculation of fine-root biomass which is now corrected (Line 505). The change has no effect on how the calculation is described in the Materials and Methods section, but the consequences is a reduced fine root biomass leading to ca 5% lower BC uptake in biomass for Ca, Mg and K. This had no impact on the conclusions and the general picture, but the substantial discrepancies between present-day weathering rates produced by the base cation budget...
and PROFILE are now slightly less pronounced. The new calculations are now included in the revised figures 4 and 5 (former Fig. 3 and 4).

- The description of how base cation budgets were calculated is now expanded with detailed information about sampling procedures and sampling sizes (section 2.5), as was requested by several reviewers. Additional graphs showing temporal changes in soil water chemistry and runoff are included in the Supplementary material (figure S4-S5; see also below). Apparently, reviewer 1 in particular got the impression that the base cation budgets were based on a quite limited sampling. We hope the present text will change that view.

- By mistake error bars in Figure 3 (now Fig 4) have been switched between K and Na and we have corrected for this.

- We have revisited our results that we obtained from applying the depletion method and came to the conclusion that the relatively low values given by the historical weathering losses is due to complicated Zr gradients observed in two soil profiles at the flakaliden site (i.e. 11B and 15A; Fig.5). By removing these profiles from the calculations (described now in Lines 363-367 and Line 904-917), predictions of historical weathering losses for Ca and Mg are more in line with the general view of declining rates over time. It makes more sense to observe Ca and Mg losses that are of similar magnitude, since both elements are contained to a similar extent in the easily weatherable mineral hornblende, which is an important mineral in the Svecofennian granitic bedrock. An editorial consequence of this was that we also moved former Fig. 5 to Fig. 2.

Referee 1:

- In order to strengthen our study we have attempted to be clear about the novelty from the beginning of the manuscript (i.e. Introduction). Furthermore, as described above, we have added an additional assessment of uncertainty of the data that are used to construct the base cation budget (Table 6).

Referee 2:

Historical weathering:

- We have corrected for the wrong unit used for Zr in former Table 2 (now Table 3).
- We have added an equation (1) to the manuscript in the method section which describes the calculation by the depletion method (Line 327).
- We have added estimated volume change (strain calculations according to a formula in White et al.1996) in the Supplements (Table S5) and a mentioning in Lines 348-352.

Steady-state weathering:

We included a short mentioning of the steady-state concept in the introduction (Line 148) and in Table 2.

- We have enlarged former Table 3 (now Table 4) and added a column that contains general information for each site. Layer-specific information is given in Supplementary Table S3-S4.

**Base cation budget:**

- We have added a more detailed description of how total deposition was calculated. The same deposition data was used for parameter setting of PROFILE and in the base cation budget.
- We have added two supplementary figures (Figure S4-S5) to illustrate monthly mean and standard deviation of drainage (mm) in soil water at 50 cm depth in the soil of the four control plots at Asa and Flakaliden (Figure S5) and mean and standard error of BC ions (mg/l) in soil water sampled at 50 cm depth in the soil of four control plots at Asa and Flakaliden (Figure S4).
- We have added a new table to the manuscript (Table 6) that contains estimated uncertainty ranges for the different terms in the base cation budget and their combined uncertainty. These uncertainties 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). A detailed description of the statistical procedure is given in Lines 582-595.

**Discussion:**

We have improved section 4.2.

**Figures:**

- We have inserted an explanation of error bars in Line 1494-1500 and in Lines 582-595.

**Referee 3**

- We have removed site names in figure 4 (now figure 5).
- Apart from issues that were already raised by the other referees, we have corrected for minor errors, such as misspellings and we have changed to "extractable concentrations" instead of "concentrations" in the table description of former Table 2 (Now Table 3).

In addition to the revised manuscript we have also provided a corresponding version with tracked changes on, so that the revisions are clearly visible. We have also been carefully through the whole text and made some additional minor revisions which we believe aid clarity.

We hope you will find our revised manuscript acceptable for publication in Biogeosciences and look forward to hearing from you in due course.
On behalf of all authors, yours sincerely,

Sophie Casetou-Gustafson,

Corresponding author