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 and assessments of critical loads of acidity. A variety of methods that differ in concept, temporal and spatial scale and data requirements are available for measuring weathering rates. In this study, causes of discrepancies in weathering rates between methods were analyzed and were classified as being either conceptual (inevitable) or random. The release rates of base cations (BC; Ca, Mg, K, Na) by 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 by 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) BC budget at stand scale, using measured deposition, leaching and changes in base cation stocks in biomass and soil over a period of 12 years. In the 0–50 cm soil horizon historical weathering of BC were 10.6 and 34.1 $mmol_c\ m^{-2}\ yr^{-1,}$ at Asa and Flakaliden, respectively. Corresponding values of PROFILE weathering rates were 37.1 and 42.7 $mmol_c\ m^{-2}\ yr^{-1}$. The PROFILE results indicated that steady-state weathering rate increased with soil depth as a function of exposed mineral surface area, reaching a maximum rate at 80 cm (Asa) and 60 cm (Flakaliden). In contrast, the depletion method indicated that the largest postglacial losses were in upper soil horizons, particularly at Flakaliden.

With the exception of Mg and Ca in shallow soil horizons, PROFILE produced higher weathering rates than the depletion method, particularly of K and Na in deeper soil horizons. The lower weathering rates of the depletion method was partly explained by natural and anthropogenic variability in Zr gradients. The base cation budget approach produced significantly higher weathering rates of BC; 134.6 $mmol_c\ m^{-2}\ yr^{-1}$ at Asa and 73.2 $mmol_c\ m^{-2}\ yr^{-1}$ at Flakaliden, due to high rates rates estimated for the nutrient elements Ca, Mg and K, whereas weathering rates were lower and similar to the depletion method (6.6 and 2.2 $mmol_c\ m^{-2}\ yr^{-1}$ at Asa and Flakaliden). The large discrepancy in weathering rates for Ca, Mg and K between the base cation budget approach and the other methods suggest additional sources for tree uptake in the soil not captured by measurements.

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

Definitions and abbreviations

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

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

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

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

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

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

1. Introduction

Silicate weathering is the major long-term source of base cations in forest ecosystems (Sverdrup and Warfvinge, 1988) and is therefore crucial for sustainable plant production and for proton consumption, counteracting soil and water acidification (Nilsson et al., 1982; Hedin et al., 1994; Likens et al., 1998; Bailey et al., 2003). These effects of weathering are important in areas where in the past high sulphur (S) deposition has caused severe acidification of forest soils and waters (Reuss and Johnson, 1986), for example in southern Scandinavia, northeastern USA and southeastern Canada, regions where felsic igneous bedrock and less readily weatherable soils are abundant (Likens and Bormann, 1974; Nilsson and Tyler, 1995). To aid the multi-lateral negotiations on reducing emissions of acidifying air pollution, the effect-based concept of critical loads of acidity was developed in the late 1980s (Lidskog and Sundqvist, 2002). One advantage of the concept was that the critical loads could be calculated and mapped for different regions at various scales. Because weathering is a key component in estimates of critical loads, reliable applications of the critical load concept required that weathering rates could be estimated with sufficient accuracy at regional scale (Sverdrup and de Vries, 1994).

By 1990 in most European countries, the trend of increasing S emissions since the 1950s started to abate (Grennfelt and Hov, 2005) with a simultaneous decrease in atmospheric deposition of base cations (Hedin et al. 1994). In Sweden, forest growth has at the same time gradually become a relatively more important source to soil acidity (Iwald et al., 2013). Besides the reduction in S deposition, this change has partly been driven by increased use of logging residues for energy production (i.e, whole-tree harvesting), and probably also by a general higher forest production over recent decades in Sweden (Binkley and Högberg 2016). Soil acidification by forest growth is principally caused by accumulation of base cations in tree biomass in excess of anion uptake (Nilsson et al., 1982). The return of base cations in remaining biomass and residues following harvesting determines to what extent the acid load can be neutralised. The soil acidification effect of whole-tree compared to stem-only harvesting has been demonstrated in long-term field experiments (Olsson et al., 1996; Zetterberg et al., 2013). The combined effects can therefore impede recovery from acidification and place increasing demands on nutrient supply.

The sustainability of increased harvest intensity of forest biomass has been questioned and analysed in many studies from various viewpoints and criteria with focus on Europe and North America (e.g. Boyle et al., 1973; Paré et al., 2002; Thiffault et al., 2011, Achat et al. 2015; De Jong et al., 2017; Ranius et al., 2018), where the role of weathering in maintaining base cation balance being one criterion. The impact of increased use of logging residues on base cation balances in Swedish forest soils has been examined in several previous studies (Sverdrup and Rosén, 1998; Akselsson et al., 2007). A regional-scale study on Swedish forest soils found that, in parts of Sweden, base cation losses can occur at rates that lead to very low base saturation of the soils, possibly leading to negative effects on e.g. soil fertility and runoff water quality within just one forest rotation (Akselsson et al., 2007). In their study, base cation depletion in the soil was found to be more common after whole-tree harvesting than stem-only harvesting, especially for Norway spruce, with deficits being more common in southern than in northern (boreal) Sweden.

In regional assessments of the sustainability of different harvesting regimes, the estimated weathering rate has a strong influence on the base cation balance. Klaminder et al. (2011) found that different approaches to estimating weathering rates for a forested catchment in northern Sweden 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 on three continents, using different methods, and found both large between-site as well as within-site differences in the values. Differences in input data can be attributed to different time scales used when acquiring different input data, challenges determining accurate mineralogical compositions and the use of field data compared with laboratory data (Van der Salm, 2001; Futter et al., 2012). Thus, they recommend that at least three different approaches be applied per study site to evaluate the precision in weathering estimates.

Different approaches to estimate weathering rates are likely to produce different estimates due to their conceptual differences, but additional sources to discrepancies of more random nature will also appear. The latter may be due to e.g. misfits in spatial scales, measurement errors or uncertainties in model parametrisation. A number of studies comparing different approaches to estimate weathering rates have been published (e.g. Kolka et al., 1996; Sverdrup et al, 1998; Van der Salm et al., 2001; Ouimet and Dechesne, 2005; Whitfield et al., 2006, 2011; Koseva et al., 2010; Klaminder et al., 2011; Stendahl et al., 2013; Futter et al., 2012; Augustin et al., 2016) such that additional studies on this issue may seem redundant. However, several of these comparison studies can be criticized for poor harmonisation with respect to the spatial scale, or that nutrient uptake in biomass and soil change have been neglected, or poorly quantified in approaches where these processes are relevant for the estimates. Poor harmonisation makes it difficult to separate conceptual from random sources of discrepancies. We therefore see a need for improved comparisons, performed with a spatially constrained and refined harmonisation in the sense of Futter et al. (2012), and combined with a focus on forest soils, tree nutrition and growth. Starting from the viewpoint that no method provides the 'true' estimate of weathering, and acknowledging that different approaches are conceptually different and use different input data, in the present paper we examined three approaches in the present paper: (1) ‘historical weathering’ based on geochemical investigation of the soil profile, (2) modelled present weathering rate and (3) present weathering rate based on cation balances at the ecosystem level.

The choice of methods was primarily based on the fact that rates of weathering may (do) 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 by models 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). Indeed, weathering estimates based on these concepts have often differed grossly from pedon to catchment scale, whereas truly harmonised 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

154 the soil available for forest growth. To our knowledge, Kolka et al. (1996) is the only study to have previously
155 used this multiple approach.
156
157 The first approach, the depletion method, makes use of soil profile based mass balances (Chadwick et al., 1990;
158 Brimhall et al., 1991) to estimate total base cation losses in the soil above a reference soil depth. An element in a
159 weathering-resistant mineral is used as a standard, most commonly zirconium (Zr, present in e.g. zircon) or
160 titanium (Ti, present in e.g. rutile) (Sudom and St. Arnaud, 1971; Harden, 1987; Chadwick et al., 1990; Bain et
161 al., 1994), due to their resistance to weathering at low temperatures (Schützel et al., 1963). To yield an annual
162 average weathering rate ($mmol_c\ m^{-2}$), calculated element losses are commonly divided by an estimated soil age.
163 In Nordic glacial tills situated above the marine limit, soil age is conventionally considered to be the number of
164 years lapsed since the site of interest was finally deglaciated at the end of the Weichselian. Because the rate of
165 weathering may vary over time (Klaminder et al., 2011; Stendahl et al., 2013), the average 'historical
166 weathering' rate may differ from the present-day weathering rate.
167
168 The second approach commonly involves the process-based PROFILE model, which has been used widely as a
169 tool to estimate critical loads of acidity in the Nordic countries (e.g. Sverdrup et al., 1992) and North America
170 (Whitfield and Watmough, 2012; Phelan et al., 2014). In PROFILE, release rates of base cations are estimated
171 based on built in assesments of the the dissolution kinetics of a user-defined set of minerals present in the soil,
172 and the physical and chemical conditions that drive the dissolution of those minerals. Because it is a mechanistic
173 model, its strength is its transparency, while its main weakness is the difficulty in setting values of model
174 parameters and input variables to which it may have high sensitivity. Akselsson et al. (2019) concluded that the
175 most important way to reduce uncertainties in modelled weathering rates is to reduce input data uncertainties,
176 e.g. regarding soil texture, although there is still a need to improve process descriptions of e.g. biological
177 weathering and weathering brakes (e.g. Erlandsson Lampa et al., this issue). The sensitivity of PROFILE to
178 variations in soil physical parameters (e.g. soil texture, soil bulk density) and mineral composition was discussed
179 by Jönsson et al. (1995) and Hodson et al. (1996). The importance of the ability to determine the precise identity
180 and quantity of the minerals was analysed by Casetou-Gustafson et al. (2019). They (ibid.) also suggested that
181 the dissolution kinetics of minerals used in the PROFILE model should be revised and the uncertainties assessed
182 to improve the accuracy in model predictions.
183
184 The third approach to estimating weathering rate is the balanced base cation budget approach. This method has
185 been applied to estimate current weathering rates at various temporal and spatial scales, mostly the catchment
186 scale (Velbel, 1985; Likens et al., 1998). In one way of using the approach, mean weathering rates of individual
187 minerals can be estimated at the catchment scale based on data for the mineralogical composition of soils along
188 with element inputs in deposition and outputs in stream water and biomass uptake (e.g. Garrels and Mackenzie,
189 1967; Velbel 1985, Velbel and Price, 2007). Others have estimated weathering as an unknown source from the
190 missing balance between known sources (deposition, soil depletion) and known sinks (uptake, leaching, increase
191 in soil BC stocks) (e.g. Sverdrup et al. 1998; Simonsson et al., 2015). The method requires measurements of
192 known fluxes within a system with defined boundaries. The high data demand restricts the application of the
193 base cation budget approach to a limited number of sites, essentially catchments with long-term monitoring of

fluxes and well-defined boundaries. However, even then estimated weathering rates may suffer from large uncertainties, as errors in the sinks and sources accumulate in the mass balance equation (Simonsson et al., 2015). Furthermore, the base cation budget approach has mostly been applied under conditions where accumulation in biomass were not directly measured but estimated to be small, or base cation stocks in the soil were assumed to be at steady-state (e.g. Kolka et al., 1996; Sverdrup et al., 1998; Whitfield et al., 2006). However, the nutrient demand is particularly large during the aggrading phase of a stand development where the foliage biomass is increasing rapidly. Hence, due to difficulties in application of the budget method to regional scale, the PROFILE model and the depletion method are the most commonly used methods in Sweden to estimate weathering rates.

The principal aim of this study was to analyse the causes of discrepancies in estimations of weathering rates, with focus on conceptual versus random sources of discrepancies, between the depletion method, the PROFILE model and the balanced base cation budget approach. To accomplish this aim, the specific aims were to (1) perform a spatially harmonized comparison, *sensu* Futter et al. (2012) of the three approaches for a set of test criteria, and (2) to place weathering in the context of other base cation fluxes in aggrading Norway spruce forests, in particular the uptake in forest biomass. The base cation budgets were estimated at the period of stand development when nutrient demand was expected to peak. In combination with access to highly accurate data on biomass production, these conditions also provided opportunities to relate weathering to base cation accumulation in biomass at high nutrient uptake rates, and possible simultaneous depletions of extractable base cation stocks in the soil. Furthermore, input data to PROFILE were characterised by high quality quantitative mineralogical data, measured directly by quantitative X-ray powder diffraction (XRPD), as previously discussed by Casetou-Gustafson et al. (2018). Discrepancies between the PROFILE model and the depletion method were analysed by testing the sensitivity of PROFILE to changes in soil physical or mineralogical composition, and by calculating the hypothetical time needed for PROFILE weathering rates to accomplish the element loss observed with the depletion method.

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

2. Materials and methods

2. 1 Study sites

Two forest sites planted with Norway spruce (*Picea abies* (L.) Karst) were chosen for the study, Flakaliden in northern Sweden (64°07'N, 19°27'E) and Asa in southern Sweden (57°08'N, 14°45'E), because they have been used for long-term experimental studies on the effects of climate and nutrient and water supply on tree growth and element cycling (Linder, 1995; Bergh et al., 1999; Ryan, 2013) (Fig. 1).

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

233 planted in1975 with two-year-old seedlings after clear-felling and soil scarification. The experimental design
234 was similar at both sites and included control, irrigation and two nutrient optimisation treatments (Bergh et al.,
235 1999). All treatments were replicated in 50 m × 50 m plots, arranged in a randomised block design. Only two of
236 the four treatments were used in the present study; the control (C) and plots receiving an annual dose of an
237 optimised mix of solid fertiliser (F), which among other elements per year contained about 10 kg ha^{-1} Ca, 8 kg
238 ha^{-1} Mg and 45 kg ha^{-1} K (Linder, 1995).
239
240 Flakaliden is located in the central boreal sub-zone with a harsh climate, with long cool days in summer and
241 short cold days in winter. Mean annual temperature for the period 1990-2009 was 2.5 °C, and mean monthly
242 temperature varied from -7.5 °C in February to 14.5 °C in July. Mean annual precipitation in the period was
243 ~650 mm, with approximately one-third falling as snow, which usually covers the frozen ground from mid-
244 October to early May. Mean length of the growing season (daily mean temperature ≥ 5 °C) was 148 days, but
245 with large between-year variations (cf. Table 1 in Sigurdsson et al., 2013).
246
247 Asa is located in the hemi-boreal zone, where the climate is milder than at Flakaliden, which is reflected in a
248 longer growing season (193 days). Mean annual temperature (1990-2009) was 6.3 °C, mean monthly
249 temperature varied from -1.9 °C in February to 16.0 °C in July and mean annual precipitation was ~750 mm.
250 The soil is periodically frozen in winter. The difference in climate is reflected in differences in site productivity,
251 which broadly follows climate gradients in Sweden (Bergh et al., 2005).
252
253 The soils at Asa and Flakaliden differ in age due to differences in the time since deglaciation (Table 1), from
254 approximately 14,300 years at Asa and 10,150 years at Flakaliden (estimated from Fredén, 2009). The soil type
255 at both sites is an Udic Spodosol, with a mor humus horizon overlying glacial till derived from felsic bedrock.
256 The soil texture is classified as sandy loam. The transition between the B- and C-horizons is mostly located at 50
257 cm depth at Flakaliden and 50-60 cm depth at Asa. The natural ground vegetation at Flakaliden is dominated by
258 *Vaccinium myrtillus* (L.) and *V. vitis-idaea* (L.) dwarf-shrubs, lichens and mosses (Kellner, 1993; Strengbom et
259 al., 2011). The ground vegetation at Asa is dominated by *Deschampisa flexuosa*, (L.) and mosses (Strengbom et
260 al., 2011; Hedwall et al., 2013).

261 **2.2. Soil sampling and analyses of geochemistry and mineralogy**

262 A detailed description of soil sampling, geochemical analyses and determination of mineralogy can be found in
263 Casetou-Gustafson et al. (2018). The procedures are summarised below. Sampling was performed in untreated
264 control plots (K1 and K4 at Asa and 10B and 14B at Flakaliden) and fertilised (F) plots (F3, F4 at Asa and 15A
265 and 11B at Flakaliden) in October 2013 (Flakaliden) and March 2014 (Asa), in the border zone of four plots at
266 each site. One intact soil core per plot at Flakaliden and in plot K1 at Asa was extracted using a rotary drill (17
267 cm inner diameter). In plots K4, F3 and F4 at Asa, soil samples were instead taken from 1 m deep manually dug
268 soil pits, due to inaccessible terrain for the rotary drill machinery. Maximum soil depth was shallower at
269 Flakaliden (70-90 cm) than at Asa (90-100 cm). The volume of stones and boulders was determined for each plot
270 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%vol.) than at Asa (28%vol.).

Soil samples were taken from each 10-cm soil horizon. Prior to chemical analysis, these samples were dried at 30-40 °C and sieved to <2 mm. Analysis of particle size distribution was performed by wet sieving and sedimentation (pipette method) in accordance with ISO 11277. Geochemical analyses were conducted by ALS Scandinavia AB and comprised inductively coupled plasma-mass spectrometry (ICP-MS) on HNO_3 extracts of fused samples that were milled and ignited (1000 °C) prior to fusion with $LiBO_2$.

Quantitative soil mineralogy was determined with the X-ray powder diffraction (XRPD) technique (Hillier 1999, 2003). Samples for measurement of XRPD patterns were prepared by spray drying slurries of soil samples (<2 mm) micronised in ethanol. A full pattern fitting approach was used for quantitative mineralogical analysis of the diffraction data (Omotoso et al., 2006). This fitting process involved the modelling of the measured diffraction pattern as a weighted sum of previously measured and verified standard reference patterns of the identified mineral components. The determination of chemical compositions of various minerals present in the soils was conducted by electron microprobe analysis (EMPA) of mineral grains subsampled from the sifted (< 2 mm) soil samples. Mineralogical composition of the soils is given in the Supplement (Table S1).

2.3 Historical weathering determined with the depletion method

2.3.1 Method description

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

$$W_{\mathrm{depletion},i} = \frac{d \cdot \rho}{100} \cdot \frac{X_c \cdot Zr_{w,i}}{Zr_c} - X_{w,i} \qquad \text{Eq. 1}$$

where W denotes loss of the ith element (g m^{-2}), X denotes mobile element concentrations (0%), Zr denotes immobile element concentrations (%), w and c denote a weathered soil horizon and the assumed unweathered reference horizon, respectively, d is horizon thickness (m), and ρ is bulk density (g m^{-3}). Zirconium is commonly used as the immobile element due to the inert nature of the mineral zircon ($ZrSiO_4$), although Ti is sometimes used due to the resistance of the Ti-containing minerals anatase and rutile (TiO_2) to weathering (Olsson and Melkerud, 1989). The unweathered reference horizon is located in the C horizon, and has X to Zr ratios that are assumed to represent pristine conditions of the presently weathered horizons above it. In the weathered horizons, X to Zr ratios are smaller; that is, Zr is enriched compared with the mobile elements (i.e. the base cations). The method is based on the assumptions that Zr, hosted in zircon, was uniformly distributed throughout the soil profile at the time of deglaciation, that weathering only occurs above the reference horizon and that zircon does not weather. The latter implies that Zr concentrations and Zr/base cation ratios are constant below the reference horizon. The reference depths for different base cations compared with Zr, which were used as the depths of immobile element concentrations, are shown in Table 3. The Zr/base cation ratio (Fig. S1) was

used to help select the reference soil horizon as it highlights heterogeneities in parent material with depth. In cases of heterogeneities in the profile, the reference horizon was chosen above this heterogeneity. This choice was precluded for soil profile 11B, where Zr concentrations and Zr/base cation ratios peaked directly below the B-horizon (i.e. at 50-60 cm).

2.3.2. Application

Prior to calculating base cation weathering rates with the depletion method, fractional volume change Vp was calculated according to White et al. (1996) in order to assess if there were any large volume changes (collapse) in the mineral soil with implications for which depth the weathering should be calculated to. Similar to White et al. (1996), it was assumed that values close to zero indicate no volumetric change, which was the case below 30-40 cm of soil depth at both sites (Table S2). The homogeneity of the parent material was also evaluated (Fig. 2) using the criterion that the ratio of Ti to Zr should be more or less constant with depth in an originally homogeneous material. Use of the ratio of two immobile elements to establish uniformity of parent material has been suggested previously (Sudom and St. Arnaud, 1971; Starr et al., 2014). The homogeneity criterion was not met using Zr in plot K1 at Asa (i.e. the Zr concentrations decreased towards the soil surface; Fig. 2); here Ti was used as the immobile element instead. Furthermore, the plots 15A and 11B at Flakaliden had to be eliminated from the calculations, because relatively large variability in both the Zr and Ti gradients was observed. These large heterogeneities led to an overall gain of base cations in the rooting zone, which is opposite to what would be expected (i.e. that losses and gains can occur at specific soil depths due to eluviation and illuviation processes in podzolic soils). For this reason, soil profiles 15A and 11B were eliminated from further consideration in calculations of historical weathering rates using the depletion method. Thus, apart from heterogeneities, transportation processes (eluviation and illuviation) and/or erratic Zr or Ti gradients could lead to "negative" weathering, i.e. leading to a calculated relative accumulation of elements. Such negative values were not considered in the calculation of historical weathering losses.

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

$$\rho = 1.3\, e^{-0.1\, x} \qquad \text{Eq. 2}$$

where □ is TOC content (% of dry matter). For Flakaliden (soil horizons 14B: 80-90cm; 10B: 60-70 cm; and 11B: 40-70 cm), the function used was:

$$\rho = 1.8\, e^{-0.2\, x} \qquad \text{Eq. 3}$$

2.4.1 The PROFILE model

2.4.1 Model description

The steady state weathering of soil profiles was estimated using the biogeochemical PROFILE model (Table 2), where weathering of the ith base cation ($W_{profile,\, i}$) is described by long-term mineral dissolution kinetics at the

interface of wetted mineral surfaces and the soil solution. PROFILE is a multilayer model, where parameters are specified for each soil layer based on field measurements and estimation methods (Warfvinge and Sverdrup, 1995).

2.4.2 PROFILE parameter estimation

A detailed description of the application of the PROFILE model to the soils and sites in the present study can be found in Casetou-Gustafson et al. (2019). The parameters used are listed in Table 4a, 4b.

Exposed mineral surface areas were estimated from soil bulk density and texture data using the algorithm specified in Warfvinge and Sverdrup (1995). Volumetric soil water content for each soil profile in Flakaliden and Asa was estimated to be 0.25 m^3 m^{-3} according to the moisture classification scheme described in Warfvinge and Sverdrup (1995) (Table S3).

The aluminium (Al) solubility coefficient, a soil chemical parameter needed for solution equilibrium reactions, was defined as $\log\{Al^{3+}\}+3pH$. It was estimated by applying a function developed from previously published data (Simonsson and Berggren, 1998) and existing total carbon and oxalate-extractable Al measurements for the sites (Casetou-Gustafson et al., 2018) (Table S3). 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 S3).

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

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

Net base cation and nitrogen uptake in aboveground tree biomass (i.e. bark, stemwood, living and dead branches, needles) was estimated as mean accumulation rate over a 100-year rotation period in Flakaliden and a 73-year rotation period in Asa. These calculations were based on Heureka simulations using the StandWise application

(Wikström et al., 2011) for biomass estimates, in combination with measured nutrient concentrations in aboveground biomass as described in section 2.5.4 below (Linder, unpubl. data).

2.4.3 PROFILE sensitivity analysis

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

2.5 The base cation budget approach

2.5.1. General concepts of the base cation budget approach

The average weathering rate of the *i*th base cation according to base cation budget, W_{budget}, i, over a period of time can be estimated with base cation budgets (Table 2) using the base cation budget approach, which assumes that total deposition (□□□) and weathering are the major sources of mobile and plant-available base cations in the soil, and that leaching (□□) and accumulation of base cations in biomass (Δ□□) are the major sinks. A change in the extractable soil stocks of base cations over time (Δ□□) is 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,

$$W_{budget,\,i} = L_i + \Delta B_i + \Delta S_i - TD_i \qquad \text{Eq. 4}$$

2.5.2 Atmospheric deposition, TD_i

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

2.5.3. Changes in exchangeable soil pools, ΔS_i

Changes in extractable base cation stocks in the soil were calculated from the difference between two soil samplings, performed in 1986 and 1998 at Flakaliden, and in 1988 and 2004 at Asa. The organic horizon 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 horizon, 25 cores were combined into one sample.

Exchangeable base cation content in the soil (<2 mm) for all Flakaliden samples and in Asa for samples from 1988 was determined by extraction of dry samples with 1 M NH_4Cl using a percolation method, where 2.5 g of

sample was leached with 100 mL of extractant at a rate of 20 mL h^{-1}. The base cations were analysed by atomic absorption spectrophotometry (AAS). For the Asa samples from 2004, batch extraction was performed using the same extractant, and the base cations were determined with ICP. A separate test was made to compare the yield of the percolation and batch extraction methods. No consistent difference between the methods was observed.

The amount of fine soil (<2 mm) per unit area was calculated from the volume of fine earth (<2 mm) in the soil profiles and the average bulk density of the soil in the 0-10, 10-20 and 20-40 cm horizons. Bulk density and volume proportion of stoniness at Flakaliden were determined from samplings in 1986 in 20 soil profiles (0.5 m × 0.5 m and about 0.5 m deep) outside plots. At Asa, stoniness was determined with the penetration method of Stendahl et al. (2009) and the bulk density of soil <2 mm was calculated using a pedotransfer function that included soil depth and measured carbon concentrations as variables.

2.5.4 Net uptake in biomass, ΔB_i

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

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

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

2.5.5. Leaching, L_i

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

Soil water was collected from five ceramic tension lysimeters (P80) installed at 50 cm depth in each experimental plot. Soil water was collected during frost-free seasons, applying an initial tension of 70 kPa in 250 mL sampling bottles, and left overnight. These soil water samples were pooled by plot. The base cation concentration in the soil solution was determined with ICP-AES. Soil water sampling was performed twice every year, i.e. in the spring and in the autumn, which are the periods of highest water fluxso that the most important leaching events were covered. The spring samples were collected soon after the snowmelt and depending on the weather in a specific year this meant that the yearly spring sampling date varied between the last week of April and the last week of May. The autumn samples were collected when frost risk increased. That meant that the autumn sampling dates varied from year to year, i.e. from the first week in September to mid-November. The seasonal variation in soil water chemistry is shown in Fig. S2.

The drainage flux out of the profile was calculated by the CoupModel (Jansson, 2012). The model was parameterised based on hydraulic soil properties measured at the sites. The model was run with hourly mean values of locally measured climate variables (precipitation, global radiation, wind speed, air temperature and humidity) and model outcomes were tested against tensiometer data, i.e. bi-weekly tensiometer readings at 15, 30 and 45 cm depth were used for model calibration. The parameters were then adjusted slightly to obtain good agreement between measured and calculated soil water content. Annual precipitation varied considerably during the period 1990-2002, ranging from 906 to 504 mm at Flakaliden (mean 649 mm) and from 888 to 575 mm at Asa (mean 736 mm). Annual evapotranspiration increased by about 50 mm at both sites, during the period 1987-2003 at Flakaliden and 1990-2002 at Asa, due to the increment in tree leaf area. Monthly means and standard deviation of drainage (mm) at 50 cm depth in the soil of control plots at Asa during 1990 – 2004 and at Flakaliden during 1988–2004 are shown in Fig. S3.

2.5.6. Assessment of data quality in base cation budget

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

2.6 Statistical analyses

Site mean values and standard error (SE) of $W_{depletion}$ and $W_{profile}$ were calculated based on the four (or two) soil profiles studied at each site. For W_{budget} 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_i) and SE(ΔS_i), 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, $u(\Delta B_i)$ and $u(TD_i)$, 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_c) was calculated as:

$$u_c\left(W_{budget,\ i}\right) = \sqrt{\left(SE(L_i)\right)^2 + \left(u(\Delta B_i)\right)^2 + \left(SE(\Delta S_i)\right)^2 + \left(u(TD_i)\right)^2} \qquad \text{Eq. 4}$$

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

3. Results

3.1 Depletion method estimates of historical weathering rates

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

3.2 PROFILE model estimates of steady state weathering rates

The steady state weathering rate estimated by the PROFILE model ($W_{profile}$) differed from the historical rate with respect to all three test criteria, i.e. (1) total weathering rate in the 0-50 cm soil horizon, (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 $mmol_c\ m^{-2}\ yr^{-1}$, Flakaliden: 42.7 $mmol_c\ m^{-2}\ yr^{-1}$) were around 3.5 and 1.3-fold higher than $W_{depletion}$ estimates, respectively. Secondly, the total modelled base cation weathering rate for the soil profile down to 90 cm was around 7-fold higher than the rate estimated using the depletion method at Asa (89.4 $mmol_c\ m^{-2}\ yr^{-1}$), and 3.4-fold higher at Flakaliden (127.6 $mmol_c\ m^{-2}\ yr^{-1}$). Unlike the historical weathering based on the depletion method, PROFILE predicted that weathering rates increased with soil depth at both sites. At Flakaliden, high contents of K- and Mg-bearing tri-octahedral mica (Casetou-Gustafson et al., 2018) gave rise to particularly high weathering

rates at 70-80 cm. Thirdly, in contrast to $W_{depletion}$, $W_{profile}$ was largest for Na at both sites, followed by Ca. However, $W_{profile}$ was larger for K than for Mg at Asa, while the reverse was true at Flakaliden.

The sensitivity analysis of the PROFILE model using homogeneous soil physical and/or mineralogical properties demonstrated that the variations in soil physical properties (i.e. soil bulk density and specific exposed mineral surface area) with depth had a greater influence than mineralogy on the observed change in $W_{profile}$ with soil depth. In terms of the ratios of sums of squares, the 'homogenous soil physics' scenario (1) produced 75% or more of the error obtained with 'homogenous soil physics and mineralogy' (scenario (3)), leaving a mere 25% or less to the 'homogenous mineralogy' of scenario (2); also see Figures S4 and S5. The soil physical inputs that were most important for PROFILE weathering rates are indicated in Figs. S4 and S5. There was a strong linear and positive relationship between exposed mineral surface area and $W_{profile}$ for all elements at both sites, with R^2 values ranging from 0.65 to 0.89 (Fig. S6). The relationship between bulk density and $W_{profile}$ was also strong and showed the same linear response, although R^2 values were lower, 0.40-0.70 (Fig. S7).

3.3 Base cation budget estimates of current weathering rates

A comparison of weathering rates estimated by base cation budgets (W_{budget}), $W_{profile}$ and $W_{depletion}$ was made for the 0–50 cm soil horizon. For most elements, W_{budget} in the 0–50 cm horizon was higher, or much higher, than $W_{profile}$ (Fig. 5). Compared with the PROFILE model estimates, the base cation budget estimates of weathering were 6- to 7-fold higher for Ca, Mg and K weathering at Asa, and about 2- to 3-fold higher for Ca, Mg and K at Flakaliden. At Asa, the sum of base cations was on average 13-fold and 3.6-fold larger than $W_{depletion}$ and $W_{profile}$, respectively. The closest resemblance between methods was found between $W_{depletion}$ and W_{budget} for Na. The budget calculations suggested that weathering was a dominant source of K and Mg, but contributed a somewhat smaller proportion of Ca (61% at Asa and 43% at Flakaliden).

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

By using the weathering estimates obtained with PROFILE and the depletion method in the base cation budget equation, Eq. (4), in combination with measured estimates of deposition, leaching and uptake in biomass, alternative soil balances were estimated (Fig. 6). Since the base cation budget method predicted much higher weathering rates than the other methods, a balance of sources and sinks consequently required more marked decreases in exchangeable soil stocks for K, Ca and Mg when weathering rates were based on PROFILE or the

depletion method. Furthermore, as a consequence of the substantially higher $W_{profile}$ for Na, the PROFILE based base cation budget suggested substantial increases in exchangeable Na stocks.

4. Discussion

In spite of the fact that this study was well harmonised at the spatial scale and originated from sites with similar soil parent material, our comparison of three approaches to estimate weathering rates showed significant discrepancies between them. Discrepancies were demonstrated for all three test criteria: the sum of weathering rates in the 0–50 cm horizon, the depth gradient of weathering within this horizon, and the element rank-order of weathering rates. In the following, the discrepancies between the depletion method and the PROFILE method is first analysed because all three test criteria can be applied.

4.1 First test: Lower weathering rates by the depletion method compared to PROFILE

Modelled ($W_{profile}$) and historical ($W_{depletion}$) base cation weathering rates were within the range of recently published data for similar forest sites on podzolised glacial till (Stendahl et al., 2013). However, the historical weathering rates at Asa were similar to the lowest historical weathering rate observed by Stendahl et al. (2013) and the historical weathering rates for Flakaliden were similar to their highest rates, at least with regard to Ca and Mg. The overall $W_{profile}$ in the 0–50 cm depth was higher than $W_{depletion}$ for Na and K. Similarly, high ratios of $W_{profile}/W_{depletion}$ were found at catchment scale by Augustin et al. (2016). At the pedon scale, Stendahl et al. (2013) found $W_{profile}/W_{depletion}$ ratios of on average 2.7 for 16 Swedish study sites (with average max. and min. ratios of 7.9 and 0.4, respectively); this ratio was larger than the one found for Flakaliden in our study (1.5) and lower than the one found for Asa (5.1). Similar to Flakaliden, low ratios have been reported for the Lake Gårdsjön site situated in south-western Sweden (Sverdrup et al., 1998; Stendahl et al., 2013). An exception to the general trend of higher steady-state PROFILE weathering rates compared to historical rates calculated by the depletion method, was found for Mg at the Flakaliden site, where $W_{depletion}$ was 1.9-fold greater than $W_{profile}$ in the upper mineral soil, but only at Flakaliden. This exception with regard to Mg was also found by Stendahl et al. (2013) for all of their 16 study sites.

The observed discreprancy between $W_{profile}$ and $W_{depletion}$ has both conceptual and random origin, where the conceptual origin is due to the different temporal scales. In contrast to the observed discrepancies referred to above, several studies have concluded that the average historical weathering rate should generally be higher than the present weathering rate, since soil development involves loss of easily weatherable minerals and ageing of mineral surfaces (Bain et al., 1993; Taylor and Blum, 1995; White et al., 1996). In a study using the Historic-SAFE model, applied to the Lake Gårdsjön catchment in southwestern Sweden, Sverdrup et al. (1998) predicted a decline in weathering rates due to assumed disappearance of fine particles and loss of minerals. Their results suggested an increase in weathering rates from deglaciation 12,000 years B.P. towards a peak at 9000 years B.P., followed by a gradual decrease to below initial levels.

The particularly low $W_{depletion}$ at Asa was largely attributed to a weakly developed depth gradient of Zr in the soil (Fig. 3). This observation has probably a random rather than a conceptual origin, because it might have been 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 horizons. In addition, clearance cairns of unknown age were found in the experimental area at Asa, indicating small-scale agriculture in the past. Moreover, if burrowing earthworms have been abundant in the past, they might have produced soil mixing in the upper soil horizons (Taylor et al., 2019), resulting in a disturbed Zr gradient and in low estimates of historical weathering in the rooting zone (Whitfield et al. 2011). High or near-neutral soil pH and deciduous litter can promote high population densities of burrowing earthworms following forest clearing and agriculture; and we note that partly deciduous vegetation dominated at Asa until only 1000-2000 years BP, with species such as *Corylus avellana* (L.), Betula spp., *Quercus* spp. and *Tilia* spp. (Greisman et al., 2009).

Apart from disturbances, natural heterogeneity in texture or mineralogy probably influenced the estimate of $W_{depletion}$ at the study sites, i.e., biases of random nature. At Flakaliden, it was reasoned that heterogeneous Zr gradients (Fig. 3) and Zr/base cation ratios (Fig. S1) disqualified two soil profiles from further analysis, which would have otherwise indicated unreasonable net gains of elements in the rooting zone (0–50 cm) (i.e. for soil profile 15A for all elements and for soil profile 11B with regard to Na and K). Whitfield et al. (2011) used the same argument for excluding single profiles from their calculations, emphasizing that overall gains in the rooting zone are not expected without external additions of base cations to the soil profiles. Several alternative reasons could have contributed to the observed peaks of Zr in 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 uniform and hereby overshadows heterogeneities observed with soil depth for both elements (Fig. 2, 3). Thus, heterogeneities in Zr gradients observed in the B/C horizon can be attributed to local heterogeneities of the parent material irrespective of if the Ti/Zr gradients are uniform at these depths.

Regardless of errors in the Zr gradients, both $W_{depletion}$ and $W_{profile}$ 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; Schaetzl and Isard, 1996), which would imply that soil 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.

4.2 Second test: PROFILE and depletion method produce different weathering gradients in the soil

Our second test, postulating similarity between $W_{depletion}$ and $W_{profile}$ concerning the weathering rate gradient with soil depth, was not fulfilled. This discrepancy was basically of conceptual nature. We may imagine a front of intense weathering moving downward through the soil profile over the millennia. Each horizon would undergo an episode, limited in time, of intense weathering followed by slower weathering in the ageing material. The sensitivity test performed with PROFILE revealed that the model output was only little affected by the

differences in mineralogy between horizons. Therefore, if processes are correctly modelled with PROFILE, the notion of a weathering front should primarily be associated with changes in bulk density and exposed mineral surface area, as also suggested by the positive correlation between $W_{profile}$ and exposed mineral surface area and bulk density (Figs. S6-S7) and by the findings of Jönsson et al. (1995).

The increase in weathering rate with soil depth simulated by PROFILE is obviously in contrast with the classic notion of weathering rates being highest in the A- or E-horizon of podzolised soils (Tamm, 1931). To test whether the high $W_{profile}$ values could be reconciled with the observed historical weathering, the hypothetical time needed for the PROFILE weathering rates to accomplish the element losses determined with the depletion method was calculated. This showed that the the highest weathering rate, presently prevailing at approximately 80 cm (Asa) or 60 cm (Flakaliden) depth according to PROFILE (Fig. 4), would cause the observed depletion losses within less than half of the soil age ('max rates' in Fig. 7), 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 horizons (Fig. 4), would often result in a more severe base cation depletion within less than the postglacial period than observed by the depletion method ('min rates' in Fig. 7), particularly at Flakaliden, and for K and Na also at Asa. Hence, even considering the concept of a possible weathering front, there appears to be a positive bias in $W_{profile}$ at the investigated sites.

4.3 Third test: Depletion method and PROFILE resulted in different element rank-order

The weathering rates of PROFILE may also be criticized based on discrepancies in the ranking order of the weathering of elements, compared to historical weathering; this is our third test criterion. At both sites, 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, whilst 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. (2019) demonstrates that K-feldspar was the dominant source of all steady state PROFILE weathering of K and previous results from similar soils suggest that the dissolution rate for K-feldspar is too high compared with mica. For example, Thompson and Ukrainczyk (2002) described differences in the plant availability of K via weathering from these two mineral groups. In addition, Simonsson et al. (2016) found that, although K-feldspar contained approximately 90% of the bulk K in the soil, 25–50% of the weathering of K had occurred in mica. Furthermore, and in more general terms, Hodson and Langan (1999) suggested that the PROFILE model overestimates weathering rates because it does not consider the decrease in mineral reactivity that has taken place over time and because it assumes that all mineral surface areas are reactive. Therefore, PROFILE can be expected to overestimate base cation weathering rates, an error that can be attributed to a combination of conceptual (conditions or processes inaccurately represented in model) and random (lack of relevant field data) sources.

4.4 Weathering in a base cation budget perspective

683 The base cation budget approach consistently resulted in much higher weathering rates than PROFILE and the
684 depletion method for all base cations except Na. However, as was shown by the large combined uncertainties
685 given in Table 6, base cation budget estimates of weathering are associated with substantial uncertainties from
686 different sources. In general, significant uncertainties in the element budget of ecosystems are common (Yanai et
687 al., 2010), and similarly large uncertainties associated with estimates of W_{budget} were observed by Simonsson et
688 al. (2015) for the Skogaby site in south-western Sweden, a Norway spruce site of similar stand age and soil
689 condition as Asa. Accounting for all sources of uncertainty, they found that the 95% confidence interval in
690 estimates of base cation weathering was 2.6 times the mean (33 $mmol_c\ m^{-2}\ yr^{-1}$).
691
692 Despite the considerable uncertainties in W_{budget} estimates, the base cation budget approach showed that
693 accumulation in biomass was a dominant sink for all base cation elements except Na, in line with findings of
694 Nykvist (2000) for two Norway spruce sites in Sweden and the findings of Simonsson et al. (2015). However,
695 this contrasts to other studies, which assumed no change in soil and tree biomass stocks of base cations over time
696 (e.g. Sverdrup et al., 1998). The higher estimated weathering rate at Asa reflected the higher productivity and
697 nutrient demand of the stand at this site (Bergh et al., 1999), which has resulted in 1.4-fold greater accumulation
698 of base cations in biomass than at Flakaliden.
699
700 Calcium and Mg uptake in forest trees is considered to be more or less passive flow driven by transpiration
701 fluxes, whereas K uptake is an energy-demanding active process (Nieves-Cordones et al., 2014). Considering
702 that Na was the dominant base cation in the soil solution at 50 cm soil depth (Fig. 6), the negligible
703 accumulation of Na in tree biomass suggests that Na uptake in trees is physiologically blocked. Low
704 concentrations of Na seem to be a general feature of terrestrial plants in boreal forests, in contrast to aquatic
705 plants, which explains why the latter are considered important Na sources for large herbivores like moose
706 (Ohlson and Staaland, 2001). Thus, as in agreement with findings by e.g. Taylor and Velbel (1991) and Velbel
707 (1995) for other types of forest ecosystems, the negligible Na accumulation in tree biomass and the particularly
708 low deposition at Flakaliden simplify the Na budget to include only three major counterbalancing fluxes:
709 weathering, deposition and leaching. Because $W_{depletion}$ and W_{budget} of Na were fairly similar, and were much
710 lower than $W_{profile}$, our results provide additional support for the claim that the PROFILE model produced
711 consistently too high Na weathering.
712
713 Accumulation in biomass was the dominant sink for Ca, Mg and K, and this term in the BC budget was
714 considered to be of moderate to high quality (Table 5). The changes observed in extractable Ca stocks in the soil
715 was considered more uncertain (Table 5), but they are consistent with observations over 22 years of aggrading
716 Norway spruce forests by Zetterberg et al. (2016), who reported exchangeable Ca depletion rates of 5-11 and 23-
717 39 $mmol_c\ m^{-2}\ yr^{-1}$ for sites in south-western and northern Sweden, respectively. The higher value for the northern
718 site reflected higher Ca saturation in the soil. The corresponding values for Asa and Flakaliden were larger, but
719 of similar magnitude (34.5 and 40.5 $mmol_c\ m^{-2}\ yr^{-1}$, respectively). Brandtberg and Olsson (2012) studied the
720 same sites as Zetterberg et al. (2016) over a 10–year period and found a general minor increase in exchangeable
721 K soil stocks and a substantial decrease in the Ca stocks, a result much similar to the findings of the present
722 study.

When an independent estimate of current weathering rate ($W_{profile}$) is introduced in the budget (Fig. 6) the high rate of accumulation in biomass is not explained by the combination of measured ($TD, \Delta S$) or modelled ($W_{profile}$) sources or sinks (L). This result suggests that forest trees have access to additional sources of Ca, Mg and K, not measured or captured by our study. We can only speculate about the nature of such sources: It is possible that depletion of ammonium-chloride-exchangeable base cations underestimates the plant-available phases of BC in the soil. Using other extract media than NH_4Cl may have revealed additional sources from e.g. oxalates (Rosenstock et al., 2019b). Additional BC release from decomposing roots, stumps and residues from the felling of the former stand was probably neglected because of difficulties to include coarse wood in soil sampling. It is also possible that the assumption made that no base cation uptake takes place below 50 cm in the soil was wrong. If trees can take up base cations from deeper soil horizons (e.g. Callesen et al., 2016; 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. Furthermore, although biological processes are represented in PROFILE, the model fail to capture biological feedback mechanisms in their entirety, in particular feedbacks generated by plant uptake and mycorrhiza (Finlay et al., 2009; Sverdrup, 2009; Smits and Wallander, 2017; Akselsson et al., 2019; Finlay et al., this issue; Rosenstock et al. 2019a).

5. Conclusions

A general observation from our comparison of three conceptually different methods was that weathering rate estimates were lower by the depletion method than the PROFILE model for the 0–50 cm soil horizon, and that the highest weathering rates were estimated by the BC budget approach. In sharp contrast to the historic weathering estimated by the depletion method, the current steady-state weathering by PROFILE increased with increasing soil depth.

The Na weathering rate was an important exception from the general finding as PROFILE estimated much higher weathering rate for Na than the other methods, which produced similar weathering rates for Na. This indicated that the high weathering rate of Ca, Mg and K by the budget method was at large an effect of high nutrient demand and uptake rate of these elements in the aggrading forest stands. Hence, weathering rates of Ca, Mg and K by the budget method were in our case most likely overestimated. An implication of this conclusion is that forest trees probably have access to additional sources of nutrients base cation, not measured or captured by our study.

Another implication of the higher weathering rate for Na by PROFILE compared to the other methods is that the model may have overestimated release rates of Na, and probably also of K. This conclusion was based on differences between historical and steady-state estimates regarding the rank-order of elements, and the fact that even the lowest PROFILE weathering rates were too high compared with observed depletions of Na and K. A possible cause to the fact that K weathering rates were overestimated by the PROFILE method was incorrect parameters for the weathering of K-bearing minerals in the model, which should be accounted for in future PROFILE based weathering estimate.

762 The depletion method resulted in generally lower weathering rates at Asa than at Flakaliden, whereas the
763 PROFILE estimates for the sites were more similar, indicating that historical weathering estimated by the
764 depletion method was probably underestimated at Asa. This was an effect of the weakly developed and possibly
765 erratic Zr gradients in the soil at Asa, which could have been caused by natural and anthropogenic disturbances.
766 Future studies based on the depletion method should ensure that the Zr gradient with depth show a net
767 enrichment of Zr towards the soil surface. This condition was not fulfilled for soil profiles at the Asa site.
768 Another important outcome of the study was to show that within-site variations in Zr gradients can be large, as
769 was the case at Flakaliden for two soil profiles.

770 **6. Authors contribution**

771 Authors contributed to the study as in the following: S. Casetou-Gustafson: study design, data treatment,
772 analyses, interpretation and writing. Magnus Simonsson: study design, analysis, interpretation and writing. Johan
773 Stendahl: study design, analysis, interpretation and writing B.A. Olsson: study design, data treatment, analysis,
774 interpretation and writing. S. Hillier: interpretation and writing. Sune Linder: Provided long-term experimental
775 data, interpretation and writing. Harald Grip: Provided long-term experimental data, interpretation, and writing.

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782 **8. References**

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

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

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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 homogeneous 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	288.1	-
	F3	60-70	1.41	0.55	0.87	1.04	282.6	-
	F4	80-90	1.26	0.49	0.85	0.98	293.3	-
Flakaliden	10B	60-70	1.09	0.57	0.88	0.87	243.8	-
	14B	60-70	1.59	0.70	0.81	1.03	336.1	-

1071 **Table 4a.** Site parameters used in the PROFILE model
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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 (mmolc m^{-2} yr^{-1})	Measured data on open field and throughfall deposition available from nearby Swedish ICP Integrated Monitoring Sites	$SO^{2-}4$: 27.0	$SO^{2-}4$: 13.1
		Cl^-: 38.3	Cl^-: 5.6
		NO^-3: 30.7	NO^-3: 10.5
		NH^+4: 21.6	NH^+4: 9.9
		Ca^{2+}: 7.2	Ca^{2+}: 5.2
		Mg^{2+}: 6.8	Mg^{2+}: 1.9
		K^+: 1.9	K^+: 1.1
		Na^+: 31.5	Na^+: 5.6
Base cation net uptake ($mmol_c$ m^{-2} yr^{-1})	Previously measured data for Asa and Flakaliden: Concentrations in biomass from Linder (unpublished data). Biomass data from Heureka simulations.	Ca^{2+}: 46.2	Ca^{2+}: 26.7
		Mg^{2+}: 10.6	Mg^{2+}: 4.4
		K^+: 17.8	K^+: 6.7
Net nitrogen uptake ($mmol_c$ m^{-2} yr^{-1})	Previously measured data from Asa and Flakaliden: Concentrations in biomass from Linder (unpublished data). Biomass data from Heureka simulations.	81.0	32.4
Base cations in litterfall ($mmol_c$ m^{-2} yr^{-1})	Literature data from Hellsten et al. (2013)	Ca^{2+}: 116.8	Ca^{2+}: 40.6
		Mg^{2+}: 15.1	Mg^{2+}: 4.6
		K^+: 10.5	K^+: 3.2
Nitrogen in litterfall ($mmol_c$ m^{-2} yr^{-1})	Literature data from Hellsten et al. (2013)	179.8	47.5
Evapo-transpiration (Fraction)	Precipitation data and runoff data. Runoff data calculated based on proportion of runoff to precipitation (R/P) at Gammtratten and Aneboda.	0.3	0.6

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1075 **Table 4b**. Soil* parameters used in the PROFILE model.
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Parameter	Unit	Source
Exposed mineral surface area	$m^2\ m^{-3}$	Own measurements used together with Eq. 5.13 in Warfvinge and Sverdrup (1995)
Soil bulk density	$kg\ m^{-3}$	Own measurements
Soil moisture	$m^3\ m^{-3}$	Based on paragraph 5.9.5 in Warfvinge and Sverdrup (1995)
Mineral composition	Weight fraction	Own measurements
Dissolved organic carbon	$mg\ L^{-1}$	Previously measured data for Asa and Flakaliden: Measurements for B-horizon from Harald Grip and previously measured data from Fröberg et al. (2013)
Aluminium solubility coefficient	$kmol\ m^{-3}$	Own measurements for total organic carbon and oxalate-extractable Al together with function developed from previously published data (Simonsson and Berggren, 1998)
Soil solution CO_2 partial pressure	atm.	Based on paragraph 5.10.2 in Warfvinge and Sverdrup (1995)

1077 *) Physical and chemical soil horizon specific input data are given in supplements (Tables S3)
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1079 **Table 5.** Judgement of data quality for terms included in the base cation budget estimate of weathering.
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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)	J. Bergholm and H. Grip, unpublished data.	Moderate/low: repeated sampling biased by differences in methods of sampling and soil extraction.
Leaching	Plot	Sampling of soil water at 50 cm depth repeated 2 times per year. Water flux modelled (COUP).	H. Grip, unpublished data	High/moderate: High spatial and temporal resolution in soil chemistry, but uncertainty in separating lateral and vertical flow (Flakaliden).
Biomass accumulation	Site (control plots)	Growth increment measured from biomass studies at start and after 12 years.	Growth Albaugh et al. (2009) Nutrient content: S: Linder unpublished data	High/moderate: High quality in growth estimates and nutrient content at treatment scale, data lacking at plot scale

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

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

Figure captions

Figure 1. Map of Scandinavia showing the location of the study sites Asa and Flakaliden.

Figure 2. Zirconium (Zr) gradient in the saoil at Asa (K1, K4, F3, F4) and Flakaliden (10B, 11B, 14B, 15A).

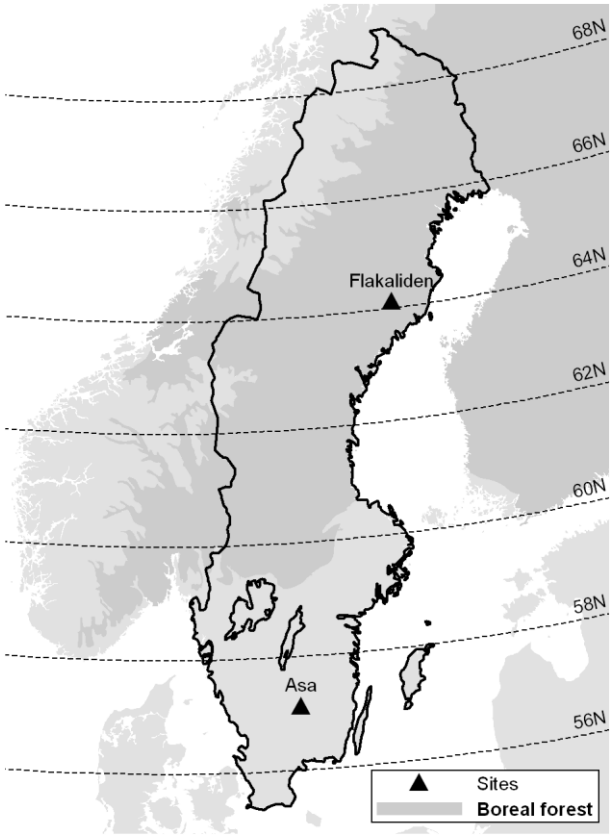
Figure 3. (Left) Historical weathering rate of base cations ($mmol_c\ m^{-2}\ yr^{-1}$) estimated by the depletion method and (right) steady-state weathering rate estimated by the PROFILE model in different soil layes at Asa and Flakaliden.

Figure 5. Site mean values and standard errors (SE) of weathering rates ($mmol_c\ m^{-2}\ yr^{-1}$) for Ca, Mg, K and Na determined with the depletion method, the PROFILE model and the base cation budegt method for the 0-50 cm horizon at Asa and Flakaliden. For the weathering rates based on the depletion method and the PROFILE model, error bars represent the SE calculated based on four soil profiles at each study site, except for Flakaliden, where the depletion method method was only applied in two soil profiles. For weathering rates based on the base cation budget approach, SE bars were calculated from combined standard uncertainties, which are based on SE 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 6. (Left) Sinks and (right) sources of base cations (BC) in ecosystem net fluxes at Asa and Flakaliden. The soil is a net source of soil BC if soil base cation stocks decrease and a net sink if they increase. 'BC budget' = current base cation weathering rate (W_{budget}) estimated with the BC budget method, including measured changes in soil exchangeable BC stocks; 'PROFILE'= soil exchangeable pools estimated from BC budget using PROFILE estimates of BC weathering rate; 'Historical'=soil exchangeable pools estimated from BC budget using estimates of historical weathering rate by the depletion method. 'Measured soil change' and 'Base cation budget estimated soil change' indicates that equation 4 was used to estimate weathering rate, or the soil change, respectively.

Figure 7. Time (years) required to achieve the measured historical element loss in different soil horizons with application of maximum or minimum PROFILE weathering rates at (a) Flakaliden and (b) Asa.

1120



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1122 **Figure 1.**

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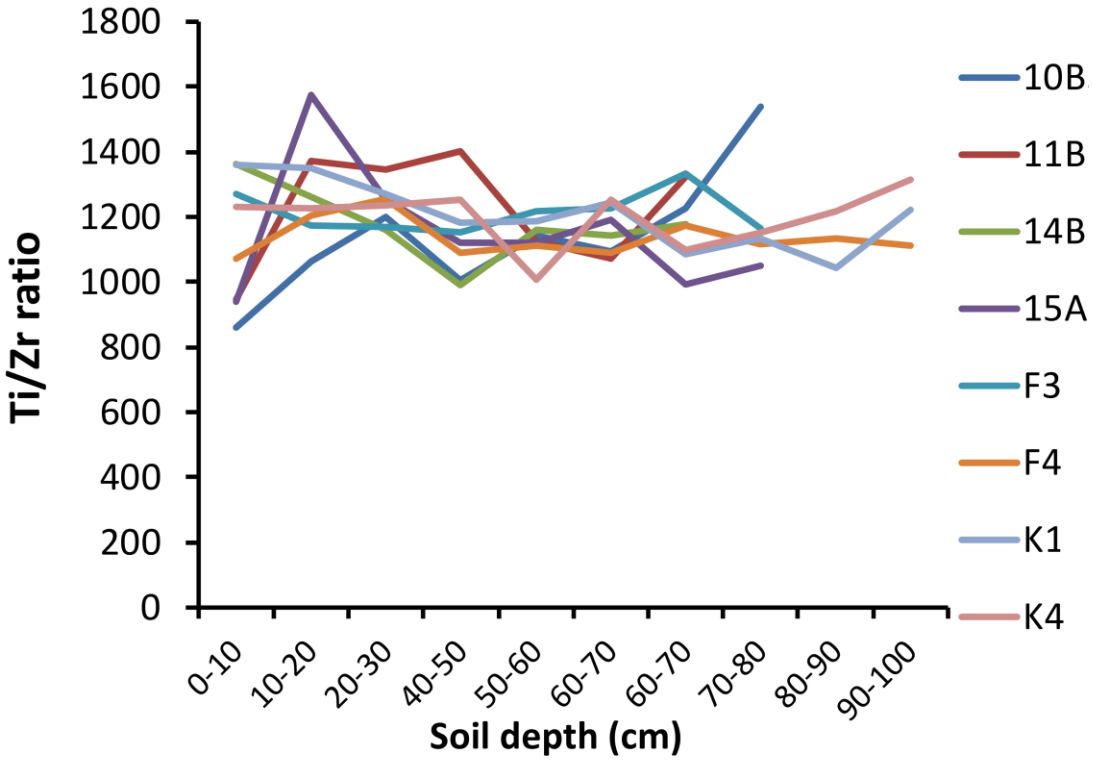

1800
1600
1400
1200
1000
800
600
400
200
0
Ti/Zr ratio
0-10
10-20
20-30
40-50
50-60
60-70
60-70
70-80
80-90
90-100
Soil depth (cm)
10B
11B
14B
15A
F3
F4
K1
K4

Figure 2.

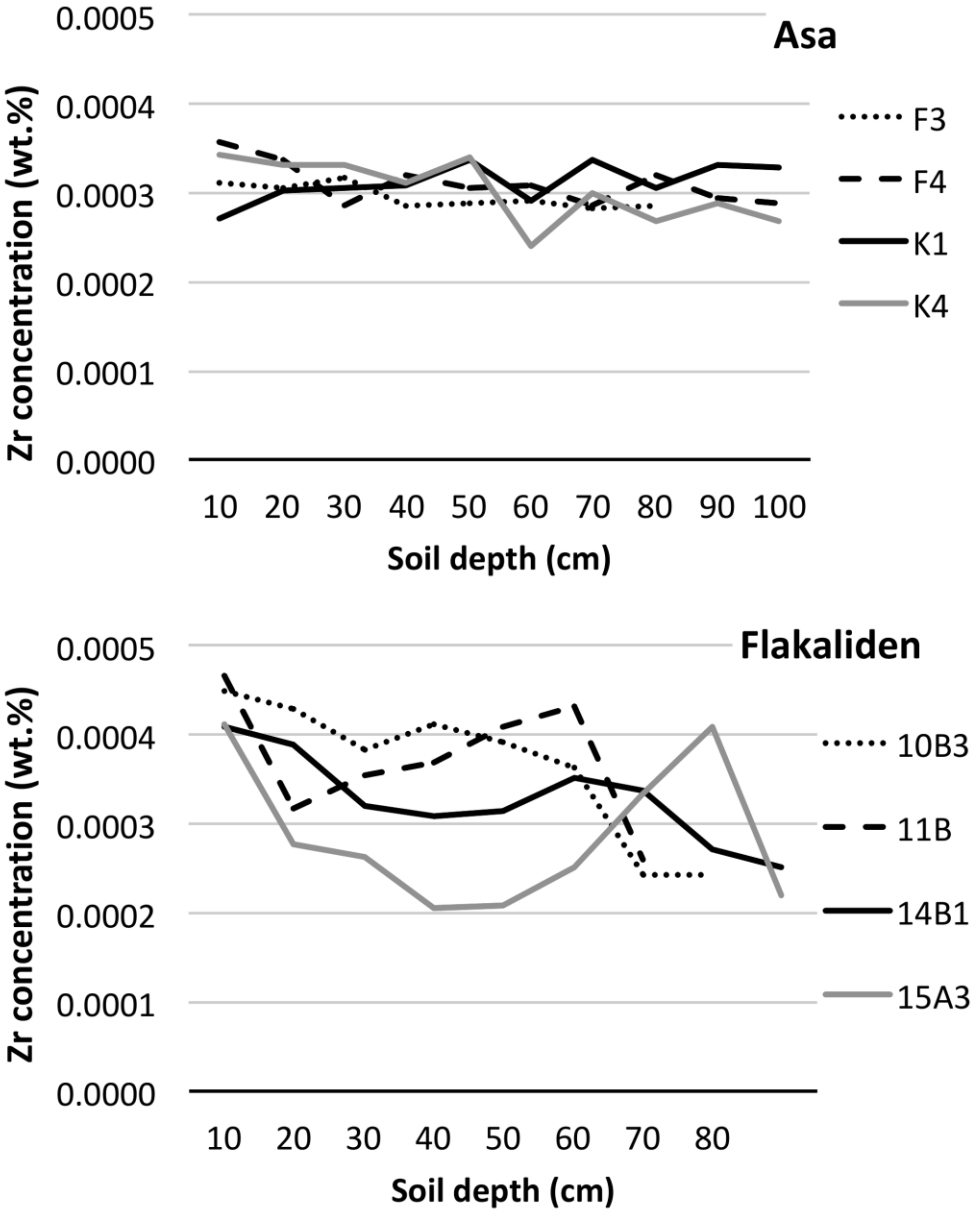

Asa
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
Zr concentration (wt.%)
10 20 30 40 50 60 70 80 90 100
Soil depth (cm)
F3
F4
K1
K4
Flakaliden
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
Zr concentration (wt.%)
10 20 30 40 50 60 70 80
Soil depth (cm)
10B3
11B
14B1
15A3

Figure 3

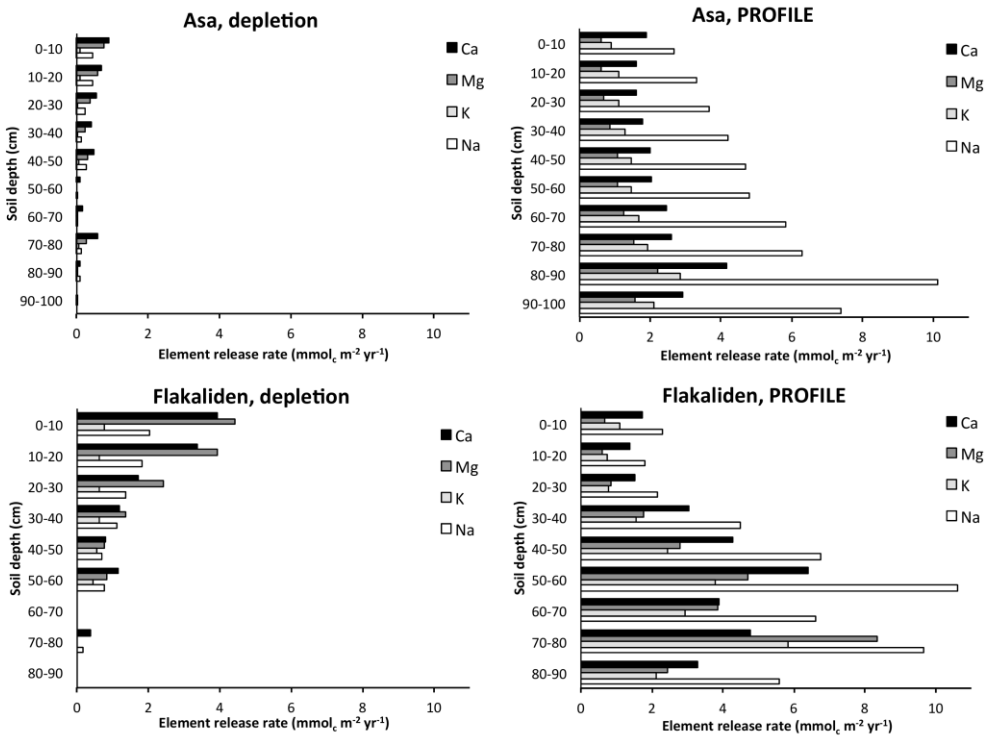
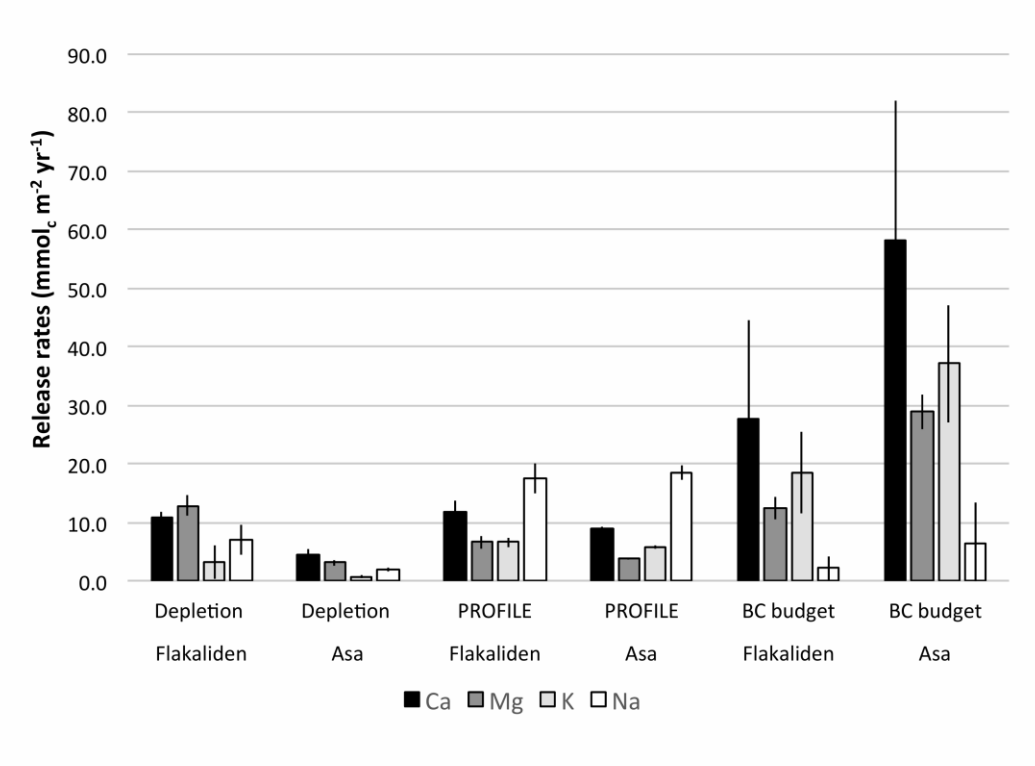

Asa, depletion
Asa, PROFILE
Flakaliden, depletion
Flakaliden, PROFILE
Soil depth (cm)
0-10
10-20
20-30
30-40
40-50
50-60
60-70
70-80
80-90
90-100
Ca
Mg
K
Na
0
2
4
6
8
10
Element release rate (mmol$_c$ m^{-2} yr^{-1})

Figure 4.



1140
1141 Figure 5.
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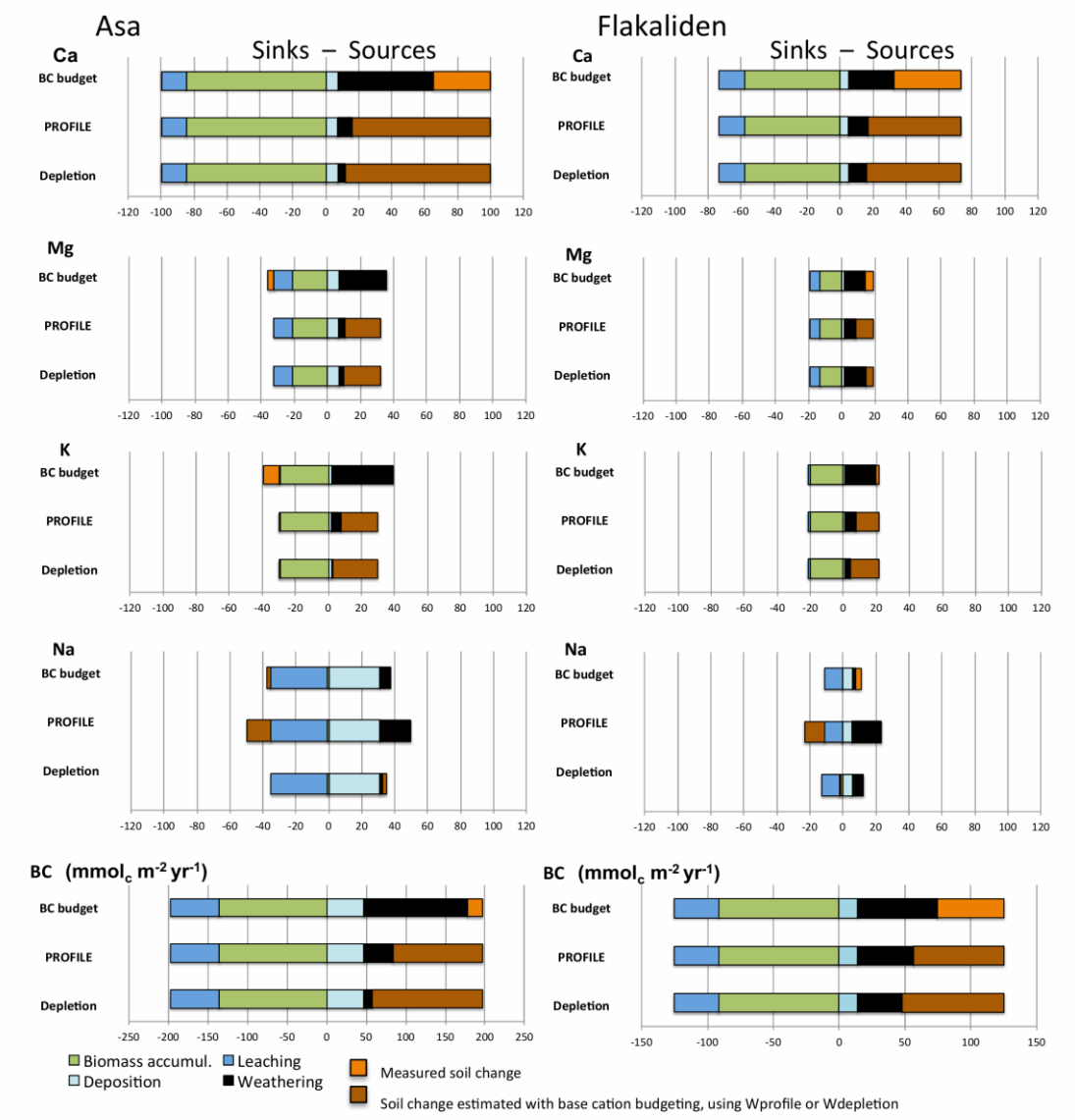
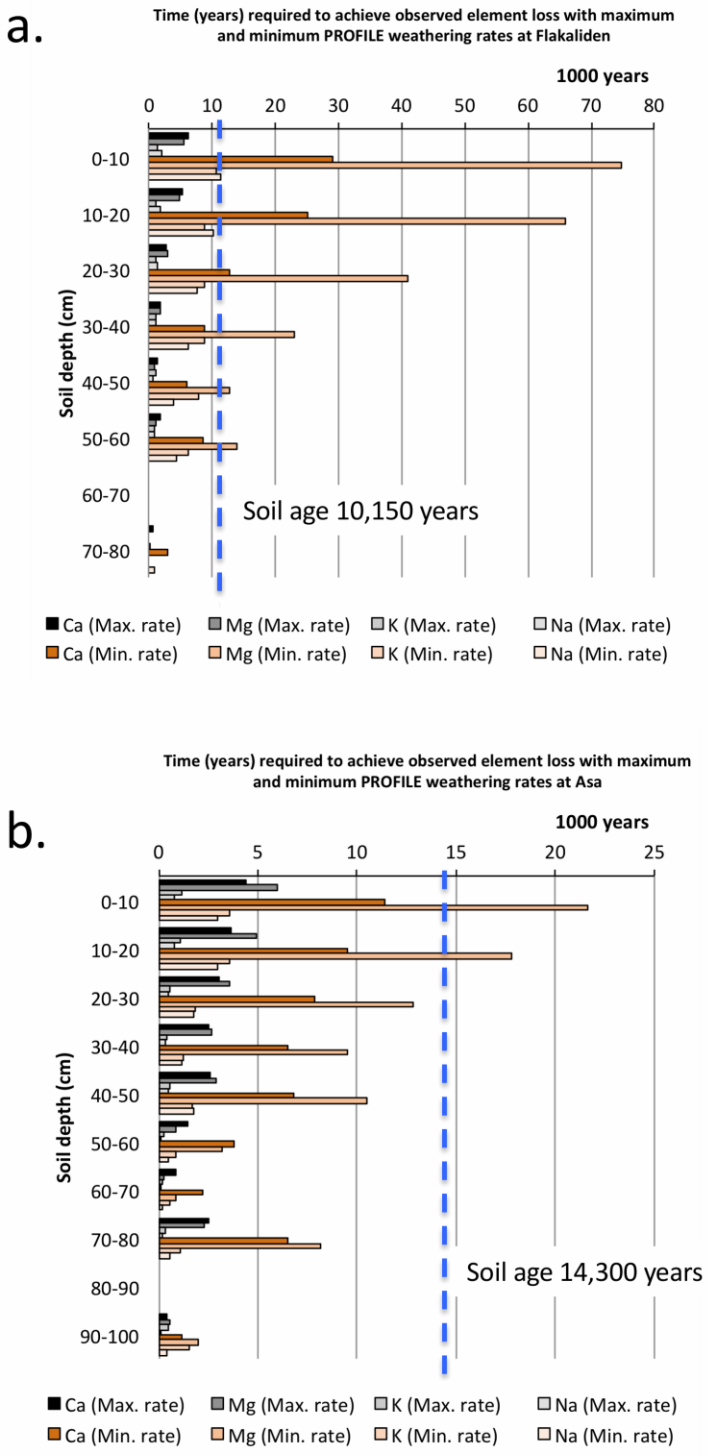

Asa
Flakaliden
Sinks – Sources
Ca
Mg
K
Na
BC budget
PROFILE
Depletion
BC (mmol$_c$ m^{-2} yr^{-1})
Biomass accumul.
Leaching
Deposition
Weathering
Measured soil change
Soil change estimated with base cation budgeting, using Wprofile or Wdepletion

Figure 6.



1148
1149 Figure 7.
1150