



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

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26 **Abstract**

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

36 In the 0-50 cm soil layer at Asa, historical weathering of Ca, Mg, K and Na estimated by the depletion
37 method was 4.7, 3.1, 0.8 and 2.0 mmol_c m⁻² yr⁻¹, respectively. Corresponding values at Flakaliden were 7.3, 9.0,
38 1.7 and 4.4 mmol_c m⁻² yr⁻¹, respectively. Steady state weathering rate for Ca, Mg, K and Na estimated with
39 PROFILE was 8.9, 3.8, 5.9 and 18.5 mmol_c m⁻² yr⁻¹, respectively, at Asa and 11.9, 6.7, 6.6 and 17.5 mmol_c m⁻²
40 yr⁻¹, respectively, at Flakaliden. Thus at both sites, the PROFILE results indicated that steady-state weathering
41 rate increased with soil depth as a function of exposed mineral surface area, reaching a maximum rate at 80 cm
42 (Asa) and 60 cm (Flakaliden). In contrast, the depletion method indicated that the largest postglacial losses were
43 in upper soil layers, particularly at Flakaliden.

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

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53 **Keywords.** Weathering; minerals; soil layers; nutrient mass-balance; *Picea abies*; PROFILE model; depletion;
54 mass balance approach

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60 **Definitions and abbreviations**

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

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

65 Weathering rate = Weathering of a mineral resulting in release of a base cation.

66 **Abbreviations:**

67 $W_{\text{depletion}}$ = Historical weathering rate based on calculation of loss of mobile elements since last deglaciation

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

69 W_{mb} = Current weathering rate based on mass balance calculations

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86 1. Introduction

87 Silicate weathering is the major long-term source of base cations in forest ecosystems (Sverdrup et al., 1988) and
88 is therefore crucial for sustainable plant production and for proton consumption, counteracting soil and water
89 acidification (Nilsson et al., 1982; Hedin et al., 1994; Likens et al., 1998; Bailey et al., 2003). These effects of
90 weathering are important in areas where historical high sulphur deposition (S) causes severe acidification of forest
91 soils and waters (Reuss and Johnson, 1986), particularly in southern Scandinavia where acid silicate bedrock and
92 less readily weatherable soils are abundant (Likens and Bormann, 1974). By 1990 in most European countries,
93 the trend of increasing S emissions since the 1950s started to abate (Grennfelt and Hov, 2005) and recovery from
94 acidification began (Warfvinge and Bertills; 2000; Bertills et al., 2007). This recovery is mainly driven by silicate
95 weathering (Evans et al., 2001; Skjelkvåle et al., 2001), but the process is slow (Akselsson et al., 2013; Futter et
96 al., 2012). At the same time, forest growth, has become a more important source of acidity caused by the
97 accumulation of base cations in tree biomass in excess over anion uptake (Nilsson et al., 1982). The biomass
98 extraction rate at harvesting determines the extent to which soil acidity produced by forest growth can be
99 neutralised by decomposition of biomass left on-site. Whole-tree harvesting can thus result in more acid, base
100 cation-depleted soils than stem-only harvesting (Olsson et al., 1996; Zetterberg et al., 2013), due to smaller return
101 of alkalinity. The combined effect of increased productivity of forests in Sweden, resulting in increased stocks of
102 forest biomass, and increased use of whole-tree harvesting for energy purposes can therefore impede recovery
103 from acidification and place increasing demands on nutrient supply. The current Swedish environmental quality
104 objective "Natural Acidification Only" targets a reduction in acid load due to forest growth and harvesting and to
105 acid deposition (Bertills et al., 2007).

106 The role of weathering in maintaining base cation balance in Swedish forest soils has been examined in several
107 previous studies (Sverdrup and Rosén, 1998; Akselsson et al., 2007). A regional-scale study on Swedish forest
108 soils found that, in parts of Sweden, base cation depletion can occur at rates that lead to negative effects on e.g.
109 soil fertility and runoff water quality within one forest rotation (Akselsson et al., 2007). The methods used to
110 determine base cation balance in that study included predicting weathering rate based on the PROFILE model and
111 analysing regional data for deposition, leaching and base cation losses in harvested biomass. Negative balances,
112 which indicate soil base cation depletion, were found to be more frequent after whole-tree harvesting than stem-
113 only harvesting, especially for Norway spruce compared with Scots pine, with the effect being more common in
114 southern than in northern (boreal) Sweden. Among the elements studied, Ca was most frequently subject to
115 depletion. However, uncertainties in estimating the terms of the base cation balance can accumulate to produce
116 large uncertainties in the overall balance, and therefore it is difficult to draw firm conclusions about the
117 sustainability of different harvesting options based on base cation balance alone. There are also conflicting
118 opinions about the consequences of long-term negative base cation balance in soils for sustainable forest
119 production (Binkley and Högberg, 2016). Experimental studies have demonstrated that growth of boreal forests
120 is strongly limited by nitrogen (N), whereas co-limitation with phosphorus (P) may occur in hemiboreal and
121 temperate forests (e.g. Tamm, 1991). Thus, concerns about base cation depletion in Swedish forest soils following
122 increasing use of whole-tree harvesting have so far been about soil acidification rather than tree nutrition,



123 expressed for example by the Swedish Forest Agency (2008) in their recommendation on nutrient compensation
124 with wood ash.

125 In regional assessments of the sustainability of different harvesting regimes, the value of weathering rate used has
126 a strong influence. Klaminder et al. (2011b) found that different approaches to estimating weathering rates yielded
127 results that differed substantially, and that uncertainties in the methods had a great influence on the predicted
128 sustainability of different harvesting practices.

129 Futter et al. (2012) compiled weathering rates estimated at 82 sites, using different methods, and found both large
130 between-site as well as within-site differences in the values. They concluded that the sources of uncertainties were
131 as follows: input data > parameters > weathering concepts/assumptions. Differences in input data can be attributed
132 to different time scales, challenges determining accurate mineralogical compositions and the use of laboratory
133 data compared with field data (Van der Salm, 2001; Klaminder et al., 2011b). Thus, they recommend that at least
134 three different approaches be applied per study site to increase the precision in weathering estimates.

135 Beside the PROFILE model, the depletion method is used in Sweden to estimate weathering rates at regional scale
136 (Olsson et al., 1993). The depletion method estimates total base cation losses since deglaciation in the soil above
137 a reference soil depth, using an element in a weathering-resistant mineral as a standard, commonly zirconium (Zr,
138 present in zircon) or titanium (Ti, present in rutile etc.) (Sudom and St.Arnaud, 1971; Harden et al., 1987;
139 Chadwick et al., 1990; Bain et al., 1994), due to their stability at low temperatures (Schützel et al., 1963). To yield
140 an annual average weathering (mmol c m^{-2}), calculated element losses are commonly divided by an estimated
141 number of years lapsed since the onset of weathering. Steady-state weathering rate may differ from the average
142 during soil formation, which is one reason why weathering rates obtained using PROFILE and the variation in
143 rate with depth in the soil can be expected to differ from those obtained using the depletion method (Stendahl
144 et al., 2013). Observed discrepancies between these methods may therefore reflect ‘true’ differences or conceptual
145 differences between the methods.

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147 The mechanistic PROFILE model estimates steady state release rates of base cations based on the dissolution
148 kinetics of a user-defined set of minerals in the soil and the physical and chemical conditions that drive dissolution
149 of minerals. Since it is a mechanistic model, its strength is its transparency, while its main weakness is the
150 difficulty in setting values of model parameters and input variables to which it may have high sensitivity.
151 Akselsson et al. (*this issue*) concluded that the most important way to reduce uncertainties in modelled weathering
152 rates is to reduce input data uncertainties, e.g. regarding soil texture, although there is also still room for
153 improvement in process descriptions of e.g. biological weathering and weathering brakes (e.g. Lampa Erlandsson
154 et al., *this issue*). The sensitivity of PROFILE to variations in soil physical parameters (e.g. soil texture, soil bulk
155 density) and mineral composition is discussed by Jönsson et al. (1995) and Hodson et al. (1996), while the
156 importance of the ability to determine the identity and quantity of the minerals is analysed by Casetou-Gustafson
157 et al. (*this issue*).

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159 An alternative approach to estimating weathering rate is the mass balance method (Likens et al., 1998; Velbel,
160 1985). It has been applied to estimate current weathering rates at various temporal and spatial scales, and elements
161 of mass balance have been used in different ways in some popular models, e.g. MAGIC (Cosby et al., 1985).
162 Using the mass balance approach, weathering rate is estimated from the difference between sinks and sources of
163 elements within a system with defined boundaries. The missing source in the mass balance equation is assumed
164 to contain the weathering, but can also contain other unidentified sources. The mass balance approach is most
165 reliable when based on long-term data from well-defined systems, although estimates of weathering tend to suffer
166 from large uncertainties, as errors can be expected to accumulate in the mass balance equation (Simonsson et al.,
167 2015). Furthermore, the mass balance approach has rarely been applied under non-steady state conditions (i.e.
168 including measures of soil exchangeable pools), due to lack of long-term data on base cation fluxes. Consequently,
169 at the pedon scale, the PROFILE model and the depletion method are the most frequently used methods in Sweden
170 to estimate weathering rate. The benefit of comparing these two methods is that, taken together, they can provide
171 complementary information about soil weathering potential (i.e. historical versus steady state weathering) in
172 individual soil layers.

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174 The main aim of this study was to quantify weathering rates in two young Norway spruce forests using the
175 depletion method and the PROFILE model and to examine possible causes of discrepancies. A second aim was
176 to quantify weathering rates by the mass balance method and to compare weathering estimates obtained by the
177 different methods against other major base cation fluxes at ecosystem scale.

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179 The different methods were applied at two ecosystem experiment sites in southern (Asa) and northern (Flakaliden)
180 Sweden, where available data allowed construction of base cation mass balances at stand scale. These study sites
181 are representative of Norway spruce forest in Sweden on soil derived from glacial till soil derived from mostly
182 acid silicate rock. They have similar soil texture and structure, but differ in climate and pedogenesis.

183 Three test criteria were used to examine the outputs of the methods: (1) similarity in weathering estimates for the
184 0-50 cm soil profile; (2) similarity in depth gradients in weathering; and (3) similarity in ranking order of the base
185 cations released.

186 2. Materials and methods

187 2.1 Study sites

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

192

193 The experiment at Flakaliden was established in 1986 in a 23-year-old Norway spruce stand, planted in 1963 with
194 four-year-old seedlings of local provenance after prescribed burning and soil scarification (Bergh et al., 1999).



195 The experiment at Asa was established one year later (1987), in a 12-year-old Norway spruce stand planted in
196 1975 with two-year-old seedlings after clear-felling and soil scarification. The experimental design was similar at
197 both sites and included control, irrigation and two nutrient optimisation treatments (Bergh et al., 1999). All
198 treatments had four replicate 50 m x 50 m plots, arranged in a randomised block design. Only two of the four
199 treatments were used in the present study; the control (C) and plots receiving an annual dose of an optimised mix
200 of solid fertiliser (F). For further details, see Linder (1995).

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202 Flakaliden is located in the central boreal sub-zone with a harsh climate, with long cool days in summer and short
203 cold days in winter. Mean annual temperature for the period 1990-2009 was 2.5 °C, and mean monthly
204 temperature varied from -7.5 °C in February to 14.5 °C in July. Mean annual precipitation in the period was ~650
205 mm, with approximately one-third falling as snow, which usually covers the frozen ground from mid-October to
206 early May. Mean length of the growing season (daily mean temperature ≥ 5 °C) was 148 days, but with large
207 between-year variations (Table 1) (cf. Sigurdsson et al., 2013).

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

214

215 The soils at Asa and Flakaliden differ in age due to differences in the time since deglaciation (Table 1). Soil age
216 is approximately 143 000 thousand years at Asa and 10 150 thousand years at Flakaliden (based on National Atlas
217 of Sweden; Fredén, 2009). The soil type at both sites is Udic Spodosol, with a mor humus layer overlying acid
218 silicate bedrock. The soil texture is classified as sandy loamy till. The B-horizon transitions to C-horizon at 35-
219 40 cm depth at Flakaliden and 40 cm depth at Asa. The natural ground vegetation at Flakaliden is dominated by
220 *Vaccinium myrtillus* (L.) and *V. vitis-idaea* (L.) dwarf-shrubs, lichens and mosses (Kellner, 1993; Strengbom et
221 al., 2011), while the ground vegetation at Asa is dominated by *Deschampsia flexuosa*, (L.) and mosses (Strengbom
222 et al., 2011; Hedwall et al., 2013).

223 2.2. Soil sampling and analyses of geochemistry and mineralogy

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

226 Soil sampling was performed in October 2013 (Flakaliden) and March 2014 (Asa), in the border zone of four plots
227 at each site. Plots selected for sampling were untreated control plots (K1 and K4 at Asa; 10B and 14B at
228 Flakaliden) and fertilised (F) plots (F3, F4 at Asa; 15A, 11B at Flakaliden). A rotary drill (17 cm inner diameter)
229 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,
230 soil samples were taken from the wall of 1 m deep soil pits, due to inaccessible terrain for forest machinery.
231 Maximum soil depth was shallower at Flakaliden (70-90 cm) than at Asa (90-100 cm). The volume of stones and



232 boulders was determined for each plot at the two study sites using the penetration method described by Viro
233 (1952) to a maximum depth of 30 cm and by applying the fitted function described by Stendahl et al. (2009).
234 Mean stone and bolder content was higher at Flakaliden (39%_{vol}) than at Asa (28%_{vol}).

235 Soil samples were taken from each 10-cm soil layer. Prior to chemical analysis, these samples were dried at 30-
236 40 °C and sieved (2 mm mesh). Particle size distribution was analysed by wet sieving and sedimentation (pipette
237 method) in accordance with ISO 11277. Geochemical analyses were conducted by ALS Scandinavia AB and
238 comprised inductively coupled plasma-mass spectrometry (ICP-MS) on HNO₃ extracts of fused samples that were
239 milled and ignited (1000 °C) prior to fusion with LiBO₂.

240 Quantitative soil mineralogy was determined with the X-ray powder diffraction technique (XRPD) (Hiller 1999,
241 2003). Samples for determination of XRPD patterns were prepared by spraying and drying slurries of micronised
242 soil samples (<2 mm) in ethanol. Quantitative mineralogical analysis of the diffraction data was performed using
243 a full pattern fitting approach (Omotoso et al., 2006). In this fitting process, the measured diffraction pattern is
244 modelled as a weighted sum of previously verified standard reference patterns of the previously identified mineral
245 components. The chemical composition of the various minerals present in the soils was determined by electron
246 microprobe analysis (EMPA) of mineral grains subsampled from the sifted (< 2 mm) soil samples.

247 **2.3 Historical weathering determined with the depletion method**

248 **2.3.1 Method description**

249 The depletion method, as defined by Marshall and Haseman (1943) and Brimhall et al. (1991), estimates the
250 accumulated mass loss since soil formation (last deglaciation for our sites) as a function of loss of a mobile
251 (weatherable) element and enrichment of an immobile (weathering resistant) element. Zirconium is commonly
252 used as the immobile element due to the inert nature of the mineral zircon (ZrSiO₄), although Ti is sometimes
253 used due to the resistance of the Ti-containing minerals anatase/rutile (TiO₂) to weathering (Olsson and
254 Melkerud, 1989). The maximum weathering depth, below which weathering is assumed to cease, is defined by a
255 reference layer and above the reference layer, Zr is enriched compared with other elements (i.e. base cations). The
256 method is based on the assumptions that zircon was uniformly distributed throughout the soil profile at the time
257 of deglaciation, that weathering only occurs above the reference layer and that zircon does not weather. The latter
258 implies that Zr gradient and Zr/BC ratio are constant below the reference layer. Table 2 shows the reference depths
259 for different base cations compared with Zr, which were used as the depths of immobile element concentrations.

260 **2.3.2. Assumption testing**

261 Prior to calculating base cation weathering rates with the depletion method, the homogeneity of the parent material
262 was evaluated (Fig. 1). Since zircon and anatase/rutile are weathering resistant minerals, it was assumed that the
263 ratio of Ti to Zr would be more or less stable as soil depth increases and, as such, uniformity of the parent material
264 could be ensured. Use of the ratio of two resistant minerals to establish uniformity of parent material has been
265 suggested previously (Sudom and St.Arnaud, 1971; Starr et al., 2014). This was the case for plots F3, K4 and F4
266 at Asa, but there was somewhat more variability in plot K1 (i.e. the Zr concentrations decreased towards the soil



267 surface; Fig. 5), consequently Ti was used as the immobile element instead of Zr for this profile. At Flakaliden,
268 variability in both the Zr and Ti gradients was observed, but the parent material was considered sufficiently
269 uniform for all plots except 15A.

270 2.3.3. Input data

271 Bulk density was estimated for each soil layer except in some plots where density measurements could not be
272 made below a certain soil depth or where a large and sudden decrease in bulk density with increasing soil depth
273 was observed. Bulk density in these cases was estimated using an exponential model for total organic carbon
274 (TOC) and bulk density (BD, g/cm³) based on our own data. For Asa (F3: soil layer 70-90 cm; F4: 0-10, 30-40,
275 50-60, 60-70, 70-80, 80-90, 90-100 cm; K4: 70-80, 80-90, 90-100 cm), the following function was used:

$$276 \text{BD} = 1.3 e^{-0.1x} \quad (1)$$

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

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

$$279 \text{BD} = 1.8 e^{-0.2x} \quad (2)$$

280 2.4 The PROFILE model

281 2.4.1 Model description

282 The biogeochemical PROFILE model can be used to estimate the steady state weathering of soil profiles, as
283 weathering is known to be primarily determined by soil physical properties at the interface of wetted mineral
284 surfaces and the soil solution. PROFILE is a multilayer model, where parameters are specified for each soil layer
285 based on field measurements and estimation methods (Warfvinge and Sverdrup, 1995).

286 2.4.2 PROFILE parameter estimation

287 A detailed description of application of the PROFILE model to the soils and sites in the present study can be found
288 in Casetou-Gustafson et al. (*this issue*). The parameters used are listed in Table 3.

289 Exposed mineral surface areas were estimated from soil bulk density and texture data using the algorithm specified
290 in Warfvinge and Sverdrup (1995). Volumetric field soil water content for each soil pit in Flakaliden and Asa was
291 estimated to be 0.25 m³ m⁻³ according to the moisture classification scheme described in Warfvinge and Sverdrup
292 (1995).

293 Aluminium (Al) solubility coefficient, a soil chemical parameter needed for solution equilibrium reactions, was
294 defined as $\log\{Al^{3+}\}+3pH$. It was estimated by applying a function developed from previously published data
295 (Simonsson and Berggren, 1998) and existing total carbon and oxalate-extractable Al measurements for our sites
296 (Casetou-Gustafson et al., 2018). For partial CO₂ pressure in the soil, the default value of Warfvinge and Sverdrup
297 (1995) was used. Data on measured dissolved organic carbon (DOC) in the soil solution at 50 cm depth were
298 available for plots K4 and K1 at Asa and plots 10B and 14B at Flakaliden, and these values were also applied for
299 deeper soil horizons. Shallower horizons (0-50 cm) were characterised by higher DOC values, based on previous
300 findings (Fröberg et al., 2013) and the DOC classification scheme in Warfvinge and Sverdrup (1995).



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

304 Total deposition was calculated using deposition data from two sites of the Swedish ICP Integrated Monitoring
305 catchments, Aneboda (for Asa) and Gammtratten (for Flakaliden) (Löfgren et al., 2011). The canopy budget
306 method of Staelens et al. (2008) was applied as in Zetterberg et al. (2016). The canopy budget model is commonly
307 used for elements that are prone to canopy leaching (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-}) or canopy uptake (NH_4^+ , NO_3^-)
308 and it calculates total deposition as the sum of dry deposition and wet deposition. Wet deposition was estimated
309 based on the contribution of dry deposition to bulk deposition, both for base cations and anions, using dry
310 deposition factors from Karlsson et al. (2012,2013).

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

316 **2.4.3 PROFILE sensitivity analysis**

317 The sensitivity of PROFILE to a change in soil physical and mineralogical input was analysed, to test whether
318 depth gradients of weathering rates predicted by PROFILE could be explained by either soil physical properties
319 or soil mineralogy. Independent PROFILE runs were performed for each of the following three test scenarios: (1)
320 homogeneous soil physical properties (soil bulk density and specific exposed mineral surface area); (2)
321 homogeneous mineralogy; and (3) homogeneous soil (i.e. soil physics and mineralogy). For homogeneous soil,
322 all soil layers (0-100 cm) were given the same value of the test variable, i.e. the average value for the actual soil
323 profile (0-100 cm).

324 **2.5 The mass balance method**

325 **2.5.1. General concepts of the mass balance method**

326 The average weathering rate of base cations (W_{BC}) over a period of time can be estimated using the mass balance
327 approach, which assumes that total deposition (TD_{BC}) and weathering are the major sources of mobile and plant-
328 available base cations in the soil, and that leaching (L_{BC}) and accumulation of base cations in biomass (B_{BC}) are
329 the major sinks. A change in the extractable soil stocks of base cations over time (ΔS_{BC}) can be considered as a
330 sink if stocks have increased, or as a source if stocks have been depleted (Simonsson et al., 2015). Each of these
331 terms is measured independently over a specific period of time. Hence,

$$332 \quad W_{\text{BC}} = L_{\text{BC}} + B_{\text{BC}} + \Delta S_{\text{BC}} - \text{TD}_{\text{BC}} \quad (3)$$

333 **2.5.2 Atmospheric deposition, TD_{BC}**



334 The same estimates of total atmospheric deposition as used in parameter setting of the PROFILE model (section
335 2.4.2) were used in the mass balance equation 3.

336 **2.5.3. Changes in exchangeable soil pools, ΔS_{BC}**

337 Changes in extractable base cation stocks in the soil were calculated from linear regressions of stocks measured
338 at repeated soil samplings. The organic layer and the mineral soil were sampled to 40 cm or deeper in 1986 and
339 1998 at Flakaliden, and in 1988 and 2004 at Asa.

340

341 At Flakaliden, soil sampling for chemical analyses was carried out in September 1986 in the border zone of plots,
342 using a 5.6 cm diameter corer for the organic layer and a 2.5 cm diameter corer for the mineral soil. The plots
343 were re-sampled in 1998 for chemical analyses, in the same way as in 1986. Soil sampling at Asa was conducted
344 in 1988, prior to the start of the experimental treatments, using the same method as at Flakaliden. The transition
345 from the humus layer to the mineral soil was less clear at Asa than at Flakaliden.

346

347 Exchangeable base cation content in the soil (<2 mm) in the Flakaliden samples from 1986 and 1998 and the Asa
348 samples from 1988 was determined by extraction of dry samples with 1 M NH_4Cl using a percolation method,
349 where 100 mL of solution was percolated through 2.5 g of sample at a rate of around 20 mL h^{-1} . The base cations
350 were analysed by atomic absorption spectrophotometry (AAS). For the Asa samples from 2004, extraction was
351 performed using the same extractant in a batch extraction method and the base cations were determined with ICP.
352 A separate test was made to compare the yield of the percolation and batch extraction methods, but the results
353 were inconclusive and therefore no correction was made to account for possible differences between the extraction
354 methods.

355

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

362 **2.5.4 Net uptake in biomass, B_{BC} (1987-2003)**

363 Accumulation of base cations in tree biomass, i.e. net uptake of base cations, was calculated as mean value of
364 control plots over the period 1989-2003. The calculations were based on increments in aboveground biomass at
365 Asa and Flakaliden for this period (Albaugh et al., 2009, 2012) and concentrations of elements in different tree
366 parts. The increment in belowground biomass was estimated from general allometric functions for Norway spruce
367 stumps and roots in Sweden (Marklund, 1988). Since Marklund's functions (1988) underestimate belowground
368 biomass by 11%, a factor to correct for this was included (Pettersson and Ståhl, 2006). Furthermore, the finest root
369 fraction (≤ 2 mm), which is not included in the functions of Marklund (1988) and Pettersson and Ståhl (2006), was



370 assumed to be 20% of needle biomass at Asa and 40% at Flakaliden, respectively, based on data from Helmisaari
371 et al. (2007).

372

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

379

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

383 **2.5.5. Leaching, L_{BC}**

384 Base cation leaching was quantified in 6-month intervals from modelled runoff multiplied by average element
385 concentrations in soil water collected with tension lysimeters at 50 cm soil depth. Runoff was calculated using
386 CoupModel (Jansson, 2012).

387

388 Annual precipitation varied considerably during the period 1990-2002, ranging from 906 to 504 mm at Flakaliden
389 (mean 649 mm) and from 888 to 575 mm at Asa (mean 736 mm).

390

391 CoupModel was parameterised based on measured hydraulic soil properties. The model was run with measured
392 climate variables (global radiation, wind speed, air temperature and humidity) and model outcomes were tested
393 against tensiometer data. The parameters were then adjusted slightly to obtain the best agreement between
394 measured and calculated soil water content. Annual evapotranspiration increased by about 50 mm at both sites,
395 during the period 1987-2003 at Flakaliden and 1990-2002 at Asa, due to the increment in tree biomass. Soil water
396 was collected from five ceramic tension lysimeters (P80) installed at 50 cm depth in each experimental plot. Soil
397 water was collected on 2-3 occasions per year during frost-free seasons, applying an initial tension of 70 kPa in
398 250 mL sampling bottles, and left overnight. These soil water samples were pooled by plot. The base cation
399 concentration in the soil solution was determined with ICP-AES.

400 **2.5.6. Judgement of data quality in mass balance**

401 The precision and accuracy of a mass balance estimate of W_{BC} is determined by the quality of estimates of each
402 individual term in equation 3, in proportion to the magnitude of each term (Simonsson et al., 2015). Significant
403 uncertainty in the estimate of a quantitatively important term will therefore dominate the overall uncertainty in
404 estimates of W_{BC} . The quality of data for each term in equation 3 was assessed based on the spatial and temporal
405 scales of measurements and the quality of measurements (Table 4). Based on these criteria, we consider the
406 estimates of deposition, leaching and accumulation in biomass to be of moderate to high quality. The



407 measurements of changes in extractable soil pools were of lower quality because of bias in methods in repeated
408 samplings, which would cause significant uncertainty if soil changes were an important part of the element budget.
409 To partly overcome this uncertainty, we used the estimates of W_{BC} obtained by the PROFILE and depletion
410 methods in additional mass balance calculations where the change in soil was determined from the mass balance.
411 These additional mass balance estimates, which are conceptually analogous to the regional mass balances
412 presented by Akselsson et al. (2007), were also used to place the PROFILE and depletion method estimates of
413 W_{BC} in the context of other base cation fluxes at ecosystem scale.

414 2.6 Statistical analyses

415 Site mean values and standard error (SE) of weathering rates were calculated based on the four soil profiles studied
416 at each site ($W_{depletion}$, $W_{profile}$) and on the W_{MB} estimates for the four control plots at each site. R (version 3.3.0)
417 (R Core Team, 2016) and Excel 2016 were used for statistical plotting of results..

418

419 3. Results

420 3.1 Depletion method estimates of historical weathering rates

421 At both Asa and Flakaliden, historical weathering rates estimated with the depletion method ($W_{depletion}$) were
422 highest in the upper soil layers and showed a gradual decrease down to the reference depth, which was defined in
423 most plots at 60-70 cm at Flakaliden and at 80-90 cm at Asa (Fig. 2). Weathering had also taken place below the
424 reference depth. In line with the younger age of the soils at Flakaliden (indicated also by higher abundance of the
425 more easily weatehrbale minerals amphibole, trioctahedral phyllosilicates and calcic plagioclase), the historical
426 annual weathering rate was higher at Flakaliden compared to Asa. The base cation weathering down to 90 cm soil
427 depth amounted to 12.8 $\text{mmol}_c \text{ m}^{-2}\text{yr}^{-1}$ at Asa and 25.1 $\text{mmol}_c \text{ m}^{-2}\text{yr}^{-1}$ at Flakaliden. The corresponding value for
428 the 0-50 cm horizon was 10.5 $\text{mmol}_c \text{ m}^{-2}\text{yr}^{-1}$ at Asa and 22.4 $\text{mmol}_c \text{ m}^{-2}\text{yr}^{-1}$ at Flakaliden. The gradients with depth
429 showed that $W_{depletion}$ increased towards the surface, although this trend was more pronounced at Flakaliden than
430 at Asa. Furthermore, at Flakaliden, $W_{depletion}$ was highest for Mg, followed by Ca, Na and K (Figs. 2 and 3). At
431 Asa, the largest average mass loss was observed for Ca, closely followed by Mg, Na and K (Figs. 2 and 3).

432 3.2 PROFILE model estimates of steady state weathering rates

433 The steady state weathering rate estimated by the PROFILE model ($W_{profile}$) differed from the historical rate with
434 respect to all aspects covered by the three starting hypotheses, i.e. total weathering rate in the 0-50 cm soil layer,
435 variation in weathering with depth and ranking order of base cations (Figs. 2 and 3).

436 PROFILE predicted that weathering rates increased with soil depth at Asa (down to 90 cm) and Flakaliden (down
437 to 60 cm). At Flakaliden, anomalously high contents of K- and Mg-bearing tri-octahedral mica (Casetou-
438 Gustafson et al., 2018) gave rise to increased weathering rates at 70-80 cm. Apart from in that specific soil layer,
439 at both sites $W_{profile}$ was largest for Na, followed by Ca. However, $W_{profile}$ was larger for K than for Mg at Asa,
440 while the reverse was true at Flakaliden.



441 In general, PROFILE also predicted much higher weathering rates than the depletion method (Fig. 2). However,
442 both methods estimated consistently higher weathering rates at Flakaliden than Asa. The total modelled base
443 cation weathering rate for the soil profile down to 90 cm was around 7-fold higher than the rate estimated using
444 the depletion method at Asa ($89.4 \text{ mmol}_c \text{ m}^{-2}\text{yr}^{-1}$), and almost 5-fold higher at Flakaliden ($127.6 \text{ mmol}_c \text{ m}^{-2}\text{yr}^{-1}$).

445 Weathering rates are often reported for the upper 50 cm soil layer, as an approximation of the root zone. On
446 restricting the base cation weathering rate to the upper 50 cm of the mineral soil, W_{profile} estimates for Asa and
447 Flakaliden were more similar (Asa: $37.1 \text{ mmol}_c \text{ m}^{-2}\text{yr}^{-1}$, Flakaliden: $42.7 \text{ mmol}_c \text{ m}^{-2}\text{yr}^{-1}$). This was not the case
448 for $W_{\text{depletion}}$ as shown above, as the estimate for Flakaliden was more than twice that obtained for Asa. However,
449 $W_{\text{depletion}}$ was higher than W_{profile} for Mg. In relative terms, the difference between sites in $W_{\text{depletion}}$ in the 0-50 cm
450 layer was similar to the difference observed for the whole soil profile.

451 The sensitivity analysis of the PROFILE model using homogeneous soil physical and/or mineralogical properties
452 demonstrated that variation in soil physical parameters (i.e. soil texture and density) with depth, rather than
453 mineralogy, was the most important input data explaining the observed change in W_{profile} with soil depth. Applying
454 homogeneous mineralogy had little effect with the original gradient of W_{profile} (Fig. 2) being similarly reproduced
455 with depth. However, when homogeneous soil physical conditions were applied (i.e. a combination of homogeneity
456 in soil physics and soil mineralogy), there were some small variations in W_{profile} between soil layers (Tables S1
457 and S2). In terms of sum of squared error, calculated from the difference in W_{profile} between actual and
458 homogeneous soil, 75-85% of the total error at Flakaliden was due to homogeneity in soil physics only, while the
459 error due to homogeneous mineralogy was 2-17%. The corresponding error values for Asa were 76-94% and 1-
460 4%, respectively. One exception to these findings was plot 10B at Flakaliden, which showed somewhat higher
461 error (17%) resulting from homogeneous mineralogy. This was due to the anomalously high content of
462 trioctahedral micas at 70-80 cm depth, as previously reported by Casetou-Gustafson et al. (2018). At Asa, an
463 outlier to the results was plot F3, where homogeneous soil physical properties produced 109% of the error
464 resulting from homogeneous soil. This was because, by coincidence, soil profile F3 had relatively high bulk
465 density and exposed mineral surface area in the uppermost soil layer, compared with the average soil physical
466 input data, and therefore the homogeneous soil test produced lower weathering rates. Soil physical input
467 parameters that were more important for PROFILE weathering rates are indicated in Figs. S1 and S2. There was
468 a strong linear and positive relationship between exposed mineral surface area and W_{profile} for all elements at both
469 sites, with R^2 values ranging from 0.65 to 0.89 (Fig. S1). The relationship between bulk density and W_{profile} was
470 also strong and showed the same linear response, although R^2 values were lower, 0.40-0.70 (Fig. S2).

471 3.3 Mass balance estimates of current weathering rates

472 A comparison of weathering rates estimated by mass balance (W_{mb}), W_{profile} and $W_{\text{depletion}}$ was made for the 0-50
473 cm soil layer. The physical boundary for the mass balance was defined by the depth of soil solution sampling (50
474 cm). It was found that, for most elements, W_{mb} in the 0-50 cm layer was higher, or much higher, than W_{profile} (Fig.
475 3). Compared with the PROFILE model estimates, the mass balance estimates of weathering were 6- to 7-fold
476 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,



477 the sum of base cations was on average 13-fold and 3.6-fold larger than average annual long-term weathering
478 rates based on the depletion method and PROFILE method, respectively. The closest fit between methods was
479 found between $W_{\text{depletion}}$ and W_{mb} for Na.

480 3.4 Base cation fluxes in measured mass balances

481 A general pattern in base cation fluxes in the mass balances was the difference between Na, on the one hand, and
482 K, Mg and Ca on the other (Fig. 4). This difference was largely due to accumulation in biomass being the dominant
483 sink for the latter elements, whereas Na uptake in biomass was negligible and leaching was the dominant sink.
484 Compared with biomass uptake, loss by leaching was a negligible sink for K, but a significant sink for Mg and
485 Na.

486
487 Deposition was a minor source of base cation inputs, except for Na at Asa. The measured decreases in soil stocks
488 of exchangeable base cations indicated that a change in this pool was a particularly important source of Ca. There
489 were minor increases in exchangeable stocks for Na, K and Mg at Asa.

490
491 In summary, the mass balance calculations indicated that weathering was a particularly dominant source of K and
492 Mg, but weathering contributed a relatively smaller proportion of the total Ca sources than for K and Mg (61% at
493 Asa and 43% at Flakaliden).

494
495 By using the weathering estimates obtained using PROFILE and the depletion method in the mass balance
496 equation (Equation 3) in combination with measured estimates of deposition, leaching and uptake in biomass,
497 alternative soil balances were estimated (Fig. 4). Since the mass balance method predicted much higher
498 weathering rates than the other methods, a balance of sources and sinks consequently required more marked
499 decreases in exchangeable soil stocks for K, Ca and Mg. Furthermore, as a consequence of the substantially higher
500 W_{profile} for Na, the PROFILE based mass balance suggested substantial increases in exchangeable Na stocks.

501 4. Discussion

502 4.1 Comparison of conceptually different methods

503 A number of studies have used multiple approaches to estimate weathering rates, with the aim of validating
504 methods and finding a best estimate for a particular site or catchment (Langan et al., 1995; Kolka et al., 1996;
505 Sverdrup et al., 1998; Futter et al., 2012). A common problem encountered is that the approaches used are so
506 conceptually different that the comparisons do not deal with similar quantities at spatial or temporal scale.
507 Concerning the spatial scale, to our knowledge the mass balance approach has most often been applied at the
508 catchment and forest stand scale, whereas the depletion method and the PROFILE model are normally applied at
509 the smaller pedon scale. In the present study, the mass balance approach included data at stand level over a period
510 when the stand showed high nutrient demand. Concerning the temporal scale, the concepts of the depletion method
511 and the PROFILE model are conceptually different, although they be applied at a similar spatial scale. These two
512 methods are based on direct measurements of soil properties, i.e. quantitative mineralogy, soil bulk density and



513 soil stone content, which is rarely the case in previous comparable studies. Since the three approaches used here
514 do not measure similar quantities at spatial and temporal scale, and all of them have obvious weaknesses, no
515 estimate can be taken as a safe reference value of the "true" weathering rate at the study sites. However, for the
516 purposes of the following discussion, we are of the view that the conceptual differences between these three
517 approaches are an asset in our case, as they provide complementary information about weathering at different
518 scales that helps identifying strengths and weaknesses of each method and provide reasons to why these methods
519 tend to overestimate or underestimate weathering rates of a particular element.

520 **4.2 Pedon scale weathering rates - a comparison with other studies**

521 A general finding of this study concerning weathering at the pedon scale was that total modelled (W_{profile}) and
522 historical ($W_{\text{depletion}}$) base cation weathering rates were in good agreement with recent published data for similar
523 forest sites on podsollic till soils (Stendahl et al., 2013). However, the historical weathering rates at Asa were of
524 similar magnitude to the lowest historical weathering rate observed by Stendahl et al. (2013). Most Nordic studies
525 on historical weathering rates have been conducted in the boreal region (Tamm, 1920, 1931; Land et al., 1999;
526 Olsson and Melkerud, 2000; Stendahl et al., 2013; Starr et al., 2014). Even though soil profile depth and soil age
527 in these weathering studies differ from those in ours, they obtained higher rates (Land et al., 1999; Olsson and
528 Melkerud, 2000; Stendahl et al., 2013), similar rates (Stendahl et al., 2013) or lower rates (Starr et al., 2014) for
529 soils developed on glacial tills.

530 **4.2.1 Depletion method estimates versus PROFILE model estimates**

531 A major finding of this study was that, in the 0-50 cm soil profile, W_{profile} was higher than $W_{\text{depletion}}$ for all elements
532 except Na, and the methods generally failed to fulfil our first test criterion concerning weathering in the soil profile
533 as a whole. However, weathering rates estimated by the depletion method and the PROFILE model can be
534 expected to differ due to differences in temporal scale. Several studies have concluded that the average historical
535 weathering rate should generally be higher than the present weathering rate, since soil development involves loss
536 of easily weatherable minerals and ageing of mineral surfaces (Bain et al., 1993; Taylor and Blum, 1995; White
537 et al., 1996). In a study using the Historic-SAFE model, applied to the Lake Gårdsjön catchment in southwestern
538 Sweden, Sverdrup et al. (1998) predicted a decline in weathering rates due to assumed disappearance of fine
539 particles and loss of minerals. Their results suggested an increase in weathering rates, from the end of the
540 glaciation 12,000 years B.P. towards a peak at 9000 years B.P., followed by a gradual decrease below initial
541 levels.

542 However, in the present study PROFILE generally yielded higher weathering rates than the depletion method at
543 both study sites. Similar results have been found in other studies, as indicated by high modelled-to-historic
544 weathering rate ratio ($W_{\text{profile}}/W_{\text{depletion}}$). At catchment scale, Augustin et al. (2016) found that weathering
545 estimated by PROFILE was on average 4-fold greater than weathering based on the depletion method. At the
546 pedon scale, Stendahl et al. (2013) found $W_{\text{profile}}/W_{\text{depletion}}$ ratios of 2.3 and 2.2 for two sites near Flakaliden,
547 Vindeln and Svartberget, which are similar values to that found for Flakaliden in our study (2.0). However, the
548 geographically closest site to Asa (Lammhult) had a much lower ratio (1.1, compared with 3.5 in our study).



549 Similarly low ratios have been reported for the Gårdsjön site situated in south-western Sweden (i.e. county of
550 Västra Götaland) (Sverdrup et al., 1998; Stendahl et al., 2013), while the high ratio we obtained for Asa was close
551 to that (4.6) reported by Stendahl et al. (2013) for Skånes Vårsjö, another site located in south-western Sweden
552 (i.e. county of Skåne). An exception to the general trend of higher steady-state PROFILE weathering rates
553 compared to historical rates calculated by the depletion method, was found for Mg at the Flakaliden site, where
554 $W_{\text{depletion}}$ was 1.3-fold greater than W_{profile} in the upper mineral soil, but only at Flakaliden.. This exception with
555 regard to Mg was also found by Stendahl et al. (2013) for all of their 16 study sites.

556 Our second test, postulating similarity between methods concerning the weathering rate gradient with soil depth,
557 was not fulfilled, because the PROFILE model predicted increasing weathering rates with increasing soil depth,
558 contrary to the depletion method. Since soil-forming processes and ageing of minerals suggest that the present
559 weathering rate might differ from the average historical value, we calculated the hypothetical time needed for the
560 simulated current weathering rates to accomplish the element losses determined with the depletion method.
561 Specifically, one can imagine a front of intense weathering moving down through the soil profile, during which a
562 pristine horizon would undergo an episode, limited in time, of intense weathering followed by slower weathering
563 in the ageing material. In concert with this notion, the highest weathering rate, presently prevailing at
564 approximately 80 cm (Asa) or 60 cm (Flakaliden) depth according to PROFILE (Fig. 2), would cause the observed
565 depletion losses within less than half of the soil age ('max rates' in Fig. 6). However, the calculation also showed
566 that the present minimum weathering rate, simulated for the topmost 1-3 layers (Fig. 2) would often "do the job"
567 in less than the postglacial period ('min rates' in Fig. 6), particularly at Flakaliden, and for K and Na also at Asa.
568 Hence, the current minimum weathering rates according to PROFILE are not generally sustainable within the
569 limits set by the depletion method, indicating either bias in either of the methods, or a current weathering pressure
570 that is correctly modelled but exceeds the historical average. Casetou-Gustafson et al. (*this issue*) could
571 demonstrate that K-feldspar was the dominant source of all steady state PROFILE weathering of K and there are
572 indications that the dissolution rate for K-feldspar is too high compared with mica. For example, Thompson and
573 Ukrainczyk (2002) described differences in the plant availability of K via weathering from these two mineral
574 groups. In addition, Simonsson et al. (2016) found that, although K-feldspar was the dominant K-bearing mineral
575 in a till soil in south-western Sweden, a large proportion of the K loss was explained by mica. Furthermore and in
576 more general terms, Hodson and Langan (1999) suggested that the PROFILE model overestimates weathering
577 rates because it does not consider the decrease in mineral reactivity that has taken place over time and because it
578 assumes that all mineral surface areas are reactive. If this is not accounted for, PROFILE can be expected to
579 generate overestimates rather than underestimates for base cation weathering rates.

580

581 As to possible errors in weathering rates according to PROFILE, the sensitivity test indicated that the within-
582 profile variability of soil physical properties had a much greater effect on simulated weathering rates than the
583 differences in mineralogy between different horizons. Therefore, the notion of a weathering front, significantly
584 changing the mineralogical composition of the soil, does not appear to be able to result in any episodic modelled
585 weathering for the studied soils; the decline in weathering rate with time is more likely to be attributable to
586 disappearance of fine particles, as also indicated by the positive correlation between W_{profile} and exposed mineral
587 surface area and bulk density (Figs. S1-S2). Moreover, given the variability of physical and mineralogical



588 properties in the investigated soils, fine-tuning parameters related to the exposed mineral surface area is most
589 likely to affect the model output, similarly to the findings of Jönsson et al. (1995). Furthermore, the discrepancy
590 between W_{profile} and $W_{\text{depletion}}$ with respect to soil depth gradient implies that the PROFILE model produces
591 weathering rate patterns that are not in line with the classic notion of weathering rates being highest in the A- or
592 E-horizon (Tamm, 1931). However, it is consistent with the more recent notion that mineral dissolution decreases
593 with increasing time/exposure to weathering (White et al., 1996; Parry et al., 2015). In line with this, the results
594 support the view that historical weathering rates do not show identical depth gradients to steady-state weathering
595 rates, and thus W_{profile} and $W_{\text{depletion}}$ could both be accurate estimates, of steady-state and historical weathering
596 rates, respectively.

597

598 As to possible bias in the historical weathering rates, underestimates are possible at Asa, where the low values of
599 $W_{\text{depletion}}$ can be attributed to the low gradient of Zr in the soil (Fig. 5). This might, in turn, be the result of soil
600 mixing by different means. Mechanical soil scarification was carried out at both Asa and Flakaliden prior to
601 planting of the present stand, which would at least have caused partial mixing or inversion of surficial soil layers.
602 In addition, clearance cairns of unknown age were found in the experimental area, indicating small-scale
603 agriculture in the past. Moreover, if burrowing earthworms have been abundant in the past, they might have
604 produced soil mixing in the upper soil horizons (Taylor et al., 2019), resulting in a complicated and erratic Zr
605 gradient (Fig. 5) resulting in low estimates of historical weathering in the rooting zone (Whitfield et al. 2011).
606 High or near-neutral soil pH and deciduous litter can promote high population densities of burrowing earthworms
607 following forest clearing and agriculture; partly deciduous vegetation indeed dominated at Asa until only 1000-
608 2000 years BP, with species such as Scots pine (*Pinus sylvestris*), *Corylus avellana* (L.), *Betula* spp., *Quercus*
609 spp. and *Tilia* spp. (Greisman et al., 2009). Apart from disturbances, natural variability in weathering rates can
610 likely be attributed to differences in soil texture (i.e. exposed mineral surface area), climate (i.e. temperature and
611 water percolation rate) and mineralogy. At Flakaliden, the small-scale variation in Zr mobility might be one of
612 the driving forces behind the large within-site variation in Zr gradient (Fig. 5). The latter is exemplified in different
613 patterns of Zr enrichment for different soil profiles (Fig. 5). An increase with depth could indicate Zr transport
614 from shallow to deeper soil layers, most significantly reflected in the Zr/base cation ratio for K (Fig. S3). In
615 relation to this, in a column experiment Hodson et al. (2002) found that K was the most sensitive element to Zr
616 mobility and that redistribution of Zr led to insignificant underestimations of base cation weathering. An
617 alternative explanation for the increased subsoil Zr content could be related to the distinct peaks of rare earth
618 metals in the B-horizons of Swedish podsol soils reported by Tyler et al. (2004), who related them to increased
619 solubility. Increasing Zr concentration in the B-horizon of forest soils in northern Sweden has also been reported
620 by Melkerud et al. (2000) and, in particular, in a study by Olsson and Melkerud (2000).

621

622 Regardless of errors in the Zr gradients, both $W_{\text{depletion}}$ and W_{profile} showed more marked gradients with soil depth
623 at Flakaliden compared to Asa. This could be expected based on the more well-developed podsol profile at
624 Flakaliden. It has been postulated that the formation of podsoles is enhanced by long duration and great depth of
625 snow cover (Jauhiainen, 1973; Schaetzl and Isard, 1996), which would imply that podsoles have developed better
626 at Flakaliden than at Asa (Lundström et al., 2000). At Flakaliden, the average mass loss of Ca and Mg was 4.0-



627 fold larger in the E-horizon than in the B-horizon, which is similar to findings by Olsson and Melkerud (2000) of
628 a 5-fold higher ratio between losses of base cations in the E- compared with the B-horizon. The average mass loss
629 since last deglaciation at Flakaliden indicated strong depletion of Ca- and Mg-bearing minerals in the beginning
630 of the pedogenesis process, which was reflected in the higher historical weathering rates than the steady-state
631 modelled rates in the upper mineral soil.

632

633 The weathering rates of PROFILE may be criticized based on discrepancies in the ranking order of weathering of
634 elements, compared to historical weathering; this is our third test criterion. PROFILE predicted the highest steady-
635 state weathering for Na at both sites. However, historical weathering at Asa was greatest for Ca among the base
636 cation elements, whereas Mg was the most abundant element released at Flakaliden. The latter was also found by
637 Olsson and Melkerud (2000), who reported the same ranking order of individual base cation weathering (i.e.
638 $Mg > Ca > Na > K$) for other sites in northern Sweden.

639 4.3 Weathering in a mass balance perspective

640 The mass balance approach resulted in consistently much higher weathering rates than PROFILE and the depletion
641 method for all base cations except Na. This discrepancy was particularly large at Asa. However, it must be stressed
642 that mass balance estimates of weathering are associated with substantial uncertainties from different sources.
643 Although the standard error in W_{MB} in the present study was moderate for all elements except Ca, the mass balance
644 approach most likely underestimated the true uncertainty. Low or moderate standard error was partly due to base
645 cation uptake in biomass and deposition being calculated as site means only, which would have reduced between-
646 plot variation in W_{MB} for elements (e.g. K) for which soil changes and leaching were small and accumulation in
647 biomass was large. Apart from between-plot variation, additional sources of uncertainties originate from
648 propagation of uncertainties in methods used for each term in the mass balance, e.g. allometric biomass functions,
649 and precision in soil sampling and chemical analyses. Simonsson et al. (2015) estimated weathering rates for the
650 Skogaby site in south-western Sweden, a Norway spruce site of similar stand age and soil condition as Asa, using
651 the same methods as in the present study. Accounting for all sources of uncertainty, they found that the 95%
652 confidence interval in estimates of base cation weathering was 2.6 times the mean ($33 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$). The
653 confidence interval was the same as the mean value for Mg, but much larger for the other elements.

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

661 The Na fluxes differed from those of the other base cations, probably because Ca, Mg and K are important plant
662 nutrients whereas Na is not. Calcium and Mg uptake in forest trees is considered to be more or less passive flow



663 driven by transpiration fluxes, whereas K uptake is an energy-demanding active process (Nieves-Cordones et al.,
664 2014). Considering that Na was the dominant base cation in the soil solution at 50 cm soil depth (Fig. 4), the
665 negligible accumulation of Na in tree biomass suggests that Na uptake in trees is physiologically blocked. Low
666 concentrations of Na seem to be a general feature of terrestrial plants in boreal forests, in contrast to aquatic plants,
667 which explains why the latter are considered important Na sources for large herbivores like moose (Ohlson and
668 Staaland, 2001). Thus, the negligible Na accumulation in tree biomass and the particularly low deposition at
669 Flakaliden simplify the Na mass balance to only three major counterbalancing fluxes: weathering, deposition and
670 leaching. Since $W_{\text{depletion}}$ and W_{mb} of Na were fairly similar, and were much lower than W_{profile} , our results provide
671 additional support for the claim that the PROFILE model produced consistently too high Na weathering.

672 Accumulation of Ca, Mg and K in biomass made up the dominant sink. Since deposition and measured depletion
673 of extractable Ca, K and Mg in the soil did not balance this sink, substantial missing sources (here estimated
674 weathering rate) were needed to reach a balance. Using the alternative weathering estimates by PROFILE and the
675 depletion method in the mass balance resulted in even larger estimated depletion in the soil to balance the sinks
676 than was actually measured. Assuming that the measurements of accumulation in biomass, deposition and
677 leaching were reasonably accurate, the results either indicate large uncertainties in measures of soil changes and/or
678 that additional sources of base cations in the soil balanced the sinks. Uncertainties in estimating soil changes were
679 probably significant, since the estimates of soil depletion were based on two single measurements over 12 years
680 and the extraction procedures were not identical over time. Nevertheless, the changes observed in extractable Ca
681 stocks in the soil are in line with observations over 22 years of aggrading Norway spruce forests by Zetterberg et
682 al. (2016), who reported exchangeable Ca depletion rates of 5-11 and 23-39 $\text{mmol}_c \text{ m}^2 \text{ yr}^{-1}$ for sites in south-
683 western and northern Sweden, respectively. The higher value for the northern site reflected higher Ca saturation
684 in the soil. The corresponding values for Asa and Flakaliden were larger, but of similar magnitude (34.5 and 40.5
685 $\text{mmol}_c \text{ m}^2 \text{ yr}^{-1}$, respectively). Moreover, exchangeable K stocks in the soil normally show little variation over time
686 (B.A. Olsson, unpublished data). Great depletion in exchangeable K stocks in the soil is therefore unlikely. The
687 results therefore suggest that other sources exist in the soil, apart from weathering ($W_{\text{depletion}}$, W_{profile}) and depletion
688 of ammonium-chloride-extractable base cation stocks. It is well known that the exchangeable nutrient stock in the
689 soil is defined by the extraction medium and procedure. A test of different extractants used on the soils in the
690 present study revealed that using NH_4OAc posed a risk of underestimating the amounts of base cations in the soil
691 and that the yield of exchangeable base cations decreased in the order aqua regia > HCl > EDTA > BaCl_2 >
692 NH_4OAc (Olofsson, 2016). Using a more potent extractant than 1 M NH_4Cl would probably have resulted in
693 different findings on the change in extractable and plant-available base cations in the soil. Regarding K, fixed or
694 structural K in clay minerals provides a dynamic pool of K that is not included in modelled weathering or in
695 NH_4Cl -extractable K (Simonsson et al., 2016). Regarding Ca and Mg, dissolution from non-crystalline/amorphous
696 compounds can be an important source in soils depleted of these elements (Van der Heijden et al., 2017).

697 Another possible explanation for the higher weathering rates with the mass balance approach is that PROFILE
698 may produce conservative estimates of weathering because the model only captures steady-state chemical
699 processes. It has been postulated that e.g. mycorrhizae play an important role in nutrient uptake in forest trees



700 through active foraging by mycelia at mineral surfaces, but the nature and potential importance of biotic control
701 of weathering has been much debated in recent decades (Finlay et al., 2008; Sverdrup, 2009; Smits and Wallander,
702 2017). Based on the results of the present study, the hypothesis of significant biological control of weathering was
703 not rejected.

704 **5. Conclusions**

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

722 **6. Authors contribution**

723 Authors contributed to the study as in the following: S. Casetou-Gustafson: study design, data treatment, analyses,
724 interpretation and writing. Magnus Simonsson: study design, analysis, interpretation and writing. Johan Stendahl:
725 study design, analysis, interpretation and writing. B.A. Olsson: study design, data treatment, analysis,
726 interpretation and writing. S. Hillier: interpretation and writing. Sune Linder: Provided long-term experimental
727 data, interpretation and writing. Herald Grip: Provided long-term experimental data, interpretation, and writing

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734

735 **8. References**

- 736 Akselsson, C., Westling, O., Sverdrup, H., Holmqvist, J., Thelin, G., Uggla, E., and Malm, G.: Impact
737 of harvest intensity on long-term base cation budgets in Swedish forest soils, *Water Air Soil Poll.:*
738 *Focus*, 7, 201-210, 2007.
- 739 Akselsson, C., Hultberg, H., Karlsson, P. E., Karlsson, G. P., and Hellsten, S.: Acidification trends in
740 south Swedish forest soils 1986–2008—Slow recovery and high sensitivity to sea-salt episodes, *Sci.*
741 *Total Environ.*, 444, 271-287, 2013.
742
- 743 Akselsson, C., Belyazid, S., Stendahl, J., Finlay, R., Olsson, B.A., Erlandsson
744 Lampa, M., Wallander, H., Gustafsson, J.P., and Bishop, K. H.: Weathering rates in Swedish forest
745 soils, In review in *Biogeosciences* (this issue).
746
- 747 Albaugh, T. J., Bergh, J., Lundmark, T., Nilsson, U., Stape, J. L., Allen, H. L., and Linder, S.: Do
748 biological expansion factors adequately estimate stand-scale aboveground component biomass for
749 Norway spruce?, *Forest Ecol. Manag.*, 258, 2628-2637, 2009.
- 750 Albaugh, T. J., Bergh, J., Lundmark, T., Nilsson, U., Stape, J. L., Allen, H. L., and Linder, S.:
751 Corrigendum to “Do biological expansion factors adequately estimate stand-scale aboveground
752 component biomass for Norway spruce?”, *Forest Ecol. Manag.*, 270, 314, 2012.
- 753 Augustin, F., Houle, D., Gagnon, C., and Courchesne, F.: Evaluation of three methods for estimating
754 the weathering rates of base cations in forested catchments, *Catena*, 144, 1-10, 2016.
- 755 Bailey, S. W., Buso, D. C., and Likens, G. E.: Implications of sodium mass balance for interpreting the
756 calcium cycle of a forested ecosystem, *Ecology*, 84, 471-484, 2003.
- 757 Bain, D. C., Mellor, A., Robertson-Rintoul, M., and Buckland, S.: Variations in weathering processes
758 and rates with time in a chronosequence of soils from Glen Feshie, Scotland, *Geoderma*, 57, 275-293,
759 1993.
- 760 Bain, D. C., Mellor, A., Wilson, M., and Duthie, D.: Chemical and mineralogical weathering rates and
761 processes in an upland granitic till catchment in Scotland, *Water Air Soil Poll.*, 73, 11-27, 1994.
- 762 Bergh, J., Linder, S., Lundmark, T., and Elfving, B.: The effect of water and nutrient availability on the
763 productivity of Norway spruce in northern and southern Sweden, *Forest Ecol. Manag.*, 119, 51-62,
764 1999.
- 765 Bergh, J., Linder, S., and Bergström, J.: Potential production of Norway spruce in Sweden, *Forest Ecol.*
766 *Manag.*, 204, 1-10, 2005.
- 767 Bertills, U., Fölster, J., and Lager, H.: Only natural acidification—in-depth assessment of the
768 environmental objective, Swedish Environmental Protection Agency Report, 5766, 116, 2007.
- 769 Binkley, D., and Högberg, P.: Does atmospheric deposition of nitrogen threaten Swedish forests?,
770 *Forest Ecol. Manag.*, 92, 119-152, 1997.
- 771 Binkley, D., and Högberg, P.: Tamm review: revisiting the influence of nitrogen deposition on Swedish
772 forests, *Forest Ecol. Manag.*, 368, 222-239, 2016.
- 773 Brimhall, G. H., Ford, C., Bratt, J., Taylor, G., and Warin, O.: Quantitative geochemical approach to
774 pedogenesis: importance of parent material reduction, volumetric expansion, and eolian influx in
775 lateritization, *Geoderma*, 51, 51-91, 1991.



- 776 Casetou-Gustafson, S., Akselsson, C., Hillier, S., and Olsson, B. A.: The importance of mineral
777 composition determinations to PROFILE base cation release rates: A case study, In review in
778 Biogeosciences (this issue).
- 779 Casetou-Gustafson, S., Hillier, S., Akselsson, C., Simonsson, M., Stendahl, J., and Olsson, B. A.:
780 Comparison of measured (XRPD) and modeled (A2M) soil mineralogies: A study of some Swedish
781 forest soils in the context of weathering rate predictions, *Geoderma*, 310, 77-88, 2018.
782
- 783 Chadwick, O. A., Brimhall, G. H., and Hendricks, D. M.: From a black to a gray box—a mass balance
784 interpretation of pedogenesis, *Geomorphology*, 3, 369-390, 1990.
- 785 Cosby, B., Hornberger, G., Galloway, J., and Wright, R.: Modeling the effects of acid deposition:
786 Assessment of a lumped parameter model of soil water and streamwater chemistry, *Water Resour. Res.*,
787 21, 51-63, 1985.
- 788 Evans, C., Cullen, J., Alewell, C., Kopáček, J., Marchetto, A., Moldan, F., Prechtel, A., Rogora, M.,
789 Veselý, J., and Wright, R.: Recovery from acidification in European surface waters, *Hydrol. Earth Syst.*
790 *Sci.*, 5, 283-298, 2001.
791
- 792 Finlay, R., Wallander, H., Smits, M., Holmstrom, S., Van Hees, P., Lian, B., and Rosling, A.: The role
793 of fungi in biogenic weathering in boreal forest soils, *Fungal Biol. Rev.*, 23, 101-106, 2009.
- 794 Fréden, C.: The National Atlas of Sweden, Geology, Third Ed. SNA Publishing House, Stockholm,
795 Sweden, 2009.
- 796 Fröberg, M., Grip, H., Tipping, E., Svensson, M., Strömgen, M., and Kleja, D. B.: Long-term effects
797 of experimental fertilization and soil warming on dissolved organic matter leaching from a spruce forest
798 in Northern Sweden, *Geoderma*, 200, 172-179, 2013.
- 799 Futter, M., Ring, E., Högbom, L., Entenmann, S., and Bishop, K.: Consequences of nitrate leaching
800 following stem-only harvesting of Swedish forests are dependent on spatial scale, *Environ. Pollut.*, 158,
801 3552-3559, 2010
- 802 Futter, M., Klaminder, J., Lucas, R., Laudon, H., and Köhler, S.: Uncertainty in silicate mineral
803 weathering rate estimates: source partitioning and policy implications, *Environ Res. Lett.*, 7, 024025,
804 2012.
- 805 Greisman, A., and Gaillard, M. J.: The role of climate variability and fire in early and mid Holocene
806 forest dynamics of southern Sweden, *J. Quaternary Sci.*, 24, 593-611, 2009.
- 807 Grennfelt, P., and Hov, Ø.: Regional air pollution at a turning point, *Ambio*, 2-10, 2005.
- 808 Harden, J. W.: Soils developed in granitic alluvium near Merced, California, Geological Survey
809 Bulletin (USA) 1590-A, Soil Chronosequences in the Western United States, Government Printing
810 Office, Washington DC, USA, A1-A65, 1987.
811
- 812 Hedin, L. O., Granat, L., Likens, G. E., Buishand, T. A., Galloway, J. N., Butler, T. J., and Rodhe, H.:
813 Steep declines in atmospheric base cations in regions of Europe and North America, *Nature*, 367, 351-
814 354, 1994.



- 815 Hedwall, P. O., Grip, H., Linder, S., Lövdahl, L., Nilsson, U., and Bergh, J.: Effects of clear-cutting
816 and slash removal on soil water chemistry and forest-floor vegetation in a nutrient optimised Norway
817 spruce stand, *Silva Fenn.*, 47, article id 933, 2013.
- 818 Hellsten, S., Helmisaari, H. S., Melin, Y., Skovsgaard, J. P., Kaakinen, S., Kukkola, M., Saarsalmi, A.,
819 Petersson, H., and Akselsson, C.: Nutrient concentrations in stumps and coarse roots of Norway spruce,
820 Scots pine and silver birch in Sweden, Finland and Denmark, *Forest Ecol. Manag.*, 290, 40-48, 2013.
821
- 822 Helmisaari, H.-S., Derome, J., Nöjd, P., and Kukkola, M.: Fine root biomass in relation to site and stand
823 characteristics in Norway spruce and Scots pine stands, *Tree Physiol.*, 27, 1493-1504, 2007.
- 824 Hillier, S.: Use of an air brush to spray dry samples for X-ray powder diffraction, *Clay Miner.*, 34, 127-
825 127, 1999.
- 826 Hillier, S.: Quantitative analysis of clay and other minerals in sandstones by X-ray powder diffraction
827 (XRPD), in: *Clay Mineral Cements in Sandstones*, edited by: Worden, R., Morad, S.: International
828 Association of Sedimentologist, Special Publication, John Wiley and Sons Ltd, Oxford, United
829 Kingdom, 34, 213-251, 2003.
- 830 Hodson, M. E., Langan, S. J., and Wilson, M. J.: A sensitivity analysis of the PROFILE model in
831 relation to the calculation of soil weathering rates, *Appl. Geochem.*, 11, 835-844, 1996.
832
- 833 Hodson, M. E., and Langan, S. J.: The influence of soil age on calculated mineral weathering rates,
834 *Appl. Geochem.*, 14, 387-394, 1999.
835
- 836 Hodson, M. E.: Experimental evidence for mobility of Zr and other trace elements in soils, *Geochim.
837 Cosmochim. Acta*, 66, 819-828, 2002.
- 838 Jansson, P.-E.: CoupModel: model use, calibration, and validation, *Trans. Am. Soc. Agric. Eng.*, 55,
839 1337-1344, 2012.
- 840 Jauhiainen, E.: Age and degree of podzolization of sand soils on the coastal plain of northwest Finland,
841 *Comm. Biol.*, 68, 1-32, 1973.
- 842 Jönsson, C., Warfvinge, P., and Sverdrup, H.: Uncertainty in predicting weathering rate and
843 environmental stress factors with the PROFILE model, *Water Air Soil Poll.*, 81, 1-23, 1995.
- 844 Karlsson, P. E., Ferm, M., Hultberg, H., Hellsten, S., Akselsson, C., and Pihl Karlsson, G.:
845 Totaldeposition av kväve till skog, IVL Swedish Environmental Research Institute, Stockholm, Sweden
846 37, 2012.
847
- 848 Karlsson, P. E., Ferm, M., Hultberg, H., Hellsten, S., Akselsson, C., and Pihl Karlsson, G.:
849 Totaldeposition av baskatjoner till skog, IVL Swedish Environmental Research Institute, Stockholm,
850 Sweden 65, 2013.
851
- 852 Kellner, O.: Effects of fertilization on forest flora and vegetation, Ph.D. thesis, Comprehensive
853 Summaries of Uppsala Dissertations from the Faculty of Science, Uppsala University, Sweden, 464, 32
854 pp., 1993.
855
- 856 Klaminder, J., Grip, H., Mörth, C.-M., and Laudon, H.: Carbon mineralization and pyrite oxidation in
857 groundwater: Importance for silicate weathering in boreal forest soils and stream base-flow chemistry,
858 *Appl. Geochem.*, 26, 319-325, 2011a.



- 859 Klaminder, J., Lucas, R., Futter, M., Bishop, K., Köhler, S., Egnell, G., and Laudon, H.: Silicate mineral
860 weathering rate estimates: Are they precise enough to be useful when predicting the recovery of nutrient
861 pools after harvesting?, *Forest Ecol. Manag.*, 261, 1-9, 2011b.
- 862 Kolka, R. K., Grigal, D., and Nater, E.: Forest soil mineral weathering rates: use of multiple approaches,
863 *Geoderma*. Vol. 73 (1): 1-21.(1996), 73, 1996.
- 864 Kronnäs, V., Akselsson, C., and Belyazid, S.: Dynamic modelling of weathering rates – Is there any
865 benefit over steady-state modelling?, *SOIL*, 5, 33-47, 2019.
- 866 Land, M., Ingri, J., and Öhlander, B.: Past and present weathering rates in northern Sweden, *Appl.*
867 *Geochem.*, 14, 761-774, 1999.
- 868 Langan, S. J., Sverdrup, H. U., and Coull, M.: The calculation of base cation release from the chemical
869 weathering of Scottish soils using the PROFILE model, *Water Air Soil Poll.*, 85, 2497-2502, 1995.
- 870 Lampa Erlandsson, M., Sverdrup, H.U., Bishop, K.H., Belyazid, S., Ameli, A., and Köhler, S. J.:
871 Catchment export of base cations: Improved mineral dissolution kinetics influence the role of water
872 transit time, In review in *Biogeosciences* (this issue).
- 873
- 874 Likens, G. E., and Bormann, F. H.: Acid rain: a serious regional environmental problem, *Science*, 184,
875 1176-1179, 1974.
- 876
- 877 Likens, G. E., Driscoll, C. T., Buso, D. C., Siccama, T. G., Johnson, C. E., Lovett, G. M., Fahey, T. J.,
878 Reiners, W. A., Ryan, D. F., Martin, C. W., and Bailey, S. W.: The biogeochemistry of calcium at
879 Hubbard Brook, *Biogeochemistry*, 41, 89-173, 1998.
- 880 Linder, S.: Foliar analysis for detecting and correcting nutrient imbalances in Norway spruce, *Ecol.*
881 *Bull.*, 178-190, 1995.
- 882 Lundström, U., Van Breemen, N., Bain, D., Van Hees, P., Giesler, R., Gustafsson, J. P., Ilvesniemi, H.,
883 Karlton, E., Melkerud, P.-A., and Olsson, M.: Advances in understanding the podzolization process
884 resulting from a multidisciplinary study of three coniferous forest soils in the Nordic Countries,
885 *Geoderma*, 94, 335-353, 2000.
- 886 Löfgren, S., Aastrup, M., Bringmark, L., Hultberg, H., Lewin-Pihlblad, L., Lundin, L., Karlsson, G. P.,
887 and Thunholm, B.: Recovery of soil water, groundwater, and streamwater from acidification at the
888 Swedish Integrated Monitoring catchments, *Ambio*, 40, 836-856, 2011.
- 889 Marklund, L. G.: Biomass functions for pine, spruce and birch in Sweden, Department of Forest Survey,
890 Swedish University of Agricultural Sciences, Umea, Sweden, Report 45, 1-73, 1988.
- 891
- 892 Marshall, C., and Haseman, J.: The quantitative evaluation of soil formation and development by heavy
893 mineral studies: A Grundy silt loam profile 1, *Soil Sci. Soc. Am. J.*, 7, 448-453, 1943.
- 894 Melkerud, P.-A., Bain, D., Jongmans, A., and Tarvainen, T.: Chemical, mineralogical and
895 morphological characterization of three podzols developed on glacial deposits in Northern Europe,
896 *Geoderma*, 94, 125-148, 2000.
- 897 Nieves-Cordones, M., Alemán, F., Martínez, V., and Rubio, F.: K⁺ uptake in plant roots. The systems
898 involved, their regulation and parallels in other organisms, *Journal of plant physiology*, 171, 688-695,
899 2014.



- 900 Nilsson, S. I., Miller, H. G., and Miller, J. D.: Forest Growth as a Possible Cause of Soil and Water
901 Acidification - an Examination of the Concepts, *Oikos*, 39, 40-49, 1982.
- 902 Nykvist, N.: Effects of clearfelling, slash removal and prescribed burning on amounts of plant nutrients
903 in biomass and soil, Swedish University of Agricultural Sciences, Department of Forest Ecology,
904 Uppsala, Sweden, 210, 2000.
905
- 906 Ohlson, M., and Staaland, H.: Mineral diversity in wild plants: benefits and bane for moose, *Oikos*, 94,
907 442-454, 2001.
- 908 Olofsson, J.: Base cations in forest soils: A pilot project to evaluate different extraction methods,
909 Swedish University of Agricultural Sciences, Uppsala, 2016.
- 910 Olsson, B. A.: Effects of biomass removal in thinnings and compensatory fertilization on exchangeable
911 base cation pools in acid forest soils, *Forest Ecol. Manag.*, 122, 29-39, 1999.
- 912 Olsson, B. A., Bengtsson, J., and Lundkvist, H.: Effects of different forest harvest intensities on the
913 pools of exchangeable cations in coniferous forest soils, *Forest Ecol. Manag.*, 84, 135-147, 1996.
914
- 915 Olsson, M., and Melkerud, P.-A.: Chemical and mineralogical changes during genesis of a Podzol from
916 till in southern Sweden, *Geoderma*, 45, 267-287, 1989.
917
- 918 Olsson, M. T., and Melkerud, P.-A.: Weathering in three podzolized pedons on glacial deposits in
919 northern Sweden and central Finland, *Geoderma*, 94, 149-161, 2000.
- 920 Olsson, M., Rosén, K., and Melkerud, P.-A.: Regional modelling of base cation losses from Swedish
921 forest soils due to whole-tree harvesting, *Appl Geochem*, 8, 189-194, 1993.
922
- 923 Omotoso, O., McCarty, D. K., Hillier, S., and Kleeberg, R.: Some successful approaches to quantitative
924 mineral analysis as revealed by the 3rd Reynolds Cup contest, *Clay Clay Miner.*, 54, 748-760, 2006.
- 925 Parry, S. A., Hodson, M. E., Kemp, S. J., and Oelkers, E. H.: The surface area and reactivity of granitic
926 soils: I. Dissolution rates of primary minerals as a function of depth and age deduced from field
927 observations, *Geoderma*, 237, 21-35, 2015.
928
- 929 Petersson, H., and Ståhl, G.: Functions for below-ground biomass of *Pinus sylvestris*, *Picea abies*,
930 *Betula pendula* and *Betula pubescens* in Sweden, *Scand. J. Forest Res.*, 21, 84-93, 2006.
- 931 R, C. T.: R: A Language and Environment for Statistical Computing. R Foundation for Statistical
932 Computing, Vienna, Austria, 2016.
- 933 Reuss, J. O., and Johnson, D.W.: Acid Deposition and the Acidification of Soils and Waters, *Ecol.*
934 *Stud.*, 95, 1986.
935
- 936 Ryan, M. G.: Three decades of research at Flakaliden advancing whole-tree physiology, forest
937 ecosystem and global change research, *Tree Physiol.*, 33, 1123-1131, 2013.
- 938 Schaetzl, R. J., and Isard, S. A.: Regional-scale relationships between climate and strength of
939 podzolization in the Great Lakes region, North America, *Catena*, 28, 47-69, 1996.



- 940 Schützel, H., Kutschke, D., and Wildner, G.: Zur Problematik der Genese der Grauen Gneise des
941 sächsischen Erzgebirges (zirkonstatistische Untersuchungen), VEB Deutscher Verlag für
942 Grundstoffindustrie, Leipzig, 1963.
- 943 Sigurdsson, B. D., Medhurst, J. L., Wallin, G., Eggertsson, O., and Linder, S.: Growth of mature boreal
944 Norway spruce was not affected by elevated [CO₂] and/or air temperature unless nutrient availability
945 was improved, *Tree Physiol.*, 33, 1192-1205, 2013.
- 946 Simonsson, M., and Berggren, D.: Aluminium solubility related to secondary solid phases in upper B
947 horizons with spodic characteristics, *Eur. J. Soil Sci.*, 49, 317-326, 1998.
- 948 Simonsson, M., Bergholm, J., Olsson, B. A., von Brömssen, C., and Öborn, I.: Estimating weathering
949 rates using base cation budgets in a Norway spruce stand on podzolised soil: analysis of fluxes and
950 uncertainties, *Forest Ecol. Manag.*, 340, 135-152, 2015.
- 951 Simonsson, M., Bergholm, J., Lemarchand, D., and Hillier, S.: Mineralogy and biogeochemistry of
952 potassium in the Skogaby experimental forest, southwest Sweden: pools, fluxes and K/Rb ratios in soil
953 and biomass, *Biogeochemistry*, 131, 77-102, 2016.
- 954 Skjelkvåle, B., Mannio, J., Wilander, A., and Andersen, T.: Recovery from acidification of lakes in
955 Finland, Norway and Sweden 1990? 1999, *Hydrol. Earth Syst. Sci.*, 5, 327-338, 2001.
956
- 957 Smits, M. M., and Wallander, H.: Role of mycorrhizal symbiosis in mineral weathering and nutrient
958 mining from soil parent material, in: *Mycorrhizal Mediation of Soil: Fertility, Structure, and Carbon
959 Storage*, edited by: Johnson, N. C., Gehring, C., and Jansa, J., Elsevier, United States, 35-46, 2017.
- 960 Staelens, J., Houle, D., De Schrijver, A., Neiryneck, J., and Verheyen, K.: Calculating dry deposition
961 and canopy exchange with the canopy budget model: review of assumptions and application to two
962 deciduous forests, *Water Air Soil Poll.*, 191, 149-169, 2008.
- 963 Starr, M., Lindroos, A.-J., and Ukonmaanaho, L.: Weathering release rates of base cations from soils
964 within a boreal forested catchment: variation and comparison to deposition, litterfall and leaching
965 fluxes, *Environ. Earth Sci.*, 72, 5101-5111, 2014.
- 966 Stendahl, J., Lundin, L., and Nilsson, T.: The stone and boulder content of Swedish forest soils, *Catena*,
967 77, 285-291, 2009.
- 968 Stendahl, J., Akselsson, C., Melkerud, P.-A., and Belyazid, S.: Pedon-scale silicate weathering:
969 comparison of the PROFILE model and the depletion method at 16 forest sites in Sweden, *Geoderma*,
970 211, 65-74, 2013.
- 971 Strengbom, J., Dahlberg, A., Larsson, A., Lindelow, A., Sandstrom, J., Widenfalk, O., and Gustafsson,
972 L.: Introducing intensively managed spruce plantations in Swedish forest landscapes will impair
973 biodiversity decline, *Forests*, 2, 610-630, 2011.
- 974 Sodom, M., and St. Arnaud, R.: Use of quartz, zirconium and titanium as indices in pedological studies,
975 *Can. J. Soil Sci.*, 51, 385-396, 1971.
- 976 Sverdrup, H.: Chemical weathering of soil minerals and the role of biological processes, *Fungal Biol.*
977 *Rev.*, 23, 94-100, 2009.
- 978 Sverdrup, H., and Rosen, K.: Long-term base cation mass balances for Swedish forests and the concept
979 of sustainability, *Forest Ecol. Manag.*, 110, 221-236, 1998.



- 980 Sverdrup, H., and Warfvinge, P.: Weathering of primary silicate minerals in the natural soil
981 environment in relation to a chemical weathering model, *Water Air Soil Poll.*, 38, 387-408, 1988.
- 982 Sverdrup, H., and Warfvinge, P.: Calculating Field Weathering Rates Using a Mechanistic Geochemical
983 Model Profile, *Appl. Geochem.*, 8, 273-283, 1993.
- 984 Sverdrup, H., Warfvinge, P., and Wickman, T.: Estimating the weathering rate at Gårdsjön using
985 different methods, in: *Experimental Reversal of Rain Effects: Gardsjön Roof Project*, edited by:
986 Hultberg, H., and Skeffington, R., John Wiley & Sons Ltd, Chichester, United Kingdom, 231-249,
987 1998.
- 988 Swedish Forest Agency: Rekommendationer vid uttag av avverkningsrester och askåterföring
989 [Recommendations for harvesting of logging residues and ash return]. *Meddelande 2–2008*. Swedish
990 Forest Agency Jönköping, 2008.
- 991 Tamm, C.-O.: Nitrogen in Terrestrial Ecosystems: Questions of Productivity, Vegetational Changes,
992 and Ecosystem Stability. *Ecological Studies* 81, Springer-Verlag, Berlin, 115, 1991.
993
- 994 Tamm, O.: Markstudier i det nordsvenska barrskogsområdet Reports of the Swedish Institute of
995 Experimental Forestry, 17(3), 49-276, 1920.
- 996 Tamm, O.: Studier över jordmånstyper och deras förhållande till markens hydrologi i nordsvenska
997 skogsterrängar barrskogsområdet, Reports of the Swedish Institute of Experimental Forestry, 26(2),
998 163-355, 1931.
- 999 Taylor, A., and Blum, J. D.: Relation between soil age and silicate weathering rates determined from
1000 the chemical evolution of a glacial chronosequence, *Geology*, 23, 979-982, 1995.
- 1001 Taylor, A., Lenoir, L., Vegerfors, B., and Persson, T.: Ant and earthworm bioturbation in cold-
1002 temperate ecosystems, *Ecosystems*, 1-14, 2019.
- 1003 Thompson, M. L., and Ukrainczyk, L.: Micas, Soil mineralogy with environmental applications, in:
1004 *Soil Mineralogy with Environmental Applications*, edited by: Dixon, J. B., and Schulze, D. G., Soil
1005 Science Society of America Inc., Madison, 431-466 pp., 2002.
- 1006 Tyler, G.: Vertical distribution of major, minor, and rare elements in a Haplic Podzol, *Geoderma*, 119,
1007 277-290, 2004.
- 1008 Van Der Heijden, G., Legout, A., Mareschal, L., Ranger, J., and Dambrine, E.: Filling the gap in Ca
1009 input-output budgets in base-poor forest ecosystems: The contribution of non-crystalline phases
1010 evidenced by stable isotopic dilution, *Geochim. Cosmochim. Acta*, 209, 135-148, 2017.
1011
- 1012 van der Salm, C.: Assessment of the regional variation in weathering rates of loess and clay soils in the
1013 Netherlands, *Water Air Soil Poll.*, 131, 217-243, 2001.
- 1014 Velbel, M. A.: Geochemical mass balances and weathering rates in forested watersheds of the southern
1015 Blue Ridge, *Am. J. Sci.*, 285, 904-930, 1985.
- 1016 Viro, P.: Kivisyiden maarittamisesta, Summary: On the determination of stoniness. *Commun. Inst. For.*
1017 *Fenn.*, 40, 8, 1952.
- 1018 Warfvinge, P., and Bertills, U.: Naturens återhämtning från försurning - aktuell kunskap och
1019 framtidsscenarier, Swedish Environmental Protection Agency Report, 5028, 98, 2000.



- 1020 Warfvinge, P., and Sverdrup, H.: Critical Loads of Acidity to Swedish Forest Soils: Methods, Data and
1021 Results, Reports in Ecology and Environmental Engineering, Dpt. of Chemical Engineering II, Lund
1022 University, Lund, Sweden, 1995.
- 1023 White, A. F., Blum, A. E., Schulz, M. S., Bullen, T. D., Harden, J. W., and Peterson, M. L.: Chemical
1024 weathering rates of a soil chronosequence on granitic alluvium: I. Quantification of mineralogical and
1025 surface area changes and calculation of primary silicate reaction rates, *Geochim. Cosmochim. Acta*, 60,
1026 2533-2550, 1996.
- 1027 Whitfield, C. J., Watmough, S. A., and Aherne, J.: Evaluation of elemental depletion weathering rate
1028 estimation methods on acid-sensitive soils of north-eastern Alberta, Canada, *Geoderma*, 166, 189-197,
1029 2011.
- 1030 Wikström, P., Edenius, L., Elfving, B., Eriksson, L. O., Lämås, T., Sonesson, J., Öhman, K.,
1031 Wallerman, J., Waller, C., and Klintebäck, F.: The Heureka forestry decision support system: an
1032 overview, *Mathematical and Computational Forestry & Natural Resource Sciences*, 3, 87, 2011.
- 1033 Zetterberg, T., Olsson, B. A., Löfgren, S., von Brömssen, C., and Brandtberg, P. O.: The effect of
1034 harvest intensity on long-term calcium dynamics in soil and soil solution at three coniferous sites in
1035 Sweden, *Forest Ecol. Manag.*, 302, 280-294, 2013.
- 1036 Zetterberg, T., Olsson, B. A., Löfgren, S., Hyvönen, R., and Brandtberg, P. O.: Long-term soil calcium
1037 depletion after conventional and whole-tree harvest, *Forest Ecol. Manag.*, 369, 102-115, 2016.
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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 (calendar years)
Asa	K1	9.49	25.04	45.30	20.18	1.10	14300
	K4	7.65	22.59	39.21	30.48	1.09	14300
	F3	4.95	25.26	40.54	29.25	0.99	14300
	F4	8.64	25.69	40.13	25.54	0.94	14300
Flakaliden	15A	1.92	9.21	68.98	19.68	1.89	10150
	14B	7.71	34.09	33.71	24.17	1.35	10150
	10B	7.75	45.17	37.23	8.90	1.36	10150
	11B	9.56	45.07	33.91	10.72	1.47	10150

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Table 2. 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 (%)	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	0.00029	-
	F3	60-70	1.41	0.55	0.87	1.04	0.00028	-
	F4	80-90	1.26	0.49	0.85	0.98	0.00029	-
Flakaliden	10B	60-70	1.09	0.57	0.88	0.87	0.00024	-
	11B	50-60	1.63	0.79	0.82	1.06	0.00043	-
	14B	60-70	1.59	0.70	0.81	1.03	0.00034	-
	15A	60-70	1.46	0.59	0.94	1.15	0.00025	-

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1065 **Table 3.** Description of parameters used in the PROFILE model

Parameter	Description	Unit	Source
Temperature	Site	°C	Measurements at Asa and Flakaliden
Precipitation	Site	m yr ⁻¹	Measurements at Asa and Flakaliden
Total deposition	Site	mmol _c 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 _c 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 _c m ⁻² yr ⁻¹	Previously measured data from Asa and Flakaliden: Concentrations in biomass from Linder (unpublished data). Biomass data from Heureka simulations.
Base cations in litterfall	Site	mmol _c m ⁻² yr ⁻¹	Literature data from Hellsten et al. (2013)
Nitrogen in litterfall	Site	mmol _c m ⁻² yr ⁻¹	Literature data from Hellsten et al. (2013)
Evapofraction	Site	Fraction	Precipitation data and runoff data. Runoff data been calculated based on proportion of runoff to precipitation (R/P) at Gamtratten and Anneboda.
Exposed mineral surface area	Soil	m ² m ⁻³	Own measurements used together with Eq. 5.13 in Warfvinge and Sverdrup (1995)
Soil bulk density	Soil	kg m ⁻³	Own measurements
Soil moisture	Soil	m ³ m ⁻³	Based on paragraph 5.9.5 in Warfvinge and Sverdrup (1995)
Mineral composition	Soil	Weight fraction	Own measurements
Dissolved organic carbon	Soil	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	Soil	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	Soil	atm.	Based on paragraph 5.10.2 in Warfvinge and Sverdrup (1995)

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1068 **Table 4.** 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/low: 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.	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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1078 **Figure captions**

1079 **Figure 1.** Titanium (Ti) to zirconium (Zr) ratio (by concentration) used as an indicator of uniform parent material
1080 in all soil layers at Asa (F3, F4, K1, K4) and Flakaliden (10B, 11B, 14B, 15A).

1081 **Figure 2.** (Left) Historical weathering rate of base cations ($\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) estimated by the depletion method
1082 and (right) steady-state weathering rate estimated by the PROFILE model in different soil layers at Asa and
1083 Flakaliden.

1084 **Figure 3.** Comparison of weathering rates ($\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) for Ca, Mg, Na and K determined with the depletion
1085 method, the PROFILE model and the mass balance method for the 0-50 cm layer at Asa and Flakaliden. Each
1086 error bar represents the standard error calculated based on four soil profiles at each study site.

1087 **Figure 4.** (Left) Sources and (right) sinks of base cations in ecosystem net fluxes at Asa and Flakaliden. The soil
1088 is a net source if soil base cation stocks decrease and a net sink if they increase. 'Mass balance' = current base
1089 cation weathering rate (W_{BC}) estimated with the mass balance method, including measured changes in soil
1090 extractable base cation stocks; 'PROFILE' = soil extractable pools estimated from mass balance using PROFILE
1091 estimates of steady-state weathering rate; 'Historical' = soil extractable pools estimated from mass balance using
1092 estimates of historical weathering rate by the depletion method. 'Measured soil change' and 'Mass balance
1093 estimated soil change' indicates that equation 3 was used to estimate weathering rate or the soil change,
1094 respectively.

1095 **Figure 5.** Zirconium (Zr) gradient in the soil at Asa (K1, K4, F3, F4) and Flakaliden (10B, 11B, 14B, 15A)

1096 **Figure 6.** Time (years) required to achieve the measured historical element loss in different soil layers with
1097 maximum or minimum PROFILE weathering rates at (a) Flakaliden and (b) Asa.

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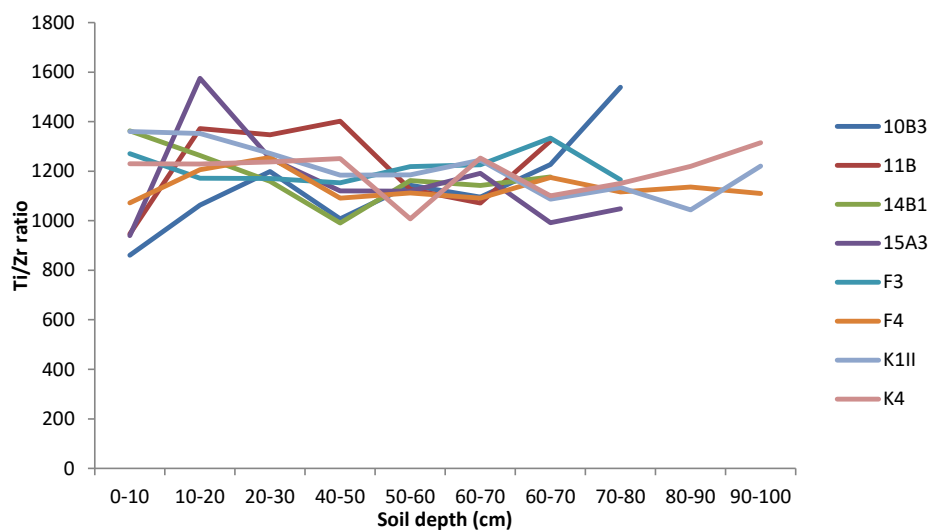
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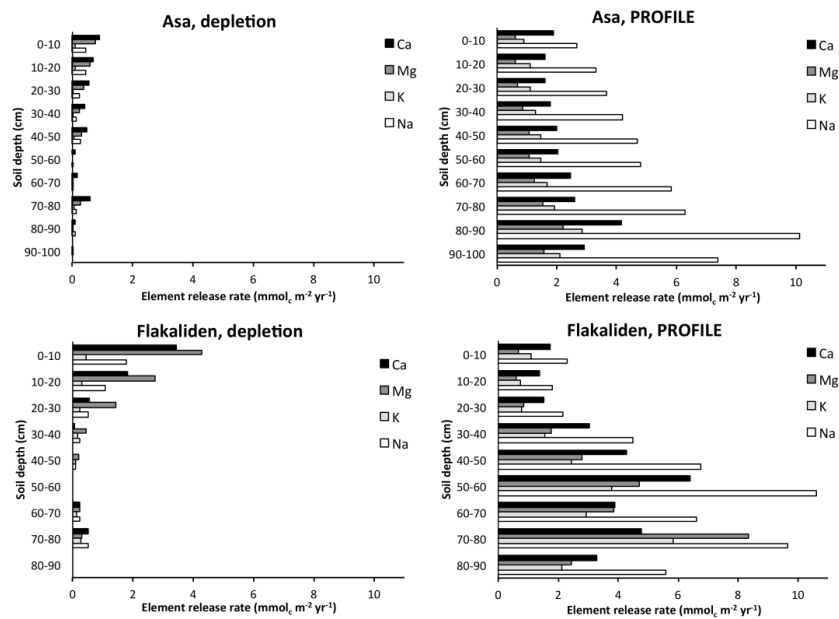


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1109 **Figure 1.**

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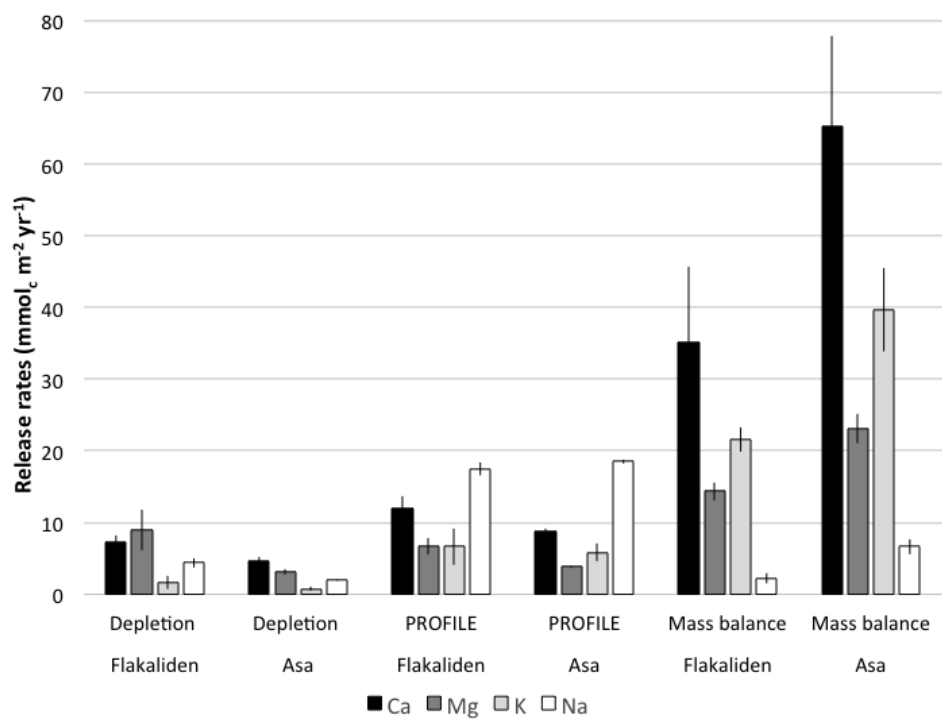
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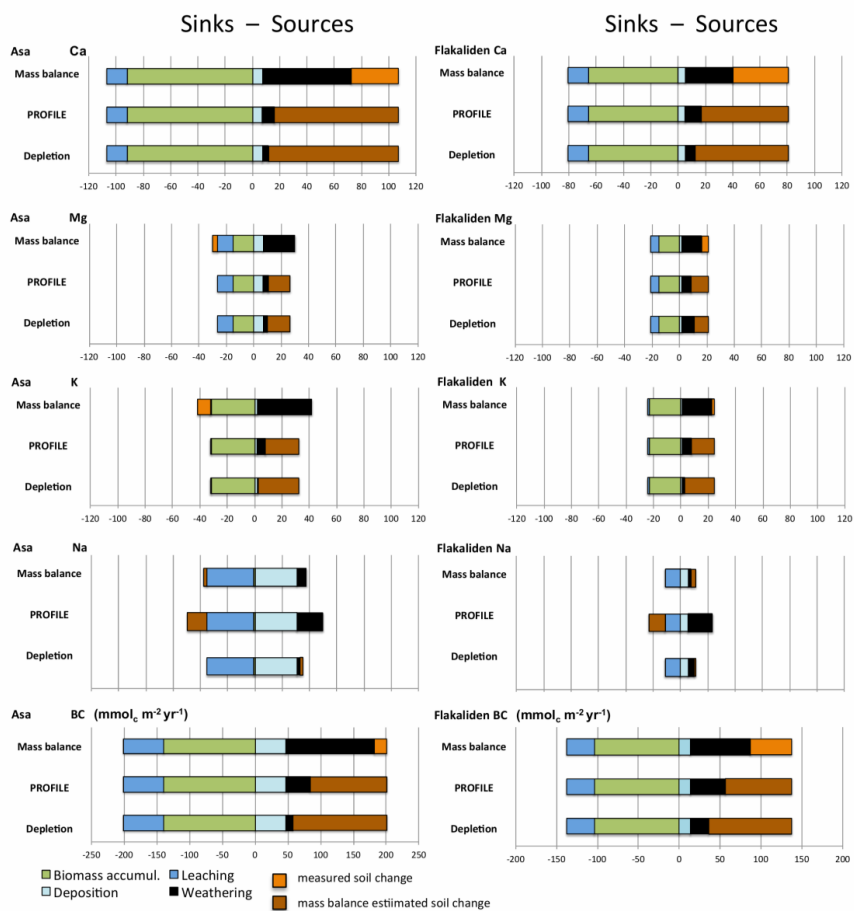
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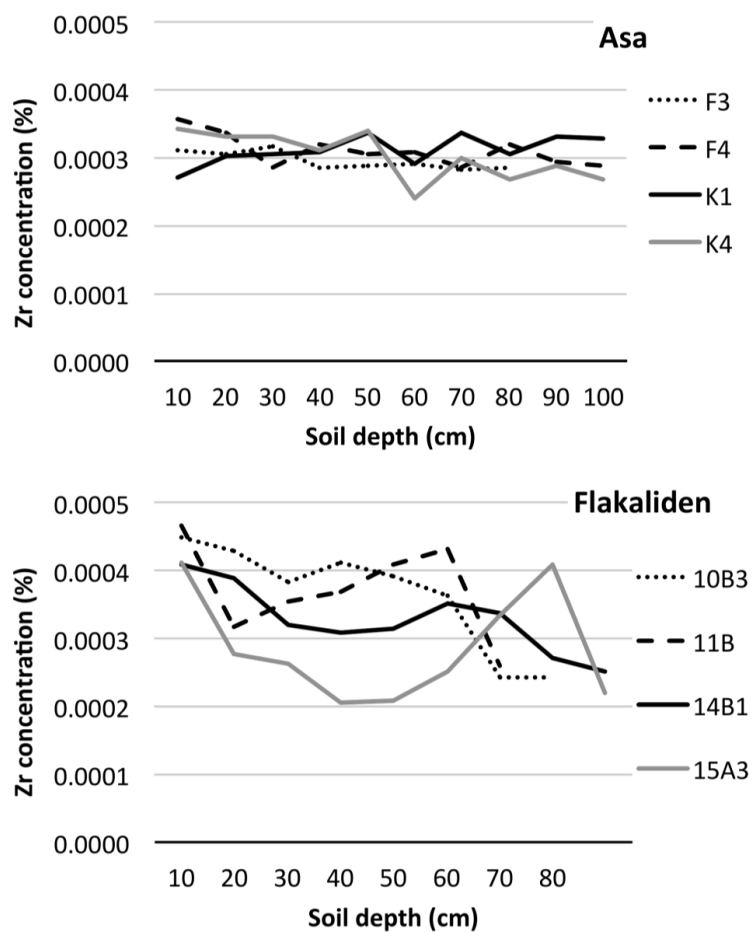
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 1121 **Figure 3.**



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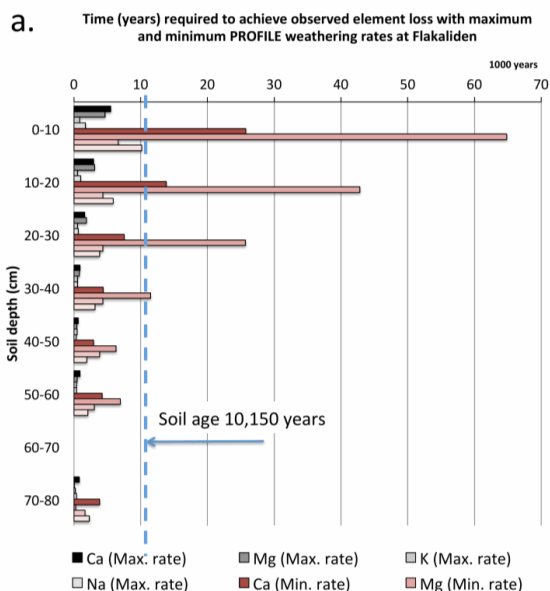
1123 **Figure 4.**

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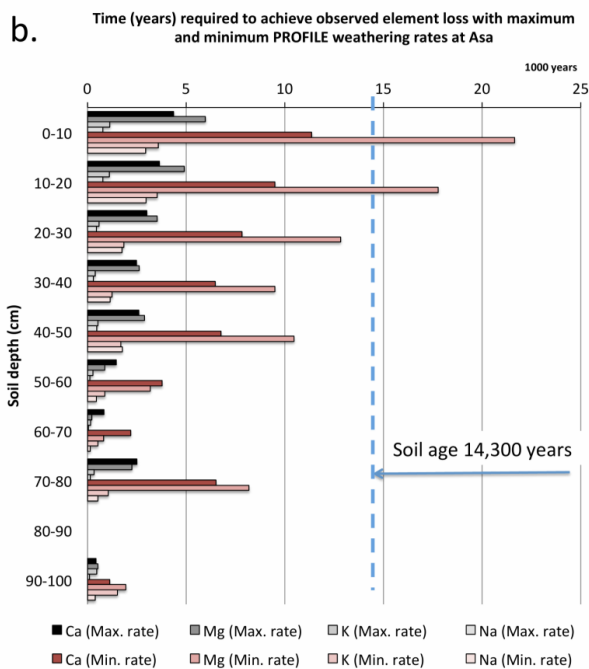


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1126 Figure 5.



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Figure 6.