

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

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27 **Abstract**

28 Reliable and accurate methods for estimating soil mineral weathering rates are required tools in
29 evaluating the sustainability of increased harvesting of forest biomass and assessments of critical loads of
30 acidity. A variety of methods that differ in concept, temporal and spatial scale and data requirements are
31 available for measuring weathering rates. In this study, causes of discrepancies in weathering rates between
32 methods were analyzed and were classified as being either conceptual (inevitable) or random. The release rates
33 of base cations (BC; Ca, Mg, K, Na) by weathering were estimated in podsolised glacial tills at two experimental
34 forest sites, Asa and Flakaliden, in southern and northern Sweden, respectively. Three different methods were
35 used: (i) historical weathering since deglaciation estimated by the depletion method, using Zr as assumed inert
36 reference; (ii) steady-state weathering rate estimated with the PROFILE model, based on quantitative analysis of
37 soil mineralogy; and (iii) BC budget at stand scale, using measured deposition, leaching and changes in base
38 cation stocks in biomass and soil over a period of 12 years. In the 0–50 cm soil horizon historical weathering of
39 BC were 10.6 and 34.1 mmol_c m⁻² yr⁻¹ at Asa and Flakaliden, respectively. Corresponding values of PROFILE
40 weathering rates were 37.1 and 42.7 mmol_c m⁻² yr⁻¹. 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 horizons, particularly at Flakaliden.

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

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

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62 **Definitions and abbreviations**

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

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

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

68

69 $W_{\text{depletion}}$ = Historical weathering rate based on calculation of loss of mobile elements since last deglaciation

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

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

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75 1. Introduction

76 Silicate weathering is the major long-term source of base cations in forest ecosystems (Sverdrup and Warfvinge,
77 1988) and is therefore crucial for sustainable plant production and for proton consumption, counteracting soil
78 and water acidification (Nilsson et al., 1982; Hedin et al., 1994; Likens et al., 1998; Bailey et al., 2003). These
79 effects of weathering are important in areas where in the past high sulphur (S) deposition has caused severe
80 acidification of forest soils and waters (Reuss and Johnson, 1986), for example in southern Scandinavia,
81 northeastern USA and southeastern Canada, regions where felsic igneous bedrock and less readily weatherable
82 soils are abundant (Likens and Bormann, 1974; Nilsson and Tyler, 1995). To aid the multi-lateral negotiations
83 on reducing emissions of acidifying air pollution, the effect-based concept of critical loads of acidity was
84 developed in the late 1980s (Lidskog and Sundqvist, 2002). One advantage of the concept was that the critical
85 loads could be calculated and mapped for different regions at various scales. Because weathering is a key
86 component in estimates of critical loads, reliable applications of the critical load concept required that
87 weathering rates could be estimated with sufficient accuracy at regional scale (Sverdrup and de Vries, 1994).

88
89 By 1990 in most European countries, the trend of increasing S emissions since the 1950s started to abate
90 (Grennfelt and Hov, 2005) with a simultaneous decrease in atmospheric deposition of base cations (Hedin et al.
91 1994). In Sweden, forest growth has at the same time gradually become a relatively more important source to
92 soil acidity (Iwald et al., 2013). Besides the reduction in S deposition, this change has partly been driven by
93 increased use of logging residues for energy production (i.e., whole-tree harvesting), and probably also by a
94 general higher forest production over recent decades in Sweden (Binkley and Högborg 2016). Soil acidification
95 by forest growth is principally caused by accumulation of base cations in tree biomass in excess of anion uptake
96 (Nilsson et al., 1982). The return of base cations in remaining biomass and residues following harvesting
97 determines to what extent the acid load can be neutralised. The soil acidification effect of whole-tree compared
98 to stem-only harvesting has been demonstrated in long-term field experiments (Olsson et al., 1996; Zetterberg et
99 al., 2013). The combined effects can therefore impede recovery from acidification and place increasing demands
100 on nutrient supply.

101
102 The sustainability of increased harvest intensity of forest biomass has been questioned and analysed in many
103 studies from various viewpoints and criteria with focus on Europe and North America (e.g. Boyle et al., 1973;
104 Paré et al., 2002; Thiffault et al., 2011, Achat et al. 2015; De Jong et al., 2017; Ranius et al., 2018), where the
105 role of weathering in maintaining base cation balance being one criterion. The impact of increased use of logging
106 residues on base cation balances in Swedish forest soils has been examined in several previous studies (Sverdrup
107 and Rosén, 1998; Akselsson et al., 2007). A regional-scale study on Swedish forest soils found that, in parts of
108 Sweden, base cation losses can occur at rates that lead to very low base saturation of the soils, possibly leading
109 to negative effects on e.g. soil fertility and runoff water quality within just one forest rotation (Akselsson et al.,
110 2007). In their study, base cation depletion in the soil was found to be more common after whole-tree harvesting
111 than stem-only harvesting, especially for Norway spruce, with deficits being more common in southern than in
112 northern (boreal) Sweden.

113

114 In regional assessments of the sustainability of different harvesting regimes, the estimated weathering rate has a
115 strong influence on the base cation balance. Klaminder et al. (2011) found that different approaches to estimating
116 weathering rates for a forested catchment in northern Sweden yielded results that differed substantially, and that
117 uncertainties in the methods had a great influence on the predicted sustainability of different harvesting
118 practices. Futter et al. (2012) compiled weathering rates estimated at 82 sites on three continents, using different
119 methods, and found both large between-site as well as within-site differences in the values. Differences in input
120 data can be attributed to different time scales used when acquiring different input data, challenges determining
121 accurate mineralogical compositions and the use of field data compared with laboratory data (Van der Salm,
122 2001; Futter et al., 2012). Thus, they recommend that at least three different approaches be applied per study site
123 to evaluate the precision in weathering estimates.

124
125 Different approaches to estimate weathering rates are likely to produce different estimates due to their
126 conceptual differences, but additional sources to discrepancies of more random nature will also appear. The
127 latter may be due to e.g. misfits in spatial scales, measurement errors or uncertainties in model parametrisation.
128 A number of studies comparing different approaches to estimate weathering rates have been published (e.g.
129 Kolka et al., 1996; Sverdrup et al, 1998; Van der Salm et al., 2001; Ouimet and Dechesne, 2005; Whitfield et al.,
130 2006, 2011; Koseva et al., 2010; Klaminder et al., 2011; Stendahl et al., 2013; Futter et al., 2012; Augustin et al.,
131 2016) such that additional studies on this issue may seem redundant. However, several of these comparison
132 studies can be criticized for poor harmonisation with respect to the spatial scale, or that nutrient uptake in
133 biomass and soil change have been neglected, or poorly quantified in approaches where these processes are
134 relevant for the estimates. Poor harmonisation makes it difficult to separate conceptual from random sources of
135 discrepancies. We therefore see a need for improved comparisons, performed with a spatially constrained and
136 refined harmonisation in the sense of Futter et al. (2012), and combined with a focus on forest soils, tree
137 nutrition and growth. Starting from the viewpoint that no method provides the 'true' estimate of weathering, and
138 acknowledging that different approaches are conceptually different and use different input data, in the present
139 paper we examined three approaches in the present paper: (1) 'historical weathering' based on geochemical
140 investigation of the soil profile, (2) modelled present weathering rate and (3) present weathering rate based on
141 cation balances at the ecosystem level.

142
143 The choice of methods was primarily based on the fact that rates of weathering may (do) vary over time
144 (Klaminder et al., 2011; Stendahl et al., 2013). The average weathering under long-term environmental change,
145 i.e. 'historical weathering', is thus different from the weathering potential under present-day environmental
146 conditions, i.e. 'present-day weathering', which is why we need to be able to consider historical weathering
147 when assessing current/present-day weathering rates. Moreover, present-day weathering rates estimated by
148 models based on the steady-state concept, which lacks the dimension of time, may differ from dynamic estimates
149 of weathering rates derived from measured base cation budgets. These three different concepts of estimating
150 weathering cannot be covered by a single method (Klaminder et al., 2011; Futter et al., 2012). Indeed,
151 weathering estimates based on these concepts have often differed grossly from pedon to catchment scale,
152 whereas truly harmonised comparisons of methods require that methods are tested uniformly at the same spatial
153 scale. This spatial scale can be the pedon, which also contains the major part of the mineral nutrient sources in

154 the soil available for forest growth. To our knowledge, Kolka et al. (1996) is the only study to have previously
155 used this multiple approach.

156

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

167

168 The second approach commonly involves the process-based PROFILE model, which has been used widely as a
169 tool to estimate critical loads of acidity in the Nordic countries (e.g. Sverdrup et al., 1992) and North America
170 (Whitfield and Watmough, 2012; Phelan et al., 2014). In PROFILE, release rates of base cations are estimated
171 based on built in assessments of the the dissolution kinetics of a user-defined set of minerals present in the soil,
172 and the physical and chemical conditions that drive the dissolution of those minerals. Because it is a mechanistic
173 model, its strength is its transparency, while its main weakness is the difficulty in setting values of model
174 parameters and input variables to which it may have high sensitivity. Akselsson et al. (2019) concluded that the
175 most important way to reduce uncertainties in modelled weathering rates is to reduce input data uncertainties,
176 e.g. regarding soil texture, although there is still a need to improve process descriptions of e.g. biological
177 weathering and weathering brakes (e.g. Erlandsson Lampa et al., this issue). The sensitivity of PROFILE to
178 variations in soil physical parameters (e.g. soil texture, soil bulk density) and mineral composition was discussed
179 by Jönsson et al. (1995) and Hodson et al. (1996). The importance of the ability to determine the precise identity
180 and quantity of the minerals was analysed by Casetou-Gustafson et al. (2019). They (ibid.) also suggested that
181 the dissolution kinetics of minerals used in the PROFILE model should be revised and the uncertainties assessed
182 to improve the accuracy in model predictions.

183

184 The third approach to estimating weathering rate is the balanced base cation budget approach. This method has
185 been applied to estimate current weathering rates at various temporal and spatial scales, mostly the catchment
186 scale (Velbel, 1985; Likens et al., 1998). In one way of using the approach, mean weathering rates of individual
187 minerals can be estimated at the catchment scale based on data for the mineralogical composition of soils along
188 with element inputs in deposition and outputs in stream water and biomass uptake (e.g. Garrels and Mackenzie,
189 1967; Velbel 1985, Velbel and Price, 2007). Others have estimated weathering as an unknown source from the
190 missing balance between known sources (deposition, soil depletion) and known sinks (uptake, leaching, increase
191 in soil BC stocks) (e.g. Sverdrup et al. 1998; Simonsson et al., 2015). The method requires measurements of
192 known fluxes within a system with defined boundaries. The high data demand restricts the application of the
193 base cation budget approach to a limited number of sites, essentially catchments with long-term monitoring of

194 fluxes and well-defined boundaries. However, even then estimated weathering rates may suffer from large
195 uncertainties, as errors in the sinks and sources accumulate in the mass balance equation (Simonsson et al.,
196 2015). Furthermore, the base cation budget approach has mostly been applied under conditions where
197 accumulation in biomass were not directly measured but estimated to be small, or base cation stocks in the soil
198 were assumed to be at steady-state (e.g. Kolka et al., 1996; Sverdrup et al., 1998; Whitfield et al., 2006).
199 However, the nutrient demand is particularly large during the aggrading phase of a stand development where the
200 foliage biomass is increasing rapidly. Hence, due to difficulties in application of the budget method to regional
201 scale, the PROFILE model and the depletion method are the most commonly used methods in Sweden to
202 estimate weathering rates.

203

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

219

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

223 2. Materials and methods

224 2.1 Study sites

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

229

230 The experiment at Flakaliden was established in 1986 in a 23-year-old Norway spruce stand, planted in 1963
231 with four-year-old seedlings of local provenance after prescribed burning and soil scarification (Bergh et al.,
232 1999). The experiment at Asa was established one year later (1987), in a 12-year-old Norway spruce stand

233 planted in 1975 with two-year-old seedlings after clear-felling and soil scarification. The experimental design
234 was similar at both sites and included control, irrigation and two nutrient optimisation treatments (Bergh et al.,
235 1999). All treatments were replicated in 50 m × 50 m plots, arranged in a randomised block design. Only two of
236 the four treatments were used in the present study; the control (C) and plots receiving an annual dose of an
237 optimised mix of solid fertiliser (F), which among other elements per year contained about 10 kg ha⁻¹ Ca, 8 kg
238 ha⁻¹ Mg and 45 kg ha⁻¹ K (Linder, 1995).

239
240 Flakaliden is located in the central boreal sub-zone with a harsh climate, with long cool days in summer and
241 short cold days in winter. Mean annual temperature for the period 1990-2009 was 2.5 °C, and mean monthly
242 temperature varied from -7.5 °C in February to 14.5 °C in July. Mean annual precipitation in the period was
243 ~650 mm, with approximately one-third falling as snow, which usually covers the frozen ground from mid-
244 October to early May. Mean length of the growing season (daily mean temperature ≥ 5 °C) was 148 days, but
245 with large between-year variations (cf. Table 1 in Sigurdsson et al., 2013).

246
247 Asa is located in the hemi-boreal zone, where the climate is milder than at Flakaliden, which is reflected in a
248 longer growing season (193 days). Mean annual temperature (1990-2009) was 6.3 °C, mean monthly
249 temperature varied from -1.9 °C in February to 16.0 °C in July and mean annual precipitation was ~750 mm.
250 The soil is periodically frozen in winter. The difference in climate is reflected in differences in site productivity,
251 which broadly follows climate gradients in Sweden (Bergh et al., 2005).

252
253 The soils at Asa and Flakaliden differ in age due to differences in the time since deglaciation (Table 1), from
254 approximately 14,300 years at Asa and 10,150 years at Flakaliden (estimated from Fredén, 2009). The soil type
255 at both sites is an Udic Spodosol, with a mor humus horizon overlying glacial till derived from felsic bedrock.
256 The soil texture is classified as sandy loam. The transition between the B- and C-horizons is mostly located at 50
257 cm depth at Flakaliden and 50-60 cm depth at Asa. The natural ground vegetation at Flakaliden is dominated by
258 *Vaccinium myrtillus* (L.) and *V. vitis-idaea* (L.) dwarf-shrubs, lichens and mosses (Kellner, 1993; Strengbom et
259 al., 2011). The ground vegetation at Asa is dominated by *Deschampsia flexuosa*, (L.) and mosses (Strengbom et
260 al., 2011; Hedwall et al., 2013).

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

262 A detailed description of soil sampling, geochemical analyses and determination of mineralogy can be found in
263 Casetou-Gustafson et al. (2018). The procedures are summarised below. Sampling was performed in untreated
264 control plots (K1 and K4 at Asa and 10B and 14B at Flakaliden) and fertilised (F) plots (F3, F4 at Asa and 15A
265 and 11B at Flakaliden) in October 2013 (Flakaliden) and March 2014 (Asa), in the border zone of four plots at
266 each site. One intact soil core per plot at Flakaliden and in plot K1 at Asa was extracted using a rotary drill (17
267 cm inner diameter). In plots K4, F3 and F4 at Asa, soil samples were instead taken from 1 m deep manually dug
268 soil pits, due to inaccessible terrain for the rotary drill machinery. Maximum soil depth was shallower at
269 Flakaliden (70-90 cm) than at Asa (90-100 cm). The volume of stones and boulders was determined for each plot
270 at the two study sites using the penetration method described by Viro (1952) to a maximum depth of 30 cm and

271 by applying the fitted function described by Stendahl et al. (2009). Mean stone and bolder content was higher at
272 Flakaliden (39%vol.) than at Asa (28%vol.).

273

274 Soil samples were taken from each 10-cm soil horizon. Prior to chemical analysis, these samples were dried at
275 30-40 °C and sieved to <2 mm. Analysis of particle size distribution was performed by wet sieving and
276 sedimentation (pipette method) in accordance with ISO 11277. Geochemical analyses were conducted by ALS
277 Scandinavia AB and comprised inductively coupled plasma-mass spectrometry (ICP-MS) on HNO₃ extracts of
278 fused samples that were milled and ignited (1000 °C) prior to fusion with LiBO₂.

279

280 Quantitative soil mineralogy was determined with the X-ray powder diffraction (XRPD) technique (Hillier 1999,
281 2003). Samples for measurement of XRPD patterns were prepared by spray drying slurries of soil samples (<2
282 mm) micronised in ethanol. A full pattern fitting approach was used for quantitative mineralogical analysis of
283 the diffraction data (Omotoso et al., 2006). This fitting process involved the modelling of the measured
284 diffraction pattern as a weighted sum of previously measured and verified standard reference patterns of the
285 identified mineral components. The determination of chemical compositions of various minerals present in the
286 soils was conducted by electron microprobe analysis (EMPA) of mineral grains subsampled from the sifted (< 2
287 mm) soil samples. Mineralogical composition of the soils is given in the Supplement (Table S1).

288 **2.3 Historical weathering determined with the depletion method**

289 **2.3.1 Method description**

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

$$295 \quad W_{\text{depletion},i} = \frac{d \cdot \rho}{100} \cdot \frac{X_c \cdot Zr_{w,i}}{Zr_c} - X_{w,i} \quad \text{Eq. 1}$$

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

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

313 2.3.2. Application

314 Prior to calculating base cation weathering rates with the depletion method, fractional volume change V_p was
315 calculated according to White et al. (1996) in order to assess if there were any large volume changes (collapse)
316 in the mineral soil with implications for which depth the weathering should be calculated to. Similar to White et
317 al. (1996), it was assumed that values close to zero indicate no volumetric change, which was the case below 30-
318 40 cm of soil depth at both sites (Table S2). The homogeneity of the parent material was also evaluated (Fig. 2)
319 using the criterion that the ratio of Ti to Zr should be more or less constant with depth in an originally
320 homogeneous material. Use of the ratio of two immobile elements to establish uniformity of parent material has
321 been suggested previously (Sudom and St. Arnaud, 1971; Starr et al., 2014). The homogeneity criterion was not
322 met using Zr in plot K1 at Asa (i.e. the Zr concentrations decreased towards the soil surface; Fig. 2); here Ti was
323 used as the immobile element instead. Furthermore, the plots 15A and 11B at Flakaliden had to be eliminated
324 from the calculations, because relatively large variability in both the Zr and Ti gradients was observed. These
325 large heterogeneities led to an overall gain of base cations in the rooting zone, which is opposite to what would
326 be expected (i.e. that losses and gains can occur at specific soil depths due to eluviation and illuviation processes
327 in podzolic soils). For this reason, soil profiles 15A and 11B were eliminated from further consideration in
328 calculations of historical weathering rates using the depletion method. Thus, apart from heterogeneities,
329 transportation processes (eluviation and illuviation) and/or erratic Zr or Ti gradients could lead to “negative”
330 weathering, i.e. leading to a calculated relative accumulation of elements. Such negative values were not
331 considered in the calculation of historical weathering losses.

332
333 Bulk density was estimated for each soil horizon except in some plots where density measurements could not be
334 made below a certain soil depth. Bulk density in these cases was estimated using an exponential model for total
335 organic carbon (TOC) and bulk density (BD, g cm^{-3}) based on our own data. For Asa (soil horizons F3: 70-90
336 cm; F4: 0-10, 30-40, 50-60, 60-70, 70-80, 80-90, 90-100 cm; and K4: 70-80, 80-90, 90-100 cm), the following
337 function was used:

$$338 \quad \rho = 1.3 e^{-0.1 x} \quad \text{Eq. 2}$$

339 where x is TOC content (% of dry matter). For Flakaliden (soil horizons 14B: 80-90cm; 10B: 60-70 cm; and
340 11B: 40-70 cm), the function used was:

$$341 \quad \rho = 1.8 e^{-0.2 x} \quad \text{Eq. 3}$$

342 2.4.1 The PROFILE model

343 2.4.1 Model description

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

346 interface of wetted mineral surfaces and the soil solution. PROFILE is a multilayer model, where parameters are
347 specified for each soil layer based on field measurements and estimation methods (Warfvinge and Sverdrup,
348 1995).

349 **2.4.2 PROFILE parameter estimation**

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

352
353 Exposed mineral surface areas were estimated from soil bulk density and texture data using the algorithm
354 specified in Warfvinge and Sverdrup (1995). Volumetric soil water content for each soil profile in Flakaliden
355 and Asa was estimated to be $0.25 \text{ m}^3 \text{ m}^{-3}$ according to the moisture classification scheme described in Warfvinge
356 and Sverdrup (1995) (Table S3).

357
358 The aluminium (Al) solubility coefficient, a soil chemical parameter needed for solution equilibrium reactions,
359 was defined as $\log\{\text{Al}^{3+}\}+3\text{pH}$. It was estimated by applying a function developed from previously published
360 data (Simonsson and Berggren, 1998) and existing total carbon and oxalate-extractable Al measurements for the
361 sites (Casetou-Gustafson et al., 2018) (Table S3). For partial CO_2 pressure in the soil, the default value of
362 Warfvinge and Sverdrup (1995) was used. Data on measured dissolved organic carbon (DOC) in the soil
363 solution at 50 cm depth were available for plots K4 and K1 at Asa and plots 10B and 14B at Flakaliden, and
364 these values were also applied for deeper soil horizons. Shallower horizons (0-50 cm) were characterised by
365 higher DOC values, based on previous findings (Fröberg et al., 2006, 2013) and the DOC classification scheme
366 in Warfvinge and Sverdrup (1995) (Table S3).

367
368 Site-specific parameters used were evapotranspiration, temperature, atmospheric deposition, precipitation, runoff
369 and nutrient uptake in biomass (Table 4a). Mean evapotranspiration per site was estimated from mean annual
370 precipitation and runoff data, using a general water balance equation.

371
372 Total deposition was calculated using deposition data from two sites of the Swedish ICP Integrated Monitoring
373 catchments, Aneboda (for Asa) and Gammtratten (for Flakaliden) (Löfgren et al., 2011). Na was used as a tracer
374 ion in order to distinguish canopy exchange from dry deposition for Ca, Mg and K. Dry deposition for Na and Cl
375 was calculated as the difference between wet and throughfall deposition. As outlined in Zetterberg et al. (2016),
376 wet deposition for all elements was calculated by correcting bulk deposition for dry deposition using wet-only to
377 bulk deposition ratio. Wet deposition was estimated based on the contribution of dry deposition to bulk
378 deposition, both for base cations and anions, using dry deposition factors from Karlsson et al. (2011, 2013).
379 Finally, total deposition for all elements was calculated from the sum of dry and wet deposition.

380
381 Net base cation and nitrogen uptake in aboveground tree biomass (i.e. bark, stemwood, living and dead branches,
382 needles) was estimated as mean accumulation rate over a 100-year rotation period in Flakaliden and a 73-year
383 rotation period in Asa. These calculations were based on Heureka simulations using the StandWise application

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

386 **2.4.3 PROFILE sensitivity analysis**

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

398 **2.5 The base cation budget approach**

399 **2.5.1. General concepts of the base cation budget approach**

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

$$407 \quad W_{\text{budget}, i} = L_i + \Delta B_i + \Delta S_i - TD_i \quad \text{Eq. 4}$$

408 **2.5.2 Atmospheric deposition, TD_i**

409 The same estimates of total atmospheric deposition as used in parameter setting of the PROFILE model (section
410 2.4.2) were used in the base cation budget, Eq. (4).

411 **2.5.3. Changes in exchangeable soil pools, ΔS_i**

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

416

417 Exchangeable base cation content in the soil (<2 mm) for all Flakaliden samples and in Asa for samples from
418 1988 was determined by extraction of dry samples with 1 M NH_4Cl using a percolation method, where 2.5 g of

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

423

424 The amount of fine soil (<2 mm) per unit area was calculated from the volume of fine earth (<2 mm) in the soil
425 profiles and the average bulk density of the soil in the 0-10, 10-20 and 20-40 cm horizons. Bulk density and
426 volume proportion of stoniness at Flakaliden were determined from samplings in 1986 in 20 soil profiles (0.5 m
427 × 0.5 m and about 0.5 m deep) outside plots. At Asa, stoniness was determined with the penetration method of
428 Stendahl et al. (2009) and the bulk density of soil <2 mm was calculated using a pedotransfer function that
429 included soil depth and measured carbon concentrations as variables.

430 **2.5.4 Net uptake in biomass, ΔB_i**

431 Accumulation of base cations in tree biomass, i.e. net uptake of base cations, was calculated as a mean value of
432 control plots over the period 1989-2003, based on increments in aboveground biomass at Asa and Flakaliden for
433 this period and on the concentrations of elements in different tree parts. The increment in aboveground biomass
434 was based on measurements of stem diameter at breast height (DBH) of all individual trees in the plots, and
435 applying DBH data to allometric functions developed for Norway spruce at the sites (Albaugh et al., 2009,
436 2012). The allometric functions were based on destructive samplings (1987 - 2003) of 93 and 180 trees at Asa
437 and Flakaliden respectively. The increment in belowground biomass was estimated from general allometric
438 functions for Norway spruce stumps and roots in Sweden (Marklund, 1988). Since Marklund's functions (1988)
439 underestimate belowground biomass by 11 %, a factor to correct for this was included (Petersson and Ståhl,
440 2006). Furthermore, the finest root fraction (≤ 2 mm), which is not included in the functions of Marklund (1988)
441 and Petersson and Ståhl (2006), was assumed to be 20% of needle biomass at Asa and 33% at Flakaliden,
442 respectively, based on data from Helmisaari et al. (2007).

443

444 Data on element concentrations in biomass were available from measurements on harvested trees (S. Linder,
445 unpublished data). At Flakaliden, total element concentrations were analysed in trees sampled for
446 biomassdetermination in 1992 and 1997. Analyses of needles and branches (dead and live) were conducted on
447 the same tree parts in the biomass sampled in 1993 and 1998. Base cation concentrations in biomass were
448 determined from acid wet digestion in HNO₃ and HClO₄, followed by determination of elements by ICP-atomic
449 emission spectrophotometry (ICP-AES) (Jobin Yvon JY-70 Plus).

450

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

454 **2.5.5. Leaching, L_i**

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

457
458 Soil water was collected from five ceramic tension lysimeters (P80) installed at 50 cm depth in each
459 experimental plot. Soil water was collected during frost-free seasons, applying an initial tension of 70 kPa in 250
460 mL sampling bottles, and left overnight. These soil water samples were pooled by plot. The base cation
461 concentration in the soil solution was determined with ICP-AES. Soil water sampling was performed twice
462 every year, i.e. in the spring and in the autumn, which are the periods of highest water flux so that the most
463 important leaching events were covered. The spring samples were collected soon after the snowmelt and
464 depending on the weather in a specific year this meant that the yearly spring sampling date varied between the
465 last week of April and the last week of May. The autumn samples were collected when frost risk increased. That
466 meant that the autumn sampling dates varied from year to year, i.e. from the first week in September to mid-
467 November. The seasonal variation in soil water chemistry is shown in Fig. S2.

468
469 The drainage flux out of the profile was calculated by the CoupModel (Jansson, 2012). The model was
470 parameterised based on hydraulic soil properties measured at the sites. The model was run with hourly mean
471 values of locally measured climate variables (precipitation, global radiation, wind speed, air temperature and
472 humidity) and model outcomes were tested against tensiometer data, i.e. bi-weekly tensiometer readings at 15,
473 30 and 45 cm depth were used for model calibration. The parameters were then adjusted slightly to obtain good
474 agreement between measured and calculated soil water content. Annual precipitation varied considerably during
475 the period 1990-2002, ranging from 906 to 504 mm at Flakaliden (mean 649 mm) and from 888 to 575 mm at
476 Asa (mean 736 mm). Annual evapotranspiration increased by about 50 mm at both sites, during the period 1987-
477 2003 at Flakaliden and 1990-2002 at Asa, due to the increment in tree leaf area. Monthly means and standard
478 deviation of drainage (mm) at 50 cm depth in the soil of control plots at Asa during 1990 – 2004 and at
479 Flakaliden during 1988–2004 are shown in Fig. S3.

480 **2.5.6. Assessment of data quality in base cation budget**

481 The precision and accuracy of a base cation budget estimate of $W_{\text{budget}, i}$ was determined by the quality of
482 estimates of each individual term in Eq. (3), in proportion to the magnitude of each term (Simonsson et al.,
483 2015). Significant uncertainty in the estimate of a quantitatively important term will therefore dominate the
484 overall uncertainty in estimates of W_{budget} . Firstly, the quality of data for each term in Eq. (3) was assessed based
485 on the spatial and temporal scales of measurements and the quality of measurements (Table 5). Using these
486 criteria, we consider the estimates of deposition, leaching and accumulation in biomass to be of moderate to high
487 quality. The measurements of changes in extractable soil pools were of lower quality because extraction methods
488 were not identical for samples collected 1986/1988 and 1998/2004, which would cause significant uncertainty if
489 soil changes were an important part of the element budget. To partly overcome this uncertainty, we used the
490 estimates obtained by the PROFILE ($W_{\text{profile}, i}$) and depletion method ($W_{\text{depletion}, i}$) in additional base cation
491 budget calculations where the change in soil was determined from the base cation budget. These additional base
492 cation budget estimates, which are conceptually analogous to the regional mass balances presented by Akselsson
493 et al. (2007), were also used to place the PROFILE and depletion method estimates of W_i in the context of other
494 base cation fluxes at the ecosystem scale.

495 **2.6 Statistical analyses**

496 Site mean values and standard error (SE) of $W_{\text{depletion}}$ and W_{profile} were calculated based on the four (or two) soil
 497 profiles studied at each site. For W_{budget} an average based on the four control plots at each site was calculated as
 498 well as a combined standard uncertainty. The latter was partly based on standard errors derived from plot-wise
 499 replicated data of the present experiments (for leaching and changes in exchangeable soil pools, $SE(L_i)$ and
 500 $SE(\Delta S_i)$, respectively), partly on standard uncertainties (u) derived from Simonsson et al. (2015), where
 501 replicated data were missing in the present study (for accumulation in biomass and total deposition, $u(\Delta B_i)$ and
 502 $u(TD_i)$, respectively). Because total deposition and bioaccumulation differed substantially from those in the
 503 study of Simonsson et al. (2015), relative standard uncertainties were derived from that study, and multiplied
 504 with the average deposition and bioaccumulation rates at Asa and Flakaliden, respectively, to yield realistic
 505 standard uncertainties for the present sites. For the weathering rate of the i th base cation according to Eq. (4), a
 506 combined standard uncertainty (u_c) was calculated as:

$$507 \quad u_c(W_{\text{budget}, i}) = \sqrt{(SE(L_i))^2 + (u(\Delta B_i))^2 + (SE(\Delta S_i))^2 + (u(TD_i))^2} \quad \text{Eq. 4}$$

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

510 3. Results

511 3.1 Depletion method estimates of historical weathering rates

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

520 3.2 PROFILE model estimates of steady state weathering rates

521 The steady state weathering rate estimated by the PROFILE model (W_{profile}) differed from the historical rate with
 522 respect to all three test criteria, i.e. (1) total weathering rate in the 0-50 cm soil horizon, (2) variation in
 523 weathering with depth and (3) ranking order of base cations (Figs. 3 and 4). Firstly, regarding base cation
 524 weathering rate in the upper 50 cm of the mineral soil, W_{profile} estimates for Asa and Flakaliden (Asa: 37.1 mmol_c
 525 $\text{m}^{-2} \text{ yr}^{-1}$, Flakaliden: $42.7 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) were around 3.5 and 1.3-fold higher than $W_{\text{depletion}}$ estimates,
 526 respectively. Secondly, the total modelled base cation weathering rate for the soil profile down to 90 cm was
 527 around 7-fold higher than the rate estimated using the depletion method at Asa ($89.4 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$), and 3.4-
 528 fold higher at Flakaliden ($127.6 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$). Unlike the historical weathering based on the depletion method,
 529 PROFILE predicted that weathering rates increased with soil depth at both sites. At Flakaliden, high contents of
 530 K- and Mg-bearing tri-octahedral mica (Casetou-Gustafson et al., 2018) gave rise to particularly high weathering

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

533
534 The sensitivity analysis of the PROFILE model using homogeneous soil physical and/or mineralogical properties
535 demonstrated that the variations in soil physical properties (i.e. soil bulk density and specific exposed mineral
536 surface area) with depth had a greater influence than mineralogy on the observed change in W_{profile} with soil
537 depth. In terms of the ratios of sums of squares, the 'homogenous soil physics' scenario (1) produced 75% or
538 more of the error obtained with 'homogenous soil physics and mineralogy' (scenario (3)), leaving a mere 25% or
539 less to the 'homogenous mineralogy' of scenario (2); also see Figures S4 and S5. The soil physical inputs that
540 were most important for PROFILE weathering rates are indicated in Figs. S4 and S5. There was a strong linear
541 and positive relationship between exposed mineral surface area and W_{profile} for all elements at both sites, with R^2
542 values ranging from 0.65 to 0.89 (Fig. S6). The relationship between bulk density and W_{profile} was also strong
543 and showed the same linear response, although R^2 values were lower, 0.40-0.70 (Fig. S7).

544 3.3 Base cation budget estimates of current weathering rates

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

553
554 As to the fluxes (terms) of the base cation budget, Na showed patterns different from those of K, Mg and Ca
555 (Fig. 6). For Na, uptake in biomass was negligible and leaching was the dominant sink. For the K, Mg and Ca,
556 accumulation in biomass was the dominant sink. Loss by leaching was negligible for K, but significant for Mg
557 and Na. Deposition generally represented only a small input, except for Na at Asa. The measured decreases in
558 soil stocks of exchangeable base cations indicated that a change in this pool was a particularly important source
559 of Ca. There were minor increases in exchangeable stocks for Na, K and Mg at Asa. Compared to Na and Mg,
560 the combined uncertainty of W_{budget} was larger for Ca and K, both dominated by the bioaccumulation term in Eq.
561 (4), than for Na and Mg (Table 6). In relation to the mean W_{budget} , the combined uncertainty was of the same
562 order of magnitude for Na, about the half for Ca, one-third for K, and lower for Mg.

563
564 By using the weathering estimates obtained with PROFILE and the depletion method in the base cation budget
565 equation, Eq. (4), in combination with measured estimates of deposition, leaching and uptake in biomass,
566 alternative soil balances were estimated (Fig. 6). Since the base cation budget method predicted much higher
567 weathering rates than the other methods, a balance of sources and sinks consequently required more marked
568 decreases in exchangeable soil stocks for K, Ca and Mg when weathering rates were based on PROFILE or the

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

571 **4. Discussion**

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

578 **4.1 First test: Lower weathering rates by the depletion method compared to PROFILE**

579 Modelled (W_{profile}) and historical ($W_{\text{depletion}}$) base cation weathering rates were within the range of recently
580 published data for similar forest sites on podzolised glacial till (Stendahl et al., 2013). However, the historical
581 weathering rates at Asa were similar to the lowest historical weathering rate observed by Stendahl et al. (2013)
582 and the historical weathering rates for Flakaliden were similar to their highest rates, at least with regard to Ca
583 and Mg. The overall W_{profile} in the 0–50 cm depth was higher than $W_{\text{depletion}}$ for Na and K. Similarly, high ratios
584 of $W_{\text{profile}}/W_{\text{depletion}}$ were found at catchment scale by Augustin et al. (2016). At the pedon scale, Stendahl et al.
585 (2013) found $W_{\text{profile}}/W_{\text{depletion}}$ ratios of on average 2.7 for 16 Swedish study sites (with average max. and min.
586 ratios of 7.9 and 0.4, respectively); this ratio was larger than the one found for Flakaliden in our study (1.5) and
587 lower than the one found for Asa (5.1). Similar to Flakaliden, low ratios have been reported for the Lake
588 Gårdsjön site situated in south-western Sweden (Sverdrup et al., 1998; Stendahl et al., 2013). An exception to
589 the general trend of higher steady-state PROFILE weathering rates compared to historical rates calculated by the
590 depletion method, was found for Mg at the Flakaliden site, where $W_{\text{depletion}}$ was 1.9-fold greater than W_{profile} in
591 the upper mineral soil, but only at Flakaliden. This exception with regard to Mg was also found by Stendahl et
592 al. (2013) for all of their 16 study sites.

593
594 The observed discrepancy between W_{profile} and $W_{\text{depletion}}$ has both conceptual and random origin, where the
595 conceptual origin is due to the different temporal scales. In contrast to the observed discrepancies referred to
596 above, several studies have concluded that the average historical weathering rate should generally be higher than
597 the present weathering rate, since soil development involves loss of easily weatherable minerals and ageing of
598 mineral surfaces (Bain et al., 1993; Taylor and Blum, 1995; White et al., 1996). In a study using the Historic-
599 SAFE model, applied to the Lake Gårdsjön catchment in southwestern Sweden, Sverdrup et al. (1998) predicted
600 a decline in weathering rates due to assumed disappearance of fine particles and loss of minerals. Their results
601 suggested an increase in weathering rates from deglaciation 12,000 years B.P. towards a peak at 9000 years B.P.,
602 followed by a gradual decrease to below initial levels.

603
604 The particularly low $W_{\text{depletion}}$ at Asa was largely attributed to a weakly developed depth gradient of Zr in the soil
605 (Fig. 3). This observation has probably a random rather than a conceptual origin, because it might have been the
606 result of soil mixing by different means. Mechanical soil scarification was carried out at both Asa and Flakaliden

607 prior to planting of the present stand, which would at least have caused partial mixing or inversion of surficial
608 soil horizons. In addition, clearance cairns of unknown age were found in the experimental area at Asa,
609 indicating small-scale agriculture in the past. Moreover, if burrowing earthworms have been abundant in the
610 past, they might have produced soil mixing in the upper soil horizons (Taylor et al., 2019), resulting in a
611 disturbed Zr gradient and in low estimates of historical weathering in the rooting zone (Whitfield et al. 2011).
612 High or near-neutral soil pH and deciduous litter can promote high population densities of burrowing
613 earthworms following forest clearing and agriculture; and we note that partly deciduous vegetation dominated at
614 Asa until only 1000-2000 years BP, with species such as *Corylus avellana* (L.), *Betula* spp., *Quercus* spp. and
615 *Tilia* spp. (Greisman et al., 2009).

616
617 Apart from disturbances, natural heterogeneity in texture or mineralogy probably influenced the estimate of
618 $W_{\text{depletion}}$ at the study sites, i.e., biases of random nature. At Flakaliden, it was reasoned that heterogeneous Zr
619 gradients (Fig. 3) and Zr/base cation ratios (Fig. S1) disqualified two soil profiles from further analysis, which
620 would have otherwise indicated unreasonable net gains of elements in the rooting zone (0–50 cm) (i.e. for soil
621 profile 15A for all elements and for soil profile 11B with regard to Na and K). Whitfield et al. (2011) used the
622 same argument for excluding single profiles from their calculations, emphasizing that overall gains in the rooting
623 zone are not expected without external additions of base cations to the soil profiles. Several alternative reasons
624 could have contributed to the observed peaks of Zr in the B/C-horizon at Flakaliden, such as local
625 heterogeneities of the deposited till, which was suggested by the unstable Ti/Zr ratio in soil profile 15A and 11B.
626 However, the observed peaks in the Ti/Zr gradients were only explained by irregularities in Ti gradients (i.e.
627 increases in the Ti/Zr ratio indicate that Ti concentrations are increasing) the latter has to be treated carefully
628 since in cases where both Zr and Ti show inconsistent patterns with soil depth, the Ti/Zr ratio will still be
629 uniform and hereby overshadows heterogeneities observed with soil depth for both elements (Fig. 2, 3). Thus,
630 heterogeneities in Zr gradients observed in the B/C horizon can be attributed to local heterogeneities of the
631 parent material irrespective of if the Ti/Zr gradients are uniform at these depths.

632
633 Regardless of errors in the Zr gradients, both $W_{\text{depletion}}$ and W_{profile} showed more marked gradients with soil depth
634 at Flakaliden compared to Asa. This could be expected based on the more well-developed podzol profile at
635 Flakaliden. It has been postulated that the formation of podzols is enhanced by long duration and great depth of
636 snow cover (Jauhiainen, 1973; Schaetzl and Isard, 1996), which would imply that soil formation had progressed
637 further at Flakaliden than at Asa (Lundström et al., 2000). At Flakaliden, the average mass loss of Ca and Mg
638 was 4.0-fold larger in the E-horizon than in the B-horizon, which is similar to findings by Olsson and Melkerud
639 (2000) of a 5-fold higher ratio between losses of base cations in the E- compared with the B-horizon.

640 **4.2 Second test: PROFILE and depletion method produce different weathering gradients in the soil**

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

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

650

651 The increase in weathering rate with soil depth simulated by PROFILE is obviously in contrast with the classic
652 notion of weathering rates being highest in the A- or E-horizon of podzolised soils (Tamm, 1931). To test
653 whether the high W_{profile} values could be reconciled with the observed historical weathering, the hypothetical
654 time needed for the PROFILE weathering rates to accomplish the element losses determined with the depletion
655 method was calculated. This showed that the the highest weathering rate, presently prevailing at approximately
656 80 cm (Asa) or 60 cm (Flakaliden) depth according to PROFILE (Fig. 4), would cause the observed depletion
657 losses within less than half of the soil age ('max rates' in Fig. 7), potentially in concert with the concept of a
658 weathering front. However, the calculation also showed that the present minimum weathering rate, presently
659 simulated for the topmost 1-3 horizons (Fig. 4), would often result in a more severe base cation depletion within
660 less than the postglacial period than observed by the depletion method ('min rates' in Fig. 7), particularly at
661 Flakaliden, and for K and Na also at Asa. Hence, even considering the concept of a possible weathering front,
662 there appears to be a positive bias in W_{profile} at the investigated sites.

663 **4.3 Third test: Depletion method and PROFILE resulted in different element rank-order**

664 The weathering rates of PROFILE may also be criticized based on discrepancies in the ranking order of the
665 weathering of elements, compared to historical weathering; this is our third test criterion. At both sites,
666 PROFILE predicted the highest steady-state weathering for Na at both sites. However, historical weathering at
667 Asa was greatest for Ca among the base cation elements, whilst Mg was the most abundant element released at
668 Flakaliden. The latter was also found by Olsson and Melkerud (2000), who reported the same ranking order of
669 individual base cation weathering (i.e. $\text{Mg} > \text{Ca} > \text{Na} > \text{K}$) for other sites in northern Sweden. At the mineralogical
670 level, Casetou-Gustafson et al. (2019) demonstrates that K-feldspar was the dominant source of all steady state
671 PROFILE weathering of K and previous results from similar soils suggest that the dissolution rate for K-feldspar
672 is too high compared with mica. For example, Thompson and Ukrainczyk (2002) described differences in the
673 plant availability of K via weathering from these two mineral groups. In addition, Simonsson et al. (2016) found
674 that, although K-feldspar contained approximately 90% of the bulk K in the soil, 25–50% of the weathering of K
675 had occurred in mica. Furthermore, and in more general terms, Hodson and Langan (1999) suggested that the
676 PROFILE model overestimates weathering rates because it does not consider the decrease in mineral reactivity
677 that has taken place over time and because it assumes that all mineral surface areas are reactive. Therefore,
678 PROFILE can be expected to overestimate base cation weathering rates, an error that can be attributed to a
679 combination of conceptual (conditions or processes inaccurately represented in model) and random (lack of
680 relevant field data) sources.

681

682 **4.4 Weathering in a base cation budget perspective**

683 The base cation budget approach consistently resulted in much higher weathering rates than PROFILE and the
684 depletion method for all base cations except Na. However, as was shown by the large combined uncertainties
685 given in Table 6, base cation budget estimates of weathering are associated with substantial uncertainties from
686 different sources. In general, significant uncertainties in the element budget of ecosystems are common (Yanai et
687 al., 2010), and similarly large uncertainties associated with estimates of W_{budget} were observed by Simonsson et
688 al. (2015) for the Skogaby site in south-western Sweden, a Norway spruce site of similar stand age and soil
689 condition as Asa. Accounting for all sources of uncertainty, they found that the 95% confidence interval in
690 estimates of base cation weathering was 2.6 times the mean ($33 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$).

691
692 Despite the considerable uncertainties in W_{budget} estimates, the base cation budget approach showed that
693 accumulation in biomass was a dominant sink for all base cation elements except Na, in line with findings of
694 Nykvist (2000) for two Norway spruce sites in Sweden and the findings of Simonsson et al. (2015). However,
695 this contrasts to other studies, which assumed no change in soil and tree biomass stocks of base cations over time
696 (e.g. Sverdrup et al., 1998). The higher estimated weathering rate at Asa reflected the higher productivity and
697 nutrient demand of the stand at this site (Bergh et al., 1999), which has resulted in 1.4-fold greater accumulation
698 of base cations in biomass than at Flakaliden.

699
700 Calcium and Mg uptake in forest trees is considered to be more or less passive flow driven by transpiration
701 fluxes, whereas K uptake is an energy-demanding active process (Nieves-Cordonos et al., 2014). Considering
702 that Na was the dominant base cation in the soil solution at 50 cm soil depth (Fig. 6), the negligible
703 accumulation of Na in tree biomass suggests that Na uptake in trees is physiologically blocked. Low
704 concentrations of Na seem to be a general feature of terrestrial plants in boreal forests, in contrast to aquatic
705 plants, which explains why the latter are considered important Na sources for large herbivores like moose
706 (Ohlson and Staaland, 2001). Thus, as in agreement with findings by e.g. Taylor and Velbel (1991) and Velbel
707 (1995) for other types of forest ecosystems, the negligible Na accumulation in tree biomass and the particularly
708 low deposition at Flakaliden simplify the Na budget to include only three major counterbalancing fluxes:
709 weathering, deposition and leaching. Because $W_{\text{depletion}}$ and W_{budget} of Na were fairly similar, and were much
710 lower than W_{profile} , our results provide additional support for the claim that the PROFILE model produced
711 consistently too high Na weathering.

712
713 Accumulation in biomass was the dominant sink for Ca, Mg and K, and this term in the BC budget was
714 considered to be of moderate to high quality (Table 5). The changes observed in extractable Ca stocks in the soil
715 was considered more uncertain (Table 5), but they are consistent with observations over 22 years of aggrading
716 Norway spruce forests by Zetterberg et al. (2016), who reported exchangeable Ca depletion rates of 5-11 and 23-
717 39 $\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$ for sites in south-western and northern Sweden, respectively. The higher value for the northern
718 site reflected higher Ca saturation in the soil. The corresponding values for Asa and Flakaliden were larger, but
719 of similar magnitude (34.5 and 40.5 $\text{mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$, respectively). Brandtberg and Olsson (2012) studied the
720 same sites as Zetterberg et al. (2016) over a 10-year period and found a general minor increase in exchangeable
721 K soil stocks and a substantial decrease in the Ca stocks, a result much similar to the findings of the present
722 study.

723

724 When an independent estimate of current weathering rate (W_{profile}) is introduced in the budget (Fig. 6) the high
725 rate of accumulation in biomass is not explained by the combination of measured ($TD, \Delta S$) or modelled (W_{profile})
726 sources or sinks (L). This result suggests that forest trees have access to additional sources of Ca, Mg and K, not
727 measured or captured by our study. We can only speculate about the nature of such sources: It is possible that
728 depletion of ammonium-chloride-exchangeable base cations underestimates the plant-available phases of BC in
729 the soil. Using other extract media than NH_4Cl may have revealed additional sources from e.g. oxalates
730 (Rosenstock et al., 2019b). Additional BC release from decomposing roots, stumps and residues from the felling
731 of the former stand was probably neglected because of difficulties to include coarse wood in soil sampling. It is
732 also possible that the assumption made that no base cation uptake takes place below 50 cm in the soil was
733 wrong. If trees can take up base cations from deeper soil horizons (e.g. Callesen et al., 2016; Brantley et al.,
734 2017), the discrepancy in weathering rates between the two methods would be reduced since PROFILE predicted
735 higher weathering rates with increasing depth. Furthermore, although biological processes are represented in
736 PROFILE, the model fail to capture biological feedback mechanisms in their entirety, in particular feedbacks
737 generated by plant uptake and mycorrhiza (Finlay et al., 2009; Sverdrup, 2009; Smits and Wallander, 2017;
738 Akselsson et al., 2019; Finlay et al., this issue; Rosenstock et al. 2019a).

739 5. Conclusions

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

745

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

753

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

761

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

770 **6. Data availability**

771 Data on geochemistry and mineralogical compositions are available in the supplement of Casetou-Gustafson et
772 al. (2018, <https://doi.org/10.1016/j.geoderma.2017.09.004>). BC budget data are available at
773 <https://doi.org/10.6084/m9.figshare.11357786>.

774 **7. Authors contribution**

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

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

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

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

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

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Table 3. Concentrations (weight %, based on geochemical analyses) of different elements at the reference depths used for calculating historical weathering rate at the Asa and Flakaliden sites.

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

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Table 4a. Site parameters used in the PROFILE model

Parameter	Source	Asa	Flakaliden
Temperature (°C)	Measurements at Asa and Flakaliden	6.1	2.3
Precipitation (m yr ⁻¹)	Measurements at Asa and Flakaliden	0.736	0.642
Total deposition (mmol _c m ⁻² yr ⁻¹)	Measured data on open field and throughfall deposition available from nearby Swedish ICP Integrated Monitoring Sites	SO ²⁻⁴ : 27.0 Cl ⁻ : 38.3 NO ³ : 30.7 NH ⁴ : 21.6 Ca ²⁺ : 7.2 Mg ²⁺ : 6.8 K ⁺ : 1.9 Na ⁺ : 31.5	SO ²⁻⁴ : 13.1 Cl ⁻ : 5.6 NO ³ : 10.5 NH ⁴ : 9.9 Ca ²⁺ : 5.2 Mg ²⁺ : 1.9 K ⁺ : 1.1 Na ⁺ : 5.6
Base cation net uptake (mmol _c m ⁻² yr ⁻¹)	Previously measured data for Asa and Flakaliden: Concentrations in biomass from Linder (unpublished data). Biomass data from Heureka simulations.	Ca ²⁺ : 46.2 Mg ²⁺ : 10.6 K ⁺ : 17.8	Ca ²⁺ : 26.7 Mg ²⁺ : 4.4 K ⁺ : 6.7
Net nitrogen uptake (mmol _c m ⁻² yr ⁻¹)	Previously measured data from Asa and Flakaliden: Concentrations in biomass from Linder (unpublished data). Biomass data from Heureka simulations.	81.0	32.4
Base cations in litterfall (mmol _c m ⁻² yr ⁻¹)	Literature data from Hellsten et al. (2013)	Ca ²⁺ : 116.8 Mg ²⁺ : 15.1 K ⁺ : 10.5	Ca ²⁺ : 40.6 Mg ²⁺ : 4.6 K ⁺ : 3.2
Nitrogen in litterfall (mmol _c m ⁻² yr ⁻¹)	Literature data from Hellsten et al. (2013)	179.8	47.5
Evapo-transpiration (Fraction)	Precipitation data and runoff data. Runoff data calculated based on proportion of runoff to precipitation (R/P) at Gammtratten and Aneboda.	0.3	0.6

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

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

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*) Physical and chemical soil horizon specific input data are given in supplements (Tables S3)

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

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

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1087 **Table 6:** Standard errors and standard uncertainties ($\text{mmol}_e \text{m}^{-2} \text{yr}^{-1}$) for the terms in the base cation budget,
 1088 Eq. (4). Combined standard uncertainty, plot average value and confidence interval for the weathering rate of
 1089 base cation i derived from base cation budgets $W_{\text{budget}, i}$ ($\text{mmol}_e \text{m}^{-2} \text{yr}^{-1}$).
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Site	Element	Deposition	Soil change	Biomass accum.	Leaching	Combined standard uncertainty	W_{budget}	Confidence interval (combined standard uncertainty $\times 3$)
Asa	Ca	1.1	12.9	19.5	3.2	24	58	± 71
	Mg	1.1	0.6	2.5	1.6	3	29	± 10
	K	0.3	0.5	9.7	0.1	10	33	± 29
	Na	4.0	0.9	0.0	5.1	7	7	± 20
Flakaliden	Ca	0.8	10.5	13.3	0.7	17	28	± 51
	Mg	0.3	1.1	1.5	0.3	2	12	± 6
	K	0.2	0.6	6.7	0.2	7	19	± 20
	Na	0.7	1.2	0.0	0.8	2	2	± 5

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1093 **Figure captions**

1094 **Figure 1.** Map of Scandinavia showing the location of the study sites Asa and Flakaliden.

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1096 **Figure 2.** Titanium (Ti) to Zirconium (Zr) ratios by concentration in the soil at Asa (K1, K4, F3, F4) and
1097 Flakaliden (10B, 11B, 14B, 15A).

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1099 **Figure 3.** Zirconium (Zr) gradient in the soil at Asa (K1, K4, F3, F4) and Flakaliden (10B, 11B, 14B, 15A).

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1101 **Figure 4.** (Left) Historical weathering rate of base cations ($\text{mmolc m}^{-2} \text{yr}^{-1}$) estimated by the depletion method
1102 and (right) steady-state weathering rate estimated by the PROFILE model in different soil layers at Asa and
1103 Flakaliden.

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1105 **Figure 5.** Site mean values and standard errors (SE) of weathering rates ($\text{mmolc m}^{-2} \text{yr}^{-1}$) for Ca, Mg, K and Na
1106 determined with the depletion method, the PROFILE model and the base cation budget method for the 0-50 cm
1107 horizon at Asa and Flakaliden. For the weathering rates based on the depletion method and the PROFILE model,
1108 error bars represent the SE calculated based on four soil profiles at each study site, except for Flakaliden, where
1109 the depletion method method was only applied in two soil profiles. For weathering rates based on the base cation
1110 budget approach, SE bars were calculated from combined standard uncertainties, which are based on SE derived
1111 from plot-wise replicated data of the present experiments (for leaching and changes in exchangeable soil pools)
1112 and on standard uncertainties derived from Simonsson et al. (2015), where replicated data were missing in the
1113 present study (for accumulation in biomass and total deposition).

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1115 **Figure 6.** (Left) Sinks and (right) sources of base cations (BC) in ecosystem net fluxes at Asa and Flakaliden.
1116 The soil is a net source of soil BC if soil base cation stocks decrease and a net sink if they increase. 'BC budget'
1117 = current base cation weathering rate (W_{budget}) estimated with the BC budget method, including measured
1118 changes in soil exchangeable BC stocks; 'PROFILE'= soil exchangeable pools estimated from BC budget using
1119 PROFILE estimates of BC weathering rate; 'Historical'=soil exchangeable pools estimated from BC budget
1120 using estimates of historical weathering rate by the depletion method. 'Measured soil change' and 'Base cation
1121 budget estimated soil change' indicates that equation 4 was used to estimate weathering rate, or the soil change,
1122 respectively.

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1124 **Figure 7.** Time (years) required to achieve the measured historical element loss in different soil horizons with
1125 application of maximum or minimum PROFILE weathering rates at (a) Flakaliden and (b) Asa.

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