

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**

4 Sophie Casetou-Gustafson¹, Harald Grip², Stephen Hillier^{3, 5}, Sune Linder⁴, Bengt A.
5 Olsson¹, Magnus Simonsson⁵ Johan Stendahl⁵
6

7 ¹Department of Ecology, Swedish University of Agricultural Sciences, (SLU), P.O. Box 7044, SE-750 07
8 Uppsala, Sweden

9 ²Department of Forest Ecology and Management, SLU, SE-901 83 Umeå, Sweden. Present address:
10 Stjernströms väg 5, SE-129 35 Hägersten, Sweden

11 ³The James Hutton Institute, Craigiebuckler, Aberdeen AB15 8QH, United Kingdom

12 ⁴Southern Swedish Forest Research Centre, SLU, P.O. Box 49, SE-230 53 Alnarp, Sweden

13 ⁵Department of Soil and Environment, SLU, P.O. Box 7014, SE-750 07 Uppsala, Sweden
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15 *Correspondence to:* Sophie Casetou-Gustafson (Sophie.Casetou@slu.se)
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26 **Abstract**

27 Reliable and accurate methods for estimating soil mineral weathering rates 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 rates. In this study, release rates of
30 base cations through weathering were estimated in podsolised glacial tills at two experimental forest sites, Asa
31 and 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 ~~budgetmass-balance~~ at stand scale, using measured deposition, leaching and
35 changes in 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 [11.0, 12.9,](#)
38 [3.2 and 7.07-3, 9.0, 1.7 and 4.4](#) mmol_c m⁻² yr⁻¹, respectively. Steady state weathering rate for Ca, Mg, K and Na
39 estimated with PROFILE was 8.9, 3.8, 5.9 and 18.5 mmol_c m⁻² yr⁻¹, respectively, at Asa and 11.9, 6.7, 6.6 and
40 17.5 mmol_c m⁻² yr⁻¹, respectively, at Flakaliden. ~~Thus a~~At both sites, the PROFILE results indicated that steady-
41 state weathering rate increased with soil depth as a function of exposed mineral surface area, reaching a maximum
42 rate at 80 cm (Asa) and 60 cm (Flakaliden). In contrast, the depletion method indicated that the largest postglacial
43 losses were 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 ~~than the depletion method~~, particularly of K and Na in deeper soil layers. In contrast, the
46 depletion method appeared to ~~to~~ produce consistently lower rather than higher weathering rates, due to natural
47 and anthropogenic variability in ~~(reference)~~Zr gradients. The ~~base cation budgetmass-balance~~ approach produced
48 significantly higher weathering rates of Ca, Mg, and K (65, 23, 40 mmol_c m⁻² yr⁻¹ at Asa and 35, 14 and 22 mmol_c
49 m⁻² yr⁻¹ at Flakaliden), but lower Na weathering rates similar to the depletion method (6.6 and 2.2 mmol_c m⁻² yr⁻¹
50 at Asa and Flakaliden). The large discrepancy in weathering rates for Ca, Mg and K between ~~the base cation~~
51 ~~budget approachmass-balance~~ and the other methods suggest that there were additional sources for tree uptake in
52 the soil besides weathering and measured depletion in exchangeable base cations.

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

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61 **Definitions and abbreviations**

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

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

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

67 Definitions/Abbreviations:

68 $W_{\text{depletion}}$ = Historical weathering rate based on calculation of loss of mobile elements since last deglaciation

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

70 $W_{\text{ms}} - W_{\text{budgeteb}}$ = Current weathering rate based on base cation budget/mass balance calculations

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87 1. Introduction

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

108 In society there is a need to know if current forestry practices are sustainable, that is if current weathering provides
109 enough base cations to at least balance their export by forestry. The role of weathering in maintaining base cation
110 balance in Swedish forest soils has been examined in several previous studies (Sverdrup and Rosén, 1998;
111 Akselsson et al., 2007). A regional-scale study on Swedish forest soils found that, in parts of Sweden, base cation
112 ~~depletion losses~~ can occur at rates that lead to very low base saturation of the soils, possibly leading to negative
113 effects on e.g. soil fertility and runoff water quality within one forest rotation (Akselsson et al., 2007). ~~The~~
114 ~~methods used to determine base cation balance in that study included predicting weathering rates based on the~~
115 ~~PROFILE model and analysing regional data for deposition, leaching and base cation losses in harvested biomass.~~
116 Negative balances, which indicate soil base cation depletion in the soil, were found to be more frequent
117 after whole-tree harvesting than stem-only harvesting, especially for Norway spruce ~~compared with Scots pine,~~
118 with the effect deficits being more common in southern than in northern (boreal) Sweden. ~~Among the elements~~
119 ~~studied, Ca was most frequently subject to losses depletion. However, uncertainties in estimating the terms of the~~
120 ~~base cation balance can accumulate to produce large uncertainties in the overall balance, and therefore it is difficult~~
121 ~~to draw firm conclusions about the sustainability of different harvesting options based on base cation balance~~
122 ~~alone. There are also conflicting opinions about the consequences of long term negative base cation balance in~~

123 soils for sustainable forest production (Binkley and Högeberg, 1997; 2016). Experimental studies have
124 demonstrated that growth of boreal forests is strongly limited by nitrogen (N), whereas co-limitation with
125 phosphorus (P) may occur in hemiboreal and temperate forests (e.g. Tamm, 1991). Thus, concerns about base
126 cation depletion in Swedish forest soils following increasing use of whole tree harvesting have so far been about
127 soil acidification rather than tree nutrition, the latter expressed for example by the Swedish Forest Agency (2008)
128 in their recommendation on nutrient compensation with wood ash.

129 In regional assessments of the sustainability of different harvesting regimes, the value of estimated weathering rate
130 used has a strong influence on the base cation balance. Klaminder et al. (2011b) found that different approaches
131 to estimating weathering rates yielded results that differed substantially, and that uncertainties in the methods had
132 a great influence on the predicted sustainability of different harvesting practices.

133 Futter et al. (2012) compiled weathering rates estimated at 82 sites, using different methods, and found both large
134 between-site as well as within-site differences in the values. They concluded that the sources of uncertainties were
135 as follows: input data > parameters > weathering concepts/assumptions. Differences in input data can be attributed
136 to different time scales used when acquiring different input data, different time scales; challenges determining
137 accurate mineralogical compositions and the use of field laboratory data compared with laboratory field data (Van
138 der Salm, 20014; Futter et al., 2012; Klaminder et al., 2011b). Thus, they recommend that at least three different
139 approaches be applied per study site to evaluate/increase the precision in weathering estimates. The approaches
140 examined in the present paper include (1) 'historical weathering' based on geochemical investigation of the soil
141 profile, (2) modelled present weathering rate and (3) present weathering rate based on cation balances at the
142 ecosystem level. Comparing weathering estimates based on these concepts requires that the methods are tested at
143 the same spatial scale. The choice of methods is primarily based on the fact that rates of weathering may vary
144 over time (Klaminder et al., 2011; Stendahl et al., 2013). The average weathering under long-term environmental
145 change, i.e. 'historical weathering', is thus different from the weathering potential under present-day
146 environmental conditions, i.e. 'present-day weathering', which is why we need to be able to consider historical
147 weathering when assessing current/present-day weathering rates. Moreover, present-day weathering rates
148 estimated based on the steady-state concept, which lacks the dimension of time, may differ from dynamic
149 estimates of weathering rates derived from measured base cation budgets. These three different concepts of
150 estimating weathering cannot be covered by a single method (Klaminder et al., 2011; Futter et al., 2012).
151 Weathering estimates based on these concepts have often differed largely from pedon to catchment scale, whereas
152 truly harmonized comparisons of methods require that methods are tested uniformly at the same spatial scale. This
153 spatial scale can be the pedon, which also contains the major part of the mineral nutrient sources in the soil
154 available for forest growth. To our knowledge, Kolka et al. (1996) is the only study to have previously used this
155 approach. To our knowledge, Kolka et al. (1996) is the only study to have previously used this approach.

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158 The first approach, the depletion method, makes use of soil profile based mass balances (Chadwick et al., 1990;
159 Brimhall et al., 1991) to estimate total base cation losses in the soil above a reference soil depth. An element in a

160 weathering-resistant mineral is used as a standard, most commonly zirconium (Zr, present in e.g. zircon) or
161 titanium (Ti, present in e.g. rutile) (Sudom and St.Arnaud, 1971; Harden et al., 1987; Chadwick et al., 1990; Bain
162 et al., 1994), due to their stability at low temperatures (Schützel et al., 1963). To yield an annual average
163 weathering rate ($\text{mmol}_e\text{m}^{-2}$), calculated element losses are commonly divided by an estimated soil age. In Nordic
164 glacial tills situated above the marine limit, soil age is conventionally considered to be the number of years lapsed
165 since the site of interest was finally deglaciated at the end of the Weichselian. Since the rate of weathering may
166 vary over time (Klaminder et al., 2011; Stendahl et al., 2013), the average 'historical weathering' rate may differ
167 from the present-day weathering rate. ~~¶The depletion method is most widely used in Sweden to estimate
168 weathering rates, specifically at the regional scale (Olsson et al., 1993).~~
169 ~~In society there is a pressing need to know if current forestry practices are sustainable, that is i.e. if current/present-
170 day weathering provides is enough base cations (BC) to at least balance BC their export by forestry. Therefore,
171 our goal should be to determine current/present day mineral weathering rates in soil. All soils are, by definition,
172 composed of biogeochemically altered material . The rates extent/rate of alteration that have occurred over the
173 past as well as that the one that occurs at present may differ (Klaminder et al., 2011; Stendahl et al.,
174 2013; Klaminder et al., 2011), (i.e. the average weathering potential under average long term environmental
175 change, i.e. 'historical weathering', is thus different from the) as well as the one that occurs at present (i.e.
176 weathering potential under present day environmental conditions, i.e. 'present day weathering', which is why we
177 need to be able to consider historical weathering when assessing current/present day weathering rates..) may differ
178 (Stendahl et al., 2013; Klaminder et al., 2011). Moreover, present-day weathering rates when estimated based on
179 the steady state concept, which lacks time the dimension of time, may differ from dynamic estimates of
180 weathering rates derived from measured base cation budgets. These three different concepts of estimating
181 weathering cannot be covered by a single method (Klaminder et al., 2011; Futter et al., 2012), and wWeathering
182 estimates based on these concepts have often differed largely from pedon to catchment scale, whereas, truly This,
183 which is the reason why they harmonized comparisons of methods requires require a should be applied
184 uniformly at the spatial scale of interest, i.e. the soil pedon. This spatial scale can be the pedon, which also
185 contains the major part of the mineral nutrient sources in the soil available for , which is the source of mineral
186 nutrients for forest growth. To our knowledge, Kolka et al. (1996) are the only ones study that have
187 previously used this approach. However, when comparing soil profile based methods, it is important to
188 understand variation with soil depth that exceeds 0-50cm, since the depletion method calculates weathering for
189 the entire soil pedon.~~

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191 ~~Beside the PROFILE model, the depletion method is most widely used in Sweden to estimate weathering rates,
192 specifically at the regional scale (Olsson et al., 1993). The depletion method makes use of soil profile based mass
193 balance estimates (Chadwick et al., 1990; Brimhall et al., 1991) to estimate total base cation losses since
194 deglaciation in the soil above a reference soil depth, using An element in a weathering-resistant mineral is used
195 as a standard, most commonly zirconium (Zr, e.g. present in zircon etc) or titanium (Ti, e.g. present in rutile etc.)
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197 at low temperatures (Schützel et al., 1963). To yield an annual average weathering rate ($\text{mmol}_e\text{m}^{-2}$), calculated
198 element losses are commonly divided by an estimated number of years lapsed since the onset of weathering.
199 Steady state weathering rate may differ from the average during soil formation, which is one reason why
200 weathering rates obtained using PROFILE and the variation in rate with depth in the soil can be expected to differ
201 from those obtained using the depletion method (Stendahl et al., 2013). Observed discrepancies between these
202 methods may therefore reflect 'true' differences or conceptual differences between the methods.

203
204 The second approach commonly involves the mechanistic PROFILE model, by which estimates steady state
205 release rates of base cations are estimated using steady state mass balances based on the dissolution kinetics of a
206 user-defined set of minerals present in the soil, and the physical and chemical conditions that drive the dissolution
207 of minerals. Since it is a mechanistic model, its strength is its transparency, while its main weakness is the
208 difficulty in setting values of model parameters and input variables to which it may have high sensitivity.
209 Akselsson et al. (*this issue*) concluded that the most important way to reduce uncertainties in modelled weathering
210 rates is to reduce input data uncertainties, e.g. regarding soil texture, although there is also still a need to improve
211 room for improvement in process descriptions of e.g. biological weathering and weathering brakes (e.g. Lampa
212 Erlandsson Lampa et al., *this issue*). The sensitivity of PROFILE to variations in soil physical parameters (e.g.
213 soil texture, soil bulk density) and mineral composition was discussed by Jönsson et al. (1995) and Hodson et al.
214 (1996), while the importance of the ability to determine the precise identity and quantity of the minerals was
215 analysed by Casetou-Gustafson et al. (*this issue*).

216
217 An alternative approach to estimating weathering rate is the base cation budget approach mass balance
218 method (Velbel, 1985; Likens et al., 1998; Velbel, 1985). This method has been applied to estimate current
219 weathering rates at various temporal and spatial scales, and components elements of the budget approach mass
220 balance have been used in different ways in some popular models, e.g. MAGIC (Cosby et al., 1985). The w. Using
221 the base cation budget based on the mass balance mass balance approach W, weathering rate is estimated indirectly
222 as by the base cation budget approach from the difference between other sinks and sources of elements base
223 cations, which are measured within a system with defined boundaries. The missing source in the mass balance
224 equation is assumed to contain represent the weathering, but can also contain other unidentified sources. The base
225 cation budget mass balance approach is most reliable when based on long-term data from well-defined systems,
226 although even then estimated rates tend to suffer from large uncertainties, as errors in the sinks
227 and sources can be expected to accumulate in the mass balance equation (Simonsson et al., 2015). The bH
228 situation where the base cation uptake in biomass is high, it dominates the flux of the elements included in the
229 base cation budget. Nevertheless Furthermore, the Bbase cation budgets mass balance approach has rarely mostly
230 been applied under non-steady state conditions where accumulation in biomass were not directly measured but
231 estimated to be small, or base cation BC stocks in the soil were assumed to be at steady state (i.e. including
232 measures of soil exchangeable pools), due to lack of long term data on base cation fluxes (e.g. Kolka et al., 1996;
233 Sverdrup et al., 1998; Whitfield et al., 2006). Consequently, at the pedon scale, the PROFILE model and the
234 depletion method are the most frequently used methods in Sweden to estimate weathering rates. The benefit of

235 ~~comparing these two methods is that, taken together, they can provide complementary information about soil~~
236 ~~weathering potential (i.e. historical versus steady-state weathering) in individual soil layers.~~

237 ~~In this study, we applied the our aim was to apply three conceptually different methods of estimating weathering~~
238 ~~on the depletion method, the PROFILE model and the BC budget approach, to two well-defined forest~~
239 ~~ecosystems, Asa and Flakaliden in southern and northern Sweden, to allow a harmonized comparison of methods,~~
240 ~~and to place weathering in the context of other base cation fluxes in aggrading Norway spruce forests. These~~
241 ~~optimum (tree) nutrition experimental sites were selected for the study to obtain a well-defined system with~~
242 ~~uniform spatial scale for observations, in line with the suggestion of by Futter et al. (2012). In addition, BC~~
243 ~~base cation budgets were estimated at the period of stand development when nutrient demand was expected to~~
244 ~~peak. In combination with access to highly accurate data on biomass production, these conditions also provided~~
245 ~~opportunities to relate weathering to base cation BC accumulation in biomass at high nutrient uptake rates, and~~
246 ~~possible simultaneous depletions of extractable base cation BC stocks in the soil. Furthermore, input data to~~
247 ~~PROFILE were as characterised by high quality quantitative mineralogical data, measured directly by X-ray~~
248 ~~powder diffraction (XRPD), as and has been critically previously discussed in by Casetou-Gustafson et al.~~
249 ~~(2018).~~

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

253 2. Materials and methods

254 2.1 Study sites

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

259
260 The experiment at Flakaliden was established in 1986 in a 23-year-old Norway spruce stand, planted in 1963 with
261 four-year-old seedlings of local provenance after prescribed burning and soil scarification (Bergh et al., 1999).

262 The experiment at Asa was established one year later (1987), in a 12-year-old Norway spruce stand planted in
263 1975 with two-year-old seedlings after clear-felling and soil scarification. The experimental design was similar at
264 both sites and included control, irrigation and two nutrient optimisation treatments (Bergh et al., 1999). All
265 treatments ~~had four replicates~~ were replicated in 50 m x 50 m plots, arranged in a randomised block design. Only
266 two of the four treatments were used in the present study; the control (C) and plots receiving an annual dose of an
267 optimised mix of solid fertiliser (F), which among other elements per year contained about 10 kg ha⁻¹ Ca, 8 kg ha⁻¹
268 Mg and 45 kg ha⁻¹ K (Linder, 1995). For further details, see Linder (1995).

269

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

276
277 Asa is located in the hemi-boreal zone, where the climate is milder than at Flakaliden, which is reflected in a
278 longer growing season (193 days). Mean annual temperature (1990-2009) was 6.3 °C, mean monthly temperature
279 varied from -1.9 °C in February to 16.0 °C in July and mean annual precipitation was ~750 mm. The soil is
280 periodically frozen in winter. The difference in climate is reflected in differences in site productivity, which
281 broadly follows climate gradients in Sweden (Bergh et al., 2005).

282
283 The soils at Asa and Flakaliden differ in age due to differences in the time since deglaciation (Table 1). ~~Soil age~~
284 ~~is from~~ approximately 14,300 ~~thousand~~ years at Asa and 10,150 ~~thousand~~ years at Flakaliden (~~based on~~
285 ~~National Atlas of Sweden; estimated from~~ Fredén, 2009). The soil type at both sites is an Udic Spodosol, with a
286 mor humus layer overlying ~~glacial till derived from felsic acid igneous silicate~~ bedrock. The soil texture is
287 classified as sandy loam ~~my till~~. The ~~transition between the B- and C-horizons~~ ~~B-horizon transitions to C-horizon~~
288 ~~is mostly located~~ at 35-50 ~~40~~ cm depth at Flakaliden and 50-60 ~~40~~ cm depth at Asa. The natural ground vegetation
289 at Flakaliden is dominated by *Vaccinium myrtillus* (L.) and *V. vitis-idaea* (L.) dwarf-shrubs, lichens and mosses
290 (Kellner, 1993; Strengbom et al., 2011). ~~T,~~ while the ground vegetation at Asa is dominated by *Deschampsia*
291 *flexuosa*, (L.) and mosses (Strengbom et al., 2011; Hedwall et al., 2013).

292 2.2. Soil sampling and analyses of geochemistry and mineralogy

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

295 ~~Soil sampling was performed in October 2013 (Flakaliden) and March 2014 (Asa), in the border zone of four plots~~
296 ~~at each site. Plots selected for~~ ~~s~~ ~~Sampling was performed in~~ ~~ere~~ untreated control plots (K1 and K4 at Asa ~~and~~; 10B
297 and 14B at Flakaliden) and fertilised (F) plots (F3, F4 at Asa ~~and~~; 15A ~~and~~; 11B at Flakaliden) ~~in October 2013~~
298 ~~(Flakaliden) and March 2014 (Asa), in the border zone of four plots at each site. One intact soil core per plot at~~
299 ~~Flakaliden and in plot K1 at Asa was extracted using a~~ ~~A~~ rotary drill (17 cm inner diameter) ~~was used to extract~~
300 ~~one intact soil core per plot at Flakaliden and in plot K1 at Asa~~. In plots K4, F3 and F4 at Asa, soil samples were
301 ~~instead~~ taken from ~~the wall of~~ 1 m deep ~~manually dug~~ soil pits, due to inaccessible terrain for ~~the rotary drill forest~~
302 machinery. Maximum soil depth was shallower at Flakaliden (70-90 cm) than at Asa (90-100 cm). The volume
303 of stones and boulders was determined for each plot at the two study sites using the penetration method described
304 by Viro (1952) to a maximum depth of 30 cm and by applying the fitted function described by Stendahl et al.
305 (2009). Mean stone and bolder content was higher at Flakaliden (39%_{vol}) than at Asa (28%_{vol}).

306 Soil samples were taken from each 10-cm soil layer. Prior to chemical analysis, these samples were dried at 30-
307 40 °C and sieved to <2 mm mesh. Analysis of particle size distribution was performed by wet sieving
308 and sedimentation (pipette method) in accordance with ISO 11277. Geochemical analyses were conducted by
309 ALS Scandinavia AB and comprised inductively coupled plasma-mass spectrometry (ICP-MS) on HNO₃ extracts
310 of fused samples that were milled and ignited (1000 °C) prior to fusion with LiBO₂.

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

320 2.3 Historical weathering determined with the depletion method

321 2.3.1 Method description

322 The depletion method (Table X2), as defined by Marshall and Haseman (1943) and Brimhall et al. (1991),
323 estimates the accumulated mass loss since soil formation (last deglaciation for our sites) as a function of loss of a
324 mobile (weatherable) element and enrichment of an immobile (weathering resistant) element according to the
325 following general function introduced by Olsson and Melkerud (1989) and based on the same theories as the mass
326 transfer function described in Brimhall et al. (1991):

$$327 W_{\text{depletion},i} = \frac{d \cdot \rho}{100} \cdot \frac{X_c \cdot Zr_{w,i}}{Zr_c} - X_{w,i} \quad (1)$$

328 where W denotes loss of the i th element (g m^{-2}), X denotes mobile element concentrations (%), Zr denotes
329 immobile element concentrations (%), w and c denote a weathered soil layer and a weathered soil layer and
330 the assumed unweathered reference layer, respectively, d is layer depth/thickness (m), and ρ is bulk density (g m^{-3}). Zirconium is commonly used as the immobile element due to the inert nature of the mineral zircon (ZrSiO_4),
331 although Ti is sometimes used due to the resistance of the Ti-containing minerals anatase and rutile (TiO_2) to
332 weathering (Olsson and Melkerud, 1989). The unweathered reference layer. The maximum weathering depth,
333 below which weathering is assumed to cease, is defined by a reference layer that is located in the soil C
334 horizon, and has X to Zr ratios that are assumed to represent pristine conditions of the presently
335 weathered layers above it. In the weathered layers, X to Zr ratios are smaller; that is, Zr is the reference layer. Zr
336 is enriched compared with the mobile other elements (i.e. the base cations). The method is based on the
337 assumptions that Zr , hosted in zircon, was uniformly distributed throughout the soil profile at the time of
338 deglaciation, that weathering only occurs above the reference layer and that zircon does not weather. The latter
339 implies that the Zr concentrations gradient and Zr /base cation ratios are constant below the reference layer.

341 Table 2-3 shows the reference depths for different base cations compared with Zr, which were used as the depths
342 of immobile element concentrations. The Zr/base cation ratio (Fig. S3) was used to help select defining the
343 reference soil layer as it highlights shows heterogeneities in parent material with depth. In cases of heterogeneities
344 in the profile, the reference layer was chosen above this heterogeneity. This choice was precluded not given for
345 soil profile 11B, where Zr concentrations and Zr/base cation Ce ratios peaked directly below the B-horizon s(i.e.
346 at 50-60 cm).

347 2.3.2. Assumption testing Application

348 Prior to calculating base cation weathering rates with the depletion method, fractional volume change (V_p) was
349 calculated according to White et al. (1996) in order to assess if there were any large volume changes (collapse)
350 in the mineral soil with implications for which depth the weathering should be calculated to. Similar to White et
351 al. (1996), it was assumed that values close to zero indicate no volumetric change, which was the case below 30-
352 40 cm of soil depth at Asa and Flakaliden both sites (Table S5). The homogeneity of the parent material was also
353 evaluated (Fig. 1) using the criterion that: Since zircon and anatase and rutile are weathering resistant minerals,
354 it was assumed that the ratio of Ti to Zr would should be more or less stable with as soil depth in an originally
355 homogeneous material increases and, as such if so, uniformity of the parent material could be assumed ensured.
356 Use of the ratio of two immobile elements resistant minerals to establish uniformity of parent material has been
357 suggested previously (Sudom and St.Arnaud, 1971; Starr et al., 2014). This was the case for plots F3, K4 and F4
358 at Asa, but in plot K1 where there was somewhat more variability in plot K1 (i.e. the Zr concentrations decreased
359 towards the soil surface; Fig. 25). Consequently, Ti was used as the immobile element instead of Zr for this
360 profile. At Flakaliden, variability in both the Zr and Ti gradients was observed, but the parent material was
361 considered sufficiently uniform for all plots except 15A, so eliminated consideration The homogeneity criterion
362 was not met using Zr in plot K1 at Asa (i.e. the Zr concentrations decreased towards the soil surface; Fig. 2); here
363 Ti was used as the immobile element instead. Furthermore, the plots 15A and 11B at Flakaliden had to be
364 eliminated from the calculations, because relatively large variability in both the Zr and Ti gradients was observed.
365 These large heterogeneities led to an overall gain of base cations in the rooting zone, which is opposite to what
366 would be expected (i.e. that losses and gains can occur at specific soil depths due to eluviation and illuviation
367 processes in podzolic soils). For this reason, soil profiles 15A and 11B were eliminated from further consideration
368 in calculations of historical weathering rates using the depletion method. Thus, apart from heterogeneities,
369 transportation processes (eluviation and illuviation) and/or erratic Zr or Ti gradients could lead to "negative"
370 weathering, i.e. leading to a calculated relative accumulation of elements. Such negative values were not
371 considered in the calculation of historical weathering losses.

372 2.3.3. Input data

373 Bulk density was estimated for each soil layer except in some plots where density measurements could not be
374 made below a certain soil depth or where a large and sudden decrease in bulk density with increasing soil depth
375 was observed. Bulk density in these cases was estimated using an exponential model for total organic carbon
376 (TOC) and bulk density (BD, g/cm^3) based on our own data. For Asa (soil layers F3: soil layer 70-90 cm; F4: 0-

377 10, 30-40, 50-60, 60-70, 70-80, 80-90, 90-100 cm; and K4: 70-80, 80-90, 90-100 cm), the following function was
378 used:

$$379 \rho_{BD} = 1.3 e^{-0.1 \times BD} = 1.3 e^{-0.1x}$$

380 (21)

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

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

$$383 \rho_{BD} = 1.8 e^{-0.2 \times BD} = 1.8 e^{-0.2x}$$

384 (32)

385 2.4 The PROFILE model

386 2.4.1 Model description

387 ~~The steady state weathering of soil profiles was estimated using t~~The biogeochemical PROFILE model (Table
388 ~~2X) can be used to estimate the steady state weathering of soil profiles, whereas weathering of the i th base cation~~
389 ~~($W_{profile,i}$) is described by long-term mineral dissolution kinetics at is known to be primarily determined by soil~~
390 ~~physical properties at~~ the interface of wetted mineral surfaces and the soil solution. PROFILE is a multilayer
391 model, where parameters are specified for each soil layer based on field measurements and estimation methods
392 (Warfvinge and Sverdrup, 1995).

393 2.4.2 PROFILE parameter estimation

394 A detailed description of ~~the~~ application of the PROFILE model to the soils and sites in the present study can be
395 found in Casetou-Gustafson et al. (*this issue*). The parameters used are listed in Table 43.

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

400 ~~The a~~Aluminium (Al) solubility coefficient, a soil chemical parameter needed for solution equilibrium reactions,
401 was defined as $\log\{\text{Al}^{3+}\} + 3\text{pH}$. It was estimated by applying a function developed from previously published data
402 (Simonsson and Berggren, 1998) and existing total carbon and oxalate-extractable Al measurements for our sites
403 (Casetou-Gustafson et al., 2018) (Table S4). For partial CO_2 pressure in the soil, the default value of Warfvinge
404 and Sverdrup (1995) was used. Data on measured dissolved organic carbon (DOC) in the soil solution at 50 cm
405 depth were available for plots K4 and K1 at Asa and plots 10B and 14B at Flakaliden, and these values were also
406 applied for deeper soil horizons. Shallower horizons (0-50 cm) were characterised by higher DOC values, based
407 on previous findings (Fröberg et al., 2006, 2013) and the DOC classification scheme in Warfvinge and Sverdrup
408 (1995) (Table S4).

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

412 Total deposition was calculated using deposition data from two sites of the Swedish ICP Integrated Monitoring
413 catchments, Aneboda (for Asa) and Gammtratten (for Flakaliden) (Löfgren et al., 2011). Na was used as a tracer
414 ion in order to distinguish canopy exchange from dry deposition for Ca, Mg and K. Na was used as a tracer ion.
415 Dry deposition for Na and Cl was calculated as the difference between wet and throughfall deposition. As outlined
416 in Zetterberg et al. (2016), wet deposition for all elements was calculated by correcting bulk deposition for dry
417 deposition using wet-only to bulk deposition ratio. Finally, total deposition for all elements was estimated by
418 summing up dry deposition and wet deposition. The canopy budget method of Staehens et al. (2008) was applied
419 as in Zetterberg et al. (2016). The canopy budget model is commonly used for elements that are prone to canopy
420 leaching (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , SO_4^{2-}) or canopy uptake (NH_4^+ , NO_3^-) and it calculates total deposition as the sum
421 of dry deposition and wet deposition. Wet deposition was estimated based on the contribution of dry deposition
422 to bulk deposition, both for base cations and anions, using dry deposition factors from Karlsson et al. (2012,2013).
423 Finally, total deposition for all elements was calculated estimated by summing from the sum of dry and wet
424 deposition.

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

430 2.4.3 PROFILE sensitivity analysis

431 The sensitivity of PROFILE to ~~a~~ changes in soil physical and mineralogical input was analysed, to test to what
432 extent whether the depth gradients of weathering rates as predicted by PROFILE were affected primarily by ~~could~~
433 be explained by either soil physical properties or by soil mineralogy. Independent PROFILE runs were performed,
434 after replacing horizon-specific input values with soil profile average values regarding either (1) soil bulk density
435 and specific exposed mineral surface area ('homogenousised soil physics'), or (2) soil mineral
436 percentages ('homogenousised mineralogy'), or (3) both ('homogenousised soil physics and mineralogy'). ~~for~~
437 each of the following three test scenarios: (1) homogeneous soil physical properties (soil bulk density and specific
438 exposed mineral surface area); (2) homogeneous mineralogy; and (3) homogeneous soil (i.e. soil physics and
439 mineralogy). For homogeneous soil, all soil layers (0-100 cm) were given the same value of the test variable,
440 which was i.e. the average value for the actual soil profile (0-100 cm). In each scenario, the squared deviation in
441 weathering rate was calculated for each base cation and horizon, compared to the normal simulation based on
442 horizon-specific inputs for soil physics and soil mineralogy. The sum of squares over base cations and horizons
443 was used as a measure of the overall error caused by the 'homogenousised' input data. The ratios of sum of

squares, of scenario (1) over (3) and of scenario (2) over (3), was used to estimate the percent contribution of soil physics and soil mineralogy, respectively, to the overall weathering gradients in the soil profile.

2.5 The base cation budget approach mass-balance method

2.5.1. General concepts of the base cation budget approach mass-balance method

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

(3)

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

2.5.2 Atmospheric deposition, TD_i

The same estimates of total atmospheric deposition as used in parameter setting of the PROFILE model (section 2.4.2) were used in the mass-balance base cation BC budget, Eq. (4) equation 43.

2.5.3. Changes in exchangeable soil pools, $\Delta S_{\text{BC}i}$

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

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

477 Exchangeable base cation content in the soil (<2 mm) ~~in the all~~ Flakaliden samples ~~from 1986 and 1998 and the in~~
478 Asa samples from 1988 was determined by extraction of dry samples with 1 M NH₄Cl using a percolation method,
479 where ~~2.5 g of sample was leached with~~ 100 mL of ~~extractant solution was percolated through 2.5 g of sample at~~
480 a rate of ~~around~~ 20 mL h⁻¹. The base cations were analysed by atomic absorption spectrophotometry (AAS). For
481 the Asa samples from 2004, ~~batch extraction was performed~~ ~~extraction was performed~~ using the same extractant
482 ~~in a batch extraction method~~, and the base cations were determined with ICP. A separate test was made to compare
483 the yield of the percolation and batch extraction methods. ~~No consistent difference between the methods was~~
484 ~~observed, but the results were inconclusive and therefore no correction was made to account for possible~~
485 ~~differences between the extraction methods.~~

486
487 The amount of fine soil (<2 mm) per unit area was calculated from the volume of fine ~~soil earth (<2 mm)~~ in the
488 soil profiles and the average bulk density of the soil in the 0-10, 10-20 and 20-40 cm layers. Bulk density and
489 volume proportion of stoniness at Flakaliden were determined from samplings in 1986 in 20 soil profiles (0.5 m
490 x 0.5 m and about 0.5 m deep) outside plots. At Asa, stoniness was determined with the penetration method of
491 Stendahl et al. (2009) and the bulk density of soil <2 mm was calculated using a pedotransfer function that
492 included soil depth and measured carbon concentrations as variables.

493 2.5.4 Net uptake in biomass, $\Delta B_i B_{BC}$ (1987-2003)

494 Accumulation of base cations in tree biomass, i.e. net uptake of base cations, was calculated as ~~a~~ mean value of
495 control plots over the period 1989-2003. ~~The calculations were~~ based on increments in aboveground biomass at
496 Asa and Flakaliden for this period ~~(Albaugh et al., 2009, 2012)~~ and ~~on the~~ concentrations of elements in different
497 tree parts. ~~The increment in aboveground biomass was based on measurements of stem diameter at breast height~~
498 ~~(DBH) of all individual trees in the plots, and applying DBH data to allometric functions developed for Norway~~
499 ~~spruce at Asa and Flakaliden the sites (Albaugh et al., 2009, 2012). The allometric functions were based on~~
500 ~~destructive samplings (1987 - 2003) of 93 and 180 trees at Asa and Flakaliden respectively.~~ The increment in
501 belowground biomass was estimated from general allometric functions for Norway spruce stumps and roots in
502 Sweden (Marklund, 1988). Since Marklund's functions (1988) underestimate belowground biomass by 11%, a
503 factor to correct for this was included (Petersson and Ståhl, 2006). Furthermore, the finest root fraction (≤ 2 mm),
504 which is not included in the functions of Marklund (1988) and Petersson and Ståhl (2006), was assumed to be
505 20% of needle biomass at Asa and 33% at Flakaliden, respectively, based on data from Helmisaari et al. (2007).

506
507 Data on element concentrations in biomass were available from measurements on harvested trees (S. Linder,
508 unpubl. ~~ished~~ data). At Flakaliden, total element concentrations were analysed in trees sampled for biomass
509 determination in 1992 and 1997. ~~Analyses of N~~ needles and branches (dead and live) were conducted on the same
510 tree parts in the biomass sampled in 1993 and 1998. Base cation concentrations in biomass were determined from
511 acid wet digestion in HNO₃ and HClO₄, followed by determination of elements by ICP-atomic emission
512 spectrophotometry (ICP-AES) (Jobin Yvon JY-70 Plus).

513

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

517 **2.5.5. Leaching, ~~Li & B.C.~~**

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

520
521 ~~Soil water was collected from five ceramic tension lysimeters (P80) installed at 50 cm depth in each experimental~~
522 ~~plot. Soil water was collected on 2-3 occasions per year during frost-free seasons, applying an initial tension of~~
523 ~~70 kPa in 250 mL sampling bottles, and left overnight. These soil water samples were pooled by plot. The base~~
524 ~~cation concentration in the soil solution was determined with ICP-AES.~~

525 ~~Soil water sampling was performed twice every year, i.e. in the spring and in the autumn, which isare the periods~~
526 ~~of highest water flux and which means that the most important leaching events arewere covered. The spring~~
527 ~~samples were collected soon after the snowmelt and depending on currentthe weather in a specific year this meant~~
528 ~~that the yearly spring sampling date varied between the last week of April and the last week of May. The~~
529 ~~fallautumn samples were collected when late, i.e. frost risk increased. That meant that the fallautumn sampling~~
530 ~~dates varied from year to year, i.e. from the first week in September to mid-November. The seasonal variation in~~
531 ~~soil water chemistry is shown in Fig. S4).~~

532
533 ~~An additional illustration of the variation in water chemistry with time of the year could be given as Fig.S4 to~~
534 ~~show base cation fluxes for this period and to compare with the drainage flux (Fig.S5). Base cation leaching was~~
535 ~~quantified in 6-month intervals from modelled runoff multiplied by average element concentrations in soil water~~
536 ~~collected with tension lysimeters at 50 cm soil depth. Runoff was calculated using CoupModel (Jansson, 2012).~~
537 ~~The drainage flux out of the profile was calculated by the CoupModel (Jansson, 2012). The model was~~
538 ~~parameterised based on hydraulic soil properties measured at the sites. The model was run with hourly mean~~
539 ~~values of locally measured climate variables (precipitation, global radiation, wind speed, air temperature and~~
540 ~~humidity) and model outcomes were tested against tensiometer data, i.e. bi-weekly tensiometer readings at 15, 30~~
541 ~~and 45 cm depth were used for model calibration. The parameters were then adjusted slightly to obtain goodthe~~
542 ~~best agreement between measured and calculated soil water content. Annual precipitation varied considerably~~
543 ~~during the period 1990-2002, ranging from 906 to 504 mm at Flakaliden (mean 649 mm) and from 888 to 575~~
544 ~~mm at Asa (mean 736 mm).~~

545 ~~Annual evapotranspiration increased by about 50 mm at both sites, during the period 1987-2003 at Flakaliden and~~
546 ~~1990-2002 at Asa, due to the increment in tree- leaf areabiomass. Monthly means and standard deviation of~~
547 ~~drainage (mm) at 50 cm depth in the soil of control plots at Asa during 1990 – 2004 and at Flakaliden during~~
548 ~~1988-2004 are shown in andFig. S5.~~

549
550 ~~Annual precipitation varied considerably during the period 1990-2002, ranging from 906 to 504 mm at Flakaliden~~
551 ~~(mean 649 mm) and from 888 to 575 mm at Asa (mean 736 mm).~~

552
553 ~~Coupled~~ was parameterised based on measured hydraulic soil properties. ~~M~~The model was run with hourly
554 ~~mean values of local measured measured~~ climate variables (global radiation, wind speed, air temperature and
555 ~~humidity) and model outcomes were tested against tensiometer data, i.e. bi-weekly tensiometer readings at 15, 30~~
556 ~~and 45 cm depth were used for model calibration.~~

557 ~~. The parameters were then adjusted slightly to obtain the best agreement between measured and calculated soil~~
558 ~~water content. Annual evapotranspiration increased by about 50 mm at both sites, during the period 1987-2003 at~~
559 ~~Flakaliden and 1990-2002 at Asa, due to the increment in tree biomass. Soil water was collected from five ceramic~~
560 ~~tension lysimeters (P80) installed at 50 cm depth in each experimental plot. Soil water was collected on 2-3~~
561 ~~occasions per year during frost free seasons, applying an initial tension of 70 kPa in 250 mL sampling bottles,~~
562 ~~and left overnight. These soil water samples were pooled by plot. The base cation concentration in the soil solution~~
563 ~~was determined with ICP-AES.~~

564 2.5.6. ~~Assessment~~Judgement of data quality in ~~base cation budget~~mass balance

565 The precision and accuracy of a ~~base cation budget~~mass balance estimate of $W_{\text{budget},j}$ was ~~was~~ $W_{\text{bc},j}$ is determined by
566 the quality of estimates of each individual term in ~~Eq. (3)~~equation 3, in proportion to the magnitude of each term
567 (Simonsson et al., 2015). Significant uncertainty in the estimate of a quantitatively important term will therefore
568 dominate the overall uncertainty in estimates of $W_{\text{budget},j}$. ~~Firstly,~~ ~~t~~The quality of data for each term in ~~Eq.~~
569 ~~(3)~~equation 3 was assessed based on the spatial and temporal scales of measurements and the quality of
570 measurements (Table 54). ~~Using~~ ~~Based on~~ these criteria, we consider the estimates of deposition, leaching and
571 accumulation in biomass to be of moderate to high quality. The measurements of changes in extractable soil pools
572 were of lower quality because ~~extraction methods were not identical for samples collected 1986/1988 and~~
573 ~~1998/2004~~of bias in methods in repeated samplings, which would cause significant uncertainty if soil changes
574 were an important part of the element budget. To partly overcome this uncertainty, we used the estimates ~~of~~ W_{bc}
575 obtained by the PROFILE ($W_{\text{profile},c}$, W_{profile}) and depletion method ($W_{\text{depletion},j}$, $W_{\text{depletion}}$)s in additional ~~base cation~~
576 ~~budget~~mass balance calculations where the change in soil was determined from the ~~base cation budget~~mass
577 ~~balance~~. These additional ~~base cation budget~~mass balance estimates, which are conceptually analogous to the
578 regional mass balances presented by Akselsson et al. (2007), were also used to place the PROFILE and depletion
579 method estimates of W_{bc} , W_j in the context of other base cation fluxes at ~~the~~ ecosystem scale.

580

581 2.6 Statistical analyses

582 Site mean values and standard error (SE) of $W_{\text{depletion}}$, W_{profile} were calculated based on the four (or two) soil profiles
583 studied at each site. For W_{budget} an average based on the four control plots at each site was calculated as well as a
584 combined standard uncertainty. The latter was partly based on standard errors derived from plot-wise replicated
585 data of the present experiments (for leaching and changes in exchangeable soil pools, $SE(L_i)$ and $SE(\Delta S_i)$,
586 respectively), partly on standard uncertainties (u) derived from Simonsson et al. 2015, where replicated data were
587 missing in the present study (for accumulation in biomass and total deposition, $u(\Delta B_i)$ and $u(TD_i)$, respectively).
588 Because total deposition and bioaccumulation differed substantially from those in the study of Simonsson et al.

589 2015, relative standard uncertainties were derived from that study, and multiplied with the average deposition and
 590 bioaccumulation rates at Asa and Flakaliden, respectively, to yield realistic standard uncertainties for the present
 591 sites. For the weathering rate of the i th base cation according to Eq. (4), a combined standard uncertainty (u_c) was
 592 calculated as:

$$593 \quad u_c(W_{budget, i}) = \sqrt{(SE(L_i))^2 + (u(\Delta B_i))^2 + (SE(\Delta S_i))^2 + (u(TD_i))^2} \quad (5)$$

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

596 ~~Site mean values and standard error (SE) of weathering rates were calculated based on the four (or two) soil
 597 profiles studied at each site ($W_{depletion}$, $W_{profile}$) and on the W_{budget} , W_{bioM} estimates for the four control plots at each
 598 site. The combined standard uncertainty of W_{budget} , W_{bioM} was estimated as the square root of the sum of squared
 599 standard errors of the from the sums of 95% confidence interval of the terms in the right hand terms side of Eq.
 600 (4) equation (4). The confidence intervals for soil change and leaching was based on measured between-plot
 601 variation (n=4) using 1.96 as coverage factor. Standard errors: The confidence interval for deposition and base
 602 cation biomass accumulation in biomass and deposition was based on calculations from Simonsson et al.
 603 (2015; Table 4-8 in that paper) of an experimental study site in southern Sweden (Skogaby), since L_i and ΔB_i , L_{GC}
 604 and B_{GC} data were not available for individuals plots. A coverage factor of 3 was then used.~~

606 3. Results

607 3.1 Depletion method estimates of historical weathering rates

608 At both Asa and Flakaliden, historical weathering rates estimated with the depletion method ($W_{depletion}$) were
 609 highest in the upper soil layers and showed a gradual decrease down to the reference depth, which was defined in
 610 ~~most plots~~ at 60-70 cm at Flakaliden and ~~for most plots~~ at 80-90 cm at Asa (Fig. 32). ~~Weathering had also taken
 611 place below the reference depth. In line with the younger age of the soils at Flakaliden (indicated also by higher
 612 abundance of the had a higher content of more easily weatehrbale weatherable minerals amphibole, trioctahedral
 613 phyllosilicates and calcic plagioclase), and also at the higher~~ historical annual weathering rate ~~to 90 cm soil
 614 depth was higher at Flakaliden, 37.8 mmol_c m⁻²yr⁻¹, compared to than Asa, 12.8 mmol_c m⁻²yr⁻¹. The base cation
 615 weathering down to 90 cm soil depth amounted to 12.8 mmol_c m⁻²yr⁻¹ at Asa and 37.825.1 mmol_c m⁻²yr⁻¹ at
 616 Flakaliden. The corresponding value for the 0-50 cm horizon depth was 34.1 mmol_c m⁻²yr⁻¹ at Flakaliden and
 617 10.5 mmol_c m⁻²yr⁻¹ at Asa and 34.122.4 mmol_c m⁻²yr⁻¹ at Flakaliden. The gradients with depth showed that $W_{depletion}$
 618 increased towards the surface, although this trend was more pronounced at Flakaliden than at Asa. Furthermore,
 619 ~~at~~ Flakaliden, $W_{depletion}$ was highest for Mg, followed by Ca, Na and K (Figs. 2 and 33 and 4); ~~at~~ Asa, the
 620 largest average mass loss was observed ~~it was highest~~ for Ca, closely followed by Mg, Na and K (Figs. 32 and 43).~~

621 3.2 PROFILE model estimates of steady state weathering rates

622 The steady state weathering rate estimated by the PROFILE model (W_{profile}) differed from the historical rate with
623 respect to all ~~aspects covered by the three starting hypotheses test criteria~~, i.e. (1) total weathering rate in the 0-50
624 cm soil layer, (2) variation in weathering with depth and (3) ranking order of base cations (Figs. 3 and 4 Figs. 2
625 and 3). ~~Firstly, regarding base cation weathering rate in the upper 50 cm of the mineral soil, W_{profile} estimates for~~
626 ~~Asa and Flakaliden (Asa: $37.1 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$, Flakaliden: $42.7 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$) were around 3.5 and 1.3-fold higher~~
627 ~~than $W_{\text{depletion}}$ estimates, respectively. Secondly, the total modelled base cation weathering rate for the soil profile~~
628 ~~down to 90 cm was around 7-fold higher than the rate estimated using the depletion method at Asa (89.4 mmol_c~~
629 ~~$\text{m}^{-2} \text{ yr}^{-1}$), and almost 3.45-fold higher at Flakaliden ($127.6 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$). U-Secondly,~~
630 ~~unlike the historical weathering based on the depletion method, PROFILE predicted that weathering rates~~
631 ~~increased with soil depth at both sites Asa (down to 90 cm) and Flakaliden (down to 60 cm). At Flakaliden,~~
632 ~~anomalously high contents of K- and Mg-bearing tri-octahedral mica (Casetou-Gustafson et al., 2018) gave rise~~
633 ~~to increased particularly high weathering rates at 70-80 cm. Thirdly, as opposed to $W_{\text{depletions}}$, Apart from in that~~
634 ~~specific soil layer, at both sites W_{profile} was largest for Na at both sites, followed by Ca. However, W_{profile} was~~
635 ~~larger for K than for Mg at Asa, while the reverse was true at Flakaliden.~~

636 ~~In general, PROFILE also predicted much higher weathering rates than the depletion method (Fig. 32). However,~~
637 ~~both methods estimated consistently higher weathering rates at Flakaliden than Asa. The total modelled base~~
638 ~~cation weathering rate for the soil profile down to 90 cm was around 7-fold higher than the rate estimated using~~
639 ~~the depletion method at Asa ($89.4 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$), and almost 5-fold higher at Flakaliden ($127.6 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$).~~

640 ~~Weathering rates are often reported for the upper 50 cm soil layer, as an approximation of the root zone. On~~
641 ~~restricting the base cation weathering rate to the upper 50 cm of the mineral soil, W_{profile} estimates for Asa and~~
642 ~~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~~
643 ~~for $W_{\text{depletion}}$ as shown above, as the estimate for Flakaliden was more than twice that obtained for Asa. However,~~
644 ~~$W_{\text{depletion}}$ was higher than W_{profile} for Mg. In relative terms, the difference between sites in $W_{\text{depletion}}$ in the 0-50 cm~~
645 ~~layer was similar to the difference observed for the whole soil profile.~~

646 The sensitivity analysis of the PROFILE model using homogeneous soil physical and/or mineralogical properties
647 demonstrated that ~~the variations in soil physical parameters properties (i.e. soil bulk density and specific exposed~~
648 ~~mineral surface area soil texture and density) with depth had a greater influence, rather than mineralogy, was the~~
649 ~~most important input data explaining on the observed change in W_{profile} with soil depth. Applying homogeneous~~
650 ~~mineralogy had little effect, with the original gradient of W_{profile} (Fig. 32) being similarly reproduced with depth.~~
651 ~~However, when homogeneous soil physical conditions were applied (i.e. a combination of homogeneity in soil~~
652 ~~physics and soil mineralogy), there were some small variations in W_{profile} between soil layers (Tables S1 and S2).~~
653 ~~In terms of the ratios of sums of squares of error, the 'homogenously calculated from the difference in W_{profile}~~
654 ~~between actual and homogeneous soil, 75-85% of the total error at Flakaliden was due to homogeneity in soil~~
655 ~~physics only, while the error due to homogeneous mineralogy was 2-17%. soil physics' of scenario (1) produced~~
656 ~~75% or more of the error obtained with 'homogenously soil physics and mineralogy' (scenario (3)), leaving a~~
657 ~~mere 25% or less to the 'homogenously mineralogy' of scenario (2); The corresponding error values for Asa~~

658 were 76-94% and 1-4%, respectively also see Tables S1 and S2. One exception to these findings was plot 10B at
659 Flakaliden, which showed somewhat higher error (17%) resulting from homogeneous mineralogy. This was due
660 to the anomalously high content of trioctahedral micas at 70-80 cm depth, as previously reported by Casetou-
661 Gustafson et al. (2018). At Asa, an outlier to the results was plot F3, where homogeneous soil physical properties
662 produced 109% of the error resulting from homogeneous soil. This was because, by coincidence, soil profile F3
663 had relatively high bulk density and exposed mineral surface area in the uppermost soil layer, compared with the
664 average soil physical input data, and therefore the homogeneous soil test produced lower weathering rates. The
665 soil physical input parameters that were more important for PROFILE weathering rates are indicated in Figs. S1
666 and S2. There was a strong linear and positive relationship between exposed mineral surface area and W_{profile} for
667 all elements at both sites, with R^2 values ranging from 0.65 to 0.89 (Fig. S1). The relationship between bulk density
668 and W_{profile} was also strong and showed the same linear response, although R^2 values were lower, 0.40-0.70 (Fig.
669 S2).

670 3.3 Base cation budget/mass-balance estimates of current weathering rates

671 A comparison of weathering rates estimated by base cation budgets/mass-balance ($W_{\text{budget/mass-balance}}$), W_{profile} and
672 $W_{\text{depletion}}$ was made for the 0-50 cm soil layer. The physical boundary for the base cation budget/mass-balance was
673 defined by the depth of soil solution sampling (50 cm). It was found that, for most elements, $W_{\text{mb}} - W_{\text{budget}} - W_{\text{beeb}}$ in
674 the 0-50 cm layer was higher, or much higher, than W_{profile} (Fig. 43). Compared with the PROFILE model
675 estimates, the base cation budget/mass-balance estimates of weathering were 6- to 7-fold higher for Ca, Mg and K
676 weathering at Asa, and about 2- to 3-fold higher for Ca, Mg and K at Flakaliden. At Asa, the sum of base cations
677 was on average 13-fold and 3.6-fold larger than $W_{\text{depletion}}$ average annual long-term weathering rates based on the
678 depletion method and W_{profile} PROFILE method, respectively. The closest fit/resemblance between methods was
679 found between $W_{\text{depletion}}$ and $W_{\text{mb}} - W_{\text{budget}} - W_{\text{beeb}}$ for Na. The budget calculations suggested that weathering was a
680 dominant source of K and Mg, but contributed a somewhat smaller proportion of Ca (61% at Asa and 43% at
681 Flakaliden).

684 3.4 Base cation fluxes in measured base cation budgets/mass-balances

685 As to the general pattern in base cation fluxes (terms) of in the base cation budget, mass-balances was the
686 difference between Na showed patterns different from those of, on the one hand, and K, Mg and Ca on the other
687 (Fig. 54). For Na, uptake in biomass was negligible and leaching was the dominant sink. For the latter three
688 elements, this difference was largely due to accumulation in biomass being was the dominant sink for the latter
689 elements, whereas Na uptake in biomass was negligible and leaching was the dominant sink. Compared with
690 biomass uptake, loss by leaching was a negligible sink for K, but significant a significant sink for Mg and Na.

691
692 Deposition generally represented only was a minor small source of base cation inputs, except for Na at Asa. The
693 measured decreases in soil stocks of exchangeable base cations indicated that a change in this pool was a
694 particularly important source of Ca. There were minor increases in exchangeable stocks for Na, K and Mg at Asa.

695
696 ~~In summary, the base cation budgetmass balance calculations indicated that weathering was a particularly~~
697 ~~dominant source of K and Mg, but weathering contributed a relatively smaller proportion of the total Ca sources~~
698 ~~than for K and Mg (61% at Asa and 43% at Flakaliden).~~

699
700 ~~The combined uncertainty of W_{budget} was larger for Ca and K, both dominated by the bioaccumulation term in~~
701 ~~Eq. (4), than for Na and Mg (Table 6). In relation to the mean W_{budget} , the combined uncertainty was of the same~~
702 ~~order of magnitude for Na, about the half for Ca, one-third for K, and lower for Mg. In relation to the mean~~
703 ~~W_{budget} , the combined uncertainty was about 3 times higher for Na, 2 times higher for Ca and of the same order~~
704 ~~or lower for K and Mg. The contribution of the combined uncertainty from the different terms in equation (4)~~
705 ~~reflected their quantitative importance in the budget for each element. For example, uncertainty in biomass~~
706 ~~accumulation dominated in the combined uncertainty for Ca and K, but was negligible for Na.~~

707
708 By using the weathering estimates obtained ~~using with~~ PROFILE and the depletion method in the ~~base cation~~
709 ~~budgetmass balance~~ equation, ~~(Eq. (43))~~, in combination with measured estimates of deposition, leaching
710 and uptake in biomass, alternative soil balances were estimated (Fig. 54). Since the ~~base cation budgetmass~~
711 ~~balance~~ method predicted much higher weathering rates than the other methods, a balance of sources and sinks
712 consequently required more marked decreases in exchangeable soil stocks for K, Ca and Mg ~~when weathering~~
713 ~~rates were based on PROFILE or the depletion method was used.~~ Furthermore, as a consequence of the
714 substantially higher W_{profile} for Na, the PROFILE based ~~base cation budgetmass balance~~ suggested substantial
715 increases in exchangeable Na stocks.

716 4. Discussion

717 4.1 Comparison of conceptually different methods

718 A number of studies have used multiple approaches to estimate weathering rates, with the aim of validating
719 methods and finding a best estimate for a particular site or catchment (Langan et al., 1995; Kolka et al., 1996;
720 Sverdrup et al., 1998; Futter et al., 2012). A common problem encountered is that ~~differences in quantities, the~~
721 ~~approaches are not only complicated to interpret due to by used are so~~ conceptually ~~differences between the~~
722 ~~approaches, but also due to by the fact that the comparisons are not carried out in an harmonized way, i.e. at the~~
723 ~~same scale (pedon/catchment), using exactly identical the same sampling locations and methods for common~~
724 ~~input data, and whenever methods are compared, using the consistent assumptions about the same weathering~~
725 ~~zone (i.e. 0-50 cm or 0-100 cm). Can that the comparisons do not deal with similar quantities at spatial or temporal~~
726 ~~scale. Concerning the spatial scale, to our knowledge, the base cation mass balance approach has most often more~~
727 ~~commonly~~ been applied at the catchment and forest stand scale, whereas the depletion method and the PROFILE
728 model are normally applied at the ~~smaller~~ pedon scale. In the present study, the ~~base cation budget mass balance~~
729 approach included data at stand level over a period when the stand showed ~~aed~~ high nutrient demand. Concerning
730 the temporal scale, the concepts of the depletion method and the PROFILE model are conceptually different,
731 although they can be applied at similar spatial scale. ~~In the present study, these two methods are based on direct~~

732 measurements of soil properties, i.e. quantitative mineralogy, soil bulk density and soil stone content, which is
733 was rarely the case in previous comparable studies. Since the three approaches used here do not measure similar
734 quantities at spatial and temporal scale, and all of them have obvious weaknesses, no estimate can be taken as a
735 safe reference value of the "true" weathering rate at the study sites. However, for the purposes of the following
736 discussion, we are of the view that the conceptual differences between these three approaches are an asset in our
737 case, as they provide complementary information about weathering at different scales that helps to identifying
738 strengths and weaknesses of each method and establish provide reasons as to why these methods tend to vary in
739 estimated overestimate or underestimate weathering rates of a particular elements.

740 4.2 Depletion method estimates versus PROFILE model estimates Pedon scale weathering rates – a 741 comparison with other studies

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

747
748
749 Our first test criterion was the overall weathering rate to see if there are similarities in weathering estimates for over
750 the 0-50 cm depth in the soil profile. A major finding of this study was that, in the 0-50 cm soil profile, W_{profile}
751 was higher than $W_{\text{depletion}}$ for Na and K, and the methods generally failed to fulfil our first test criterion concerning
752 weathering in the soil profile as a whole. Similarly, high ratios of $W_{\text{profile}}/W_{\text{depletion}}$ of 4 were found at catchment
753 scale by Augustin et al. (2016). At the pedon scale, Stendahl et al. (2013) found $W_{\text{profile}}/W_{\text{depletion}}$ ratios of
754 average 2.7 for 16 Swedish study sites (with average max. and min. ratios of 7.9 and 0.4, respectively) 2.3 and 2.2
755 at Vindeln and Svartberget close to Flakaliden; this ratio was larger than the one found for are even larger
756 than obtained for Flakaliden in our study (1.53) and lower than the one found for Asa (5.1). By contrast, the
757 geographically closest site to Asa (Lammhult, approx. 10 km) had a much lower ratio (1.1, compared with 3.5 in
758 our study). Similar to Flakaliden, low ratios have been reported for the Lake Gårdsjön site situated in south-
759 western Sweden (Sverdrup et al., 1998; Stendahl et al., 2013), while the high ratio we obtained for Asa was close
760 to that (4.6) reported by Stendahl et al. (2013) for Skånes Vårsjö, another site located in south-western Sweden
761 (in the county of Skåne). An exception to the general trend of higher steady-state PROFILE weathering rates
762 compared to historical rates calculated by the depletion method, was found for Mg at the Flakaliden site, where
763 $W_{\text{depletion}}$ was 1.9-fold greater than W_{profile} in the upper mineral soil, but only at Flakaliden. This exception with
764 regard to Mg was also found by Stendahl et al. (2013) for all of their 16 study sites.

765
766 However, the estimated weathering rates are relevant for estimated by the depletion method and the PROFILE
767 model can be expected to differ due to differences in different temporal scales. Several studies have concluded
768 that the average historical weathering rate should generally be higher than the present weathering rate, since soil
769 development involves loss of easily weatherable minerals and ageing of mineral surfaces (Bain et al., 1993; Taylor

770 and Blum, 1995; White et al., 1996). In a study using the Historic-SAFE model, applied to the Lake Gårdsjön
771 catchment in southwestern Sweden, Sverdrup et al. (1998) predicted a decline in weathering rates due to assumed
772 disappearance of fine particles and loss of minerals. Their results suggested an increase in weathering rates, from
773 the end of the deglaciation 12,000 years B.P. towards a peak at 9000 years B.P., followed by a gradual decrease
774 to below initial levels.

775
776 With this background, it may not seem surprising that our

777 Further, the comparison of results from testing our first criterion with results from other studies can be done by
778 estimates from the magnitude of weathering for soils of similar pedogenesis but also from the proportions of the
779 estimates of depletion versus PROFILE. In terms of the magnitude of the estimates, a general finding of this
780 study concerning weathering at the pedon scale was that total modelled (W_{profile}) and historical ($W_{\text{depletion}}$) base
781 cation weathering rates were lies within the range of in good agreement with recent published data for similar
782 forest sites on podsolc till soils (Stendahl et al., 2013). However, the historical weathering rates at Asa were of
783 similar magnitude to the lowest historical weathering rate observed by Stendahl et al. (2013) and the historical
784 weathering rates for Flakaliden were of similar magnitude to their highest rates, at least with regard to Ca and Mg.
785 Most Nordic studies on historical weathering rates have been conducted in the boreal region
786 (Tamm, 1920, 1931; Land et al., 1999; Olsson and Melkerud, 2000; Stendahl et al., 2013; Starr et al., 2014). Even
787 though soil profile depth and soil age in these weathering studies differ from those in ours, they obtained higher
788 rates (Land et al., 1999; Olsson and Melkerud, 2000; Stendahl et al., 2013), similar rates (Stendahl et al., 2013)
789 or lower rates (Starr et al., 2014) for soils developed on glacial tills.

790 4.2.1 Depletion method estimates versus PROFILE model estimates

791 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
792 except Na, and the methods generally failed to fulfil our first test criterion concerning weathering in the soil profile
793 as a whole. However, weathering rates estimated by the depletion method and the PROFILE model can be
794 expected to differ due to differences in temporal scale. Several studies have concluded that the average historical
795 weathering rate should generally be higher than the present weathering rate, since soil development involves loss
796 of easily weatherable minerals and ageing of mineral surfaces (Bain et al., 1993; Taylor and Blum, 1995; White
797 et al., 1996). In a study using the Historic-SAFE model, applied to the Lake Gårdsjön catchment in southwestern
798 Sweden, Sverdrup et al. (1998) predicted a decline in weathering rates due to assumed disappearance of fine
799 particles and loss of minerals. Their results suggested an increase in weathering rates, from the end of the
800 glaciation 12,000 years B.P. towards a peak at 9000 years B.P., followed by a gradual decrease below initial
801 levels.

802 In terms of the proportion of the estimates of depletion versus PROFILE, However, in the present study PROFILE
803 generally yielded higher weathering rates than the depletion method at both study sites. Similar results have been
804 found in other studies, as indicated by high modelled to historic weathering rate ratio ($W_{\text{profile}}/W_{\text{depletion}}$). At
805 catchment scale, Augustin et al. (2016) found that weathering estimated by PROFILE was on average 4 fold
806 greater than weathering based on the depletion method. At the pedon scale, Stendahl et al. (2013) found
807 $W_{\text{profile}}/W_{\text{depletion}}$ ratios of 2.3 and 2.2 for two sites near Flakaliden, namely Vindeln and Svartberget, which are
808 similar larger than values compared to that found for Flakaliden in our study (1.2-3.0). However, the geographically

809 closest site to Asa (Lammhult, approx. 10 km) had a much lower ratio (1.1, compared with 3.5 in our study).
810 Similarly low ratios have been reported for the Gårdsjön site situated in south-western Sweden (i.e. county of
811 Västra Götaland) (Sverdrup et al., 1998; Stendahl et al., 2013), while the high ratio we obtained for Asa was close
812 to that (4.6) reported by Stendahl et al. (2013) for Skånes Vårsjö, another site located in south-western Sweden
813 (i.e. in the county of Skåne). An exception to the general trend of higher steady state PROFILE weathering rates
814 compared to historical rates calculated by the depletion method, was found for Mg at the Flakaliden site, where
815 $W_{\text{depletion}}$ was 1.193-fold greater than W_{profile} in the upper mineral soil, but only at Flakaliden. This exception with
816 regard to Mg was also found by Stendahl et al. (2013) for all of their 16 study sites.

817
818 Our second test, postulating similarity between methods concerning the weathering rate gradient with soil depth,
819 was not fulfilled. We may imagine a front of intense weathering moving downward through the soil profile over
820 the millennia. Each horizon would undergo an episode, limited in time, of intense weathering followed by slower
821 weathering in the ageing material. The sensitivity test performed with PROFILE revealed that the model output
822 was only little affected by the differences in mineralogy between horizons. Therefore, if processes are correctly
823 modelled with PROFILE, the notion of a weathering front should primarily be associated with changes in bulk
824 density and exposed mineral surface area, as also suggested by the positive correlation between W_{profile} and
825 exposed mineral surface area and bulk density (Figs. S1-S2) and by the findings of Jönsson et al. (1995).

826
827 The intense weathering at depth simulated by PROFILE is obviously in contrast with the classic notion of
828 weathering rates being highest in the A- or E-horizon of podzolised soils (Tamm, 1931). To test whether the high
829 W_{profile} values were possible to reconcile with the observed historical weathering, because the PROFILE model
830 predicted increasing weathering rates with increasing soil depth, which was contrary to the depletion method.
831 Since soil forming processes and ageing of minerals suggest that the present weathering rate might differ from
832 the average historical value, we calculated the hypothetical time needed for the simulated current PROFILE
833 weathering rates to accomplish the element losses determined with the depletion method was calculated.
834 Specifically, one can imagine. This approach corresponds to a situation where there is a front of intense weathering
835 moving down through the soil profile, during which a pristine horizon would undergo an episode, limited in time,
836 of intense weathering followed by slower weathering in the ageing material. In concert with this notion, the highest
837 weathering rate, presently prevailing at approximately 80 cm (Asa) or 60 cm (Flakaliden) depth according to
838 PROFILE (Fig. 2), would cause the observed depletion losses within less than half of the soil age ('max rates' in
839 Fig. 6), potentially in concert with the concept of a weathering front. However, the calculation also showed that
840 the present minimum weathering rate, presently simulated for the topmost 1-3 layers (Fig. 2), would often result
841 in a more severe base cation depletion with suffice "do the job" in less than the postglacial period than observed
842 by the depletion method ('min rates' in Fig. 6), particularly at Flakaliden, and for K and Na also at Asa. Hence,
843 the current minimum weathering rates according to PROFILE are not generally sustainable within the limits set
844 by the depletion method. Provided that the current weathering rate did not substantially exceed the historical
845 average, this suggests a positive bias in W_{profile} at the investigated sites, indicating either bias in either of the
846 methods, or a current weathering pressure that is correctly modelled but exceeds the historical average.

847

848 ~~The weathering rates of PROFILE may also be criticized based on discrepancies in the ranking order of weathering~~
849 ~~of elements, compared to historical weathering; this is our third test criterion. PROFILE predicted the highest~~
850 ~~steady-state weathering for Na at both sites. However, historical weathering at Asa was greatest for Ca among the~~
851 ~~base cation elements, whereas Mg was the most abundant element released at Flakaliden. The latter was also~~
852 ~~found by Olsson and Melkerud (2000), who reported the same ranking order of individual base cation weathering~~
853 ~~(i.e. Mg>Ca>Na>K) for other sites in northern Sweden. At the mineralogical level, Casetou-Gustafson et al. (this~~
854 ~~issue) could demonstrate that K-feldspar was the dominant source of all steady state PROFILE weathering of K~~
855 ~~and there are indications that the dissolution rate for K-feldspar is too high compared with mica. For example,~~
856 ~~Thompson and Ukrainczyk (2002) described differences in the plant availability of K via weathering from these~~
857 ~~two mineral groups. In addition, Simonsson et al. (2016) found that, although K-feldspar contained approximately~~
858 ~~90% of the bulk was the dominant K in the soil, 25-50% of the weathering of K had occurred in bearing mineral~~
859 ~~in a till soil in south-western Sweden, a large proportion of the K loss was explained by mica. Furthermore, and~~
860 ~~in more general terms, Hodson and Langan (1999) suggested that the PROFILE model overestimates weathering~~
861 ~~rates because it does not consider the decrease in mineral reactivity that has taken place over time and because it~~
862 ~~assumes that all mineral surface areas are reactive. If this is not accounted for, PROFILE can be expected to~~
863 ~~generate overestimates rather than underestimates for base cation weathering rates. The weathering rates of~~
864 ~~PROFILE may be criticized based on discrepancies in the ranking order of weathering of elements, compared to~~
865 ~~historical weathering; this is our third test criterion. PROFILE predicted the highest steady state weathering for~~
866 ~~Na at both sites. However, historical weathering at Asa was greatest for Ca among the base cation elements,~~
867 ~~whereas Mg was the most abundant element released at Flakaliden. The latter was also found by Olsson and~~
868 ~~Melkerud (2000), who reported the same ranking order of individual base cation weathering (i.e. Mg>Ca>Na>K)~~
869 ~~for other sites in northern Sweden.~~

870
871
872 ~~As to possible errors in weathering rates according to PROFILE, the sensitivity test indicated that the within-~~
873 ~~profile variability of soil physical properties had a much greater effect on simulated weathering rates than the~~
874 ~~differences in mineralogy between different horizons. Therefore, the notion of a weathering front, significantly~~
875 ~~changing the mineralogical composition of the soil, does not appear to be able to result in any episodic modelled~~
876 ~~weathering for the studied soils; the decline in weathering rate with time is more likely to be attributable to~~
877 ~~disappearance of fine particles, as also indicated by the positive correlation between W_{profile} and exposed mineral~~
878 ~~surface area and bulk density (Figs. S1-S2). Moreover, given the variability of physical and mineralogical~~
879 ~~properties in the investigated soils, fine tuning parameters related to the exposed mineral surface area is most~~
880 ~~likely to affect the model output, similarly to the findings of Jönsson et al. (1995). Furthermore, the discrepancy~~
881 ~~between W_{profile} and $W_{\text{depletion}}$ with respect to soil depth gradient implies that the PROFILE model produces~~
882 ~~weathering rate patterns that are not in line with the classic notion of weathering rates being highest in the A- or~~
883 ~~E horizon (Tamm, 1931). However, it is consistent with the more recent notion that mineral dissolution decreases~~
884 ~~with increasing time/exposure to weathering (White et al., 1996; Parry et al., 2015). In line with this, the results~~
885 ~~support the view that historical weathering rates do not show identical depth gradients to steady state weathering~~

886 rates, and thus W_{profile} and $W_{\text{depletion}}$ could both be accurate estimates, of steady-state and historical weathering
887 rates, respectively.

888

889 As to possible bias in the historical weathering rates, underestimates are possible at Asa, where the low values of
890 $W_{\text{depletion}}$ can be attributed to the low gradient of Zr in the soil (Fig. 5). This might, in turn, be the result of soil
891 mixing by different means. Mechanical soil scarification was carried out at both Asa and Flakaliden prior to
892 planting of the present stand, which would at least have caused partial mixing or inversion of surficial soil layers.
893 In addition, clearance cairns of unknown age were found in the experimental area at Asa, indicating small-scale
894 agriculture in the past. Moreover, if burrowing earthworms have been abundant in the past, they might have
895 produced soil mixing in the upper soil horizons (Taylor et al., 2019), resulting in a complicated and erratic
896 disturbed Zr gradient (Fig. 25) and resulting in low estimates of historical weathering in the rooting zone (Whitfield
897 et al. 2011). High or near-neutral soil pH and deciduous litter can promote high population densities of burrowing
898 earthworms following forest clearing and agriculture; partly deciduous vegetation indeed dominated at Asa until
899 only 1000-2000 years BP, with species such as Scots pine (*Pinus sylvestris*), *Corylus avellana* (L.), *Betula* spp.,
900 *Quercus* spp. and *Tilia* spp. (Greisman et al., 2009).

901

902 Apart from disturbances, natural variability in weathering rates can likely be attributed to differences in soil
903 texture (i.e. exposed mineral surface area), climate (i.e. temperature and water percolation rate) and mineralogy.
904 At Flakaliden, it was reasoned that complicated heterogeneous Zr gradients (Fig. 25) and Zr/base cation ratios
905 (Fig. S3) disqualified two soil profiles from further analysis, which would have otherwise indicated caused
906 unreasonable net gains of elements in the rooting zone (0-50 cm) (i.e. for soil profile 15A for all elements and
907 for soil profile 11B with regard to Na and K). Whitfield et al. (2011) used the same argumentation for excluding
908 single profiles from their calculations, emphasizing that overall gains in the rooting zone are not expected without
909 external additions of base cations to the soil profiles. Several alternative reasons could have contributed to the
910 observed peaks of Zr in the B/C-horizon at Flakaliden, such as local heterogeneities of the deposited till, which
911 was suggested indicated by the unstable Ti/Zr ratio in soil profile 15A and 11B. However, the observed peaks in
912 the Ti/Zr gradients were only explained by irregularities in Ti gradients (i.e. increases in the Ti/Zr ratio indicate
913 that Ti concentrations are increasing) the latter has to be treated carefully since in cases where both Zr and Ti
914 show inconsistent patterns with soil depth, the Ti/Zr ratio will still be stable and hereby overshadows
915 heterogeneities observed with soil depth for both elements (Fig. S3 and Fig. SX1, 2). Thus,
916 heterogeneities in Zr gradients observed in the B/C horizon can be attributed to local heterogeneities
917 of the parent material irrespective of if the Ti/Zr gradients are stable at these depths. At Flakaliden,
918 the small-scale variation in Zr mobility might be one of the driving forces behind the large within-site variation
919 in Zr gradient (Fig. 25). The latter is exemplified in different patterns of Zr enrichment for different soil profiles
920 (Fig. 25). An increase with depth could indicate Zr transport from shallow to deeper soil layers, most significantly
921 reflected in the Zr/base cation ratio for K (Fig. S3). In relation to this, in a column experiment Hodson et al. (2002)
922 found that K was the most sensitive element to Zr mobility and that redistribution of Zr led to insignificant
923 underestimations of base cation weathering. An alternative explanation for the increased subsoil Zr content could
924 be related to the distinct peaks of rare earth metals in the B-horizons of Swedish podsollic soils reported by Tyler

et al. (2004), who related them to increased solubility. Increasing Zr concentration in the B-horizon of forest soils in northern Sweden has also been reported by Melkerud et al. (2000) and, in particular, in a study by Olsson and Melkerud (2000).

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

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

4.3 Weathering in a base cation budget/mass balance perspective

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

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

Despite the considerable uncertainties in W_{budget} and $W_{\text{depletion}}$ estimates, the mass balance approach illustrated that accumulation in biomass was a dominant sink for all base cation elements except Na. This is in line with findings by Nykvist (2000) for two Norway spruce sites in Sweden and by Simonsson et al. (2015) for an aggrading

961 Norway spruce forest in south-western Sweden. However, it ~~contrasts to conditions~~ contradicts findings in other
962 studies of no change in soil and tree biomass stocks of base cations (e.g. Sverdrup et al., 1998). The higher
963 estimates of weathering rate at Asa reflected the higher productivity and nutrient demand of the stand at this site
964 (Bergh et al., 1999), which has resulted in 1.4 fold greater accumulation of base cations in biomass than at
965 Flakaliden.

966 The Na fluxes differed from those of the other base cations, probably because Ca, Mg and K are important plant
967 nutrients whereas Na is not. Calcium and Mg uptake in forest trees is considered to be more or less passive flow
968 driven by transpiration fluxes, whereas K uptake is an energy-demanding active process (Nieves-Cordones et al.,
969 2014). Considering that Na was the dominant base cation in the soil solution at 50 cm soil depth (Fig. 5), the
970 negligible accumulation of Na in tree biomass suggests that Na uptake in trees is physiologically blocked. Low
971 concentrations of Na seem to be a general feature of terrestrial plants in boreal forests, in contrast to aquatic plants,
972 which explains why the latter are considered important Na sources for large herbivores like moose (Ohlson and
973 Staaland, 2001). Thus, the negligible Na accumulation in tree biomass and the particularly low deposition at
974 Flakaliden simplify the Na ~~budget mass balance~~ to only three major counterbalancing fluxes: weathering,
975 deposition and leaching. Since $W_{\text{depletion}}$ and $W_{\text{min}} - W_{\text{budget}}$ of Na were fairly similar, and were much lower than
976 W_{profile} , our results provide additional support for the claim that the PROFILE model produced consistently too
977 high Na weathering.

978 Accumulation of Ca, Mg and K in biomass made up the dominant sink. Since deposition and measured depletion
979 of extractable Ca, K and Mg in the soil did not balance this sink, substantial missing sources, (here estimated as
980 an apparent weathering rate,) were needed to reach a balance. Using the alternative weathering estimates by
981 PROFILE and the depletion method in the ~~base cation budget mass balance~~ resulted in even larger estimated
982 depletion in the soil to balance the sinks than was actually measured. ~~Assuming that the measurements of~~
983 ~~accumulation in biomass, deposition and leaching were reasonably accurate, the results either indicate large~~
984 ~~uncertainties in measures of soil changes and/or that additional sources of base cations in the soil balanced the~~
985 ~~sinks.~~ Uncertainties in estimating soil changes were probably significant, since the estimates of soil depletion
986 were based on two single measurements over 12 years and the extraction procedures were not identical over time.
987 Nevertheless, the changes observed in extractable Ca stocks in the soil are in line with observations over 22 years
988 of aggrading Norway spruce forests by Zetterberg et al. (2016), who reported exchangeable Ca depletion rates of
989 5-11 and 23-39 mmol_c m⁻² yr⁻¹ for sites in south-western and northern Sweden, respectively. The higher value for
990 the northern site reflected higher Ca saturation in the soil. The corresponding values for Asa and Flakaliden were
991 larger, but of similar magnitude (34.5 and 40.5 mmol_c m⁻² yr⁻¹, respectively). Brandtberg and Olsson (2012)
992 studied the same sites as Zetterberg et al. (2016) over a 10-year period and found a general minor increase in
993 extractable K soil stocks and a substantial decrease in the Ca stocks, a result much similar to the findings of the
994 present study. Moreover, exchangeable K stocks in the soil normally show little variation over time (B.A. Olsson,
995 unpublished data). Great depletion in exchangeable K stocks in the soil is therefore unlikely. The results therefore
996 suggest that other sources of nutrient base cations exist in the soil, apart from weathering ($W_{\text{depletion}}$, W_{profile}) and
997 depletion of ammonium-chloride-extractable base cation stocks. It is well known that the exchangeable

1008 ~~extractable nutrient stock in the soil is defined by the extraction medium and procedure. A test of different~~
1009 ~~extractants used on the soils in the present study revealed that using NH₄OAc posed a risk of underestimating the~~
1000 ~~amounts of base cations in the soil and that the yield of exchangeable extractable base cations decreased in the~~
1001 ~~order aqua regia > HCl > EDTA > BaCl₂ > NH₄OAc (Olofsson, 2016). Using a more potent extractant than 1 M~~
1002 ~~NH₄Cl would probably have resulted in different findings on the change in extractable and plant available base~~
1003 ~~cations in the soil. Regarding K, fixed or structural K in clay minerals provides a dynamic pool of K that is not~~
1004 ~~included in modelled weathering or in NH₄Cl-extractable K (Simonsson et al., 2016). Regarding Ca and Mg,~~
1005 ~~dissolution from non-crystalline/amorphous compounds can be an important source in soils depleted of these~~
1006 ~~elements (Van der Heijden et al., 2017).~~

1007 ~~There are Another possible explanations for the higher weathering rates with the base cation budget/mass balance~~
1008 ~~approach is compared to that PROFILE for K, Mg and Ca. First, it is possible that the assumption made that no~~
1009 ~~base cation/BC uptake takes place below 50 cm in the soil was wrong. If trees can take up base cations/BC from~~
1010 ~~deeper soil horizons (e.g. Brantley et al., 2017), the discrepancy in weathering rates between the two methods~~
1011 ~~would be reduced since PROFILE predicted higher weathering rates with increasing depth. Second, PROFILE~~
1012 ~~may produce conservative estimates of present-day weathering because the model only captures steady-state~~
1013 ~~chemical processes. It has been postulated that e.g. mycorrhizae play an important role in nutrient uptake in forest~~
1014 ~~trees through active foraging by mycelia at mineral surfaces, but the nature and potential-quantitative importance~~
1015 ~~of biotic control or stimulation of weathering has been much debated in recent decades (Finlay et al., 2009;~~
1016 ~~Sverdrup, 2009; Smits and Wallander, 2017; Finlay et al., this issue). Based on the results of the present study,~~
1017 ~~the hypothesis of significant biological control of weathering was not rejected. Thus, the results from the present~~
1018 ~~study do not contradict the view that such processes can be quantitatively important in field situations.~~

1020 **5. Conclusions**

1021 ~~The release rate of important plant nutrients from the mineral soil has been previously shown to differ largely~~
1022 ~~when estimated with different methods due to a lack of uniformity in method comparison and data collection,~~
1023 ~~which has made it impossible to understand conceptual similarities and dissimilarities between methods. Three~~
1024 ~~conceptually different methods were compared in a harmonized fashion for 8 soil profiles at two long-term~~
1025 ~~experimental forest sites with the aim of quantifying variability in weathering rate estimates and making concrete~~
1026 ~~suggestions for an improved future applicability of these methods. We compared in a first step weathering rates~~
1027 ~~estimates by the PROFILE model and the depletion method in the 0-100 cm horizon, since a detailed assessment~~
1028 ~~of the latter method can only be made by consideration of the whole soil profile where a reference depth is defined.~~
1029 ~~In a second step, weathering rate estimates of the three methods were compared for the upper 0-50 cm soil~~
1030 ~~horizon.~~

1032 ~~In the first comparison,~~†The results indicated that historical weathering estimated by the depletion method was
1033 ~~probably underestimated, particularly at Asa, or was reasonably accurate (Ca, Mg). Reasons for underestimated~~
1034 ~~weathering rates at Asa was that all criteria for application of the method were ~~as~~ not well fulfilled. The weakly~~

1035 developed and possibly erratic Zr gradients in the soil at Asa could have been caused by natural and anthropogenic
1036 disturbances. Future studies based on the depletion method should ensure that the Zr gradient with depth show a
1037 net enrichment of Zr towards the soil surface. This condition was not fulfilled for soil profiles at the Asa site.
1038 Another important outcome of the study was to show that within-site variations in Zr gradients can be large, as
1039 was the case at Flakaliden. At that site, two soil profiles showed obviously erratic Zr gradients for unknown
1040 reasons and were not included in estimates of site mean weathering rates. In sharp contrast to the depletion method,
1041 steady-state weathering by PROFILE increased with increasing soil depth, and weathering rates were also
1042 generally higher. PROFILE probably produced reasonably accurate estimates of present-day weathering
1043 rates, rather than underestimates, but likely overestimated weathering of Na and K. This conclusion was based on
1044 differences between historical and steady-state estimates in rank-order of elements, and that the back-calculation
1045 of current PROFILE weathering rates to simulate historic base cation BC losses suggested a rapid depletion of Na
1046 and K even at the lowest PROFILE weathering rates. A possible reason for that also K weathering rates were also
1047 overestimated by the PROFILE method were inaccurate dissolution rates for K-bearing minerals
1048 applied in the model, which should be accounted for in future PROFILE based weathering estimate.

1049
1050 In the second comparison including three methods, the base cation budget method produced much higher
1051 estimates of present-day weathering compared to estimates by the other methods, except for Na. This discrepancy
1052 was largely an effect of the large uptake rates of Ca, K and Mg in the biomass, in contrast to negligible
1053 accumulation of Na, and that this uptake was only partly balanced by measured depletion of extractable soil pools,
1054 Ca in particular for Ca. The large discrepancy in weathering rates between the base cation budget method and
1055 the other methods suggest that there were additional sources available for uptake of particularly of Ca and K by
1056 trees in the soil besides weathering and the measured depletion in extractable base cations.

1060 **5. Conclusions**

1061 The depletion method, PROFILE model and mass balance approach was used to estimate weathering rates at two
1062 coniferous forest sites in Sweden. The methods estimated weathering rates at different spatial and temporal scale,
1063 and no estimate was taken as a reference value of the true (current) weathering rate. There was no similarity in
1064 weathering estimates between the depletion method and the PROFILE model with respect to BC weathering in
1065 the 0–50 cm soil layer and the soil depth gradient in weathering rates except that both methods indicated higher
1066 weathering rates and more marked depth gradients at Flakaliden compared to Asa. The PROFILE model produced
1067 consistently higher weathering rates than the depletion method except for Mg, and while the depletion method
1068 estimated decreasing weathering rates with increasing soil depth, the PROFILE model predicted the opposite. The
1069 mass balance method produced significantly higher weathering rates for all elements except Na. A cross-
1070 examination of the estimates stressed the importance of that all criteria for application of the depletion method
1071 must be satisfied. Erratic or weakly developed Zr gradients in the soil, possibly caused by natural and

1072 anthropogenic disturbances can be a cause to why the depletion method underestimates weathering rates. The
1073 higher weathering rates of K by PROFILE compared to the depletion method could be an indication of that
1074 inaccurate dissolution rates of K-bearing minerals was used in the model. On the other hand, high mass balance
1075 estimates for K, Ca and Mg weathering suggests that there were additional sources of base cations for tree uptake
1076 in the soil besides weathering and measured depletion in exchangeable base cations, and that PROFILE produced
1077 conservative estimates of base cation supply to forest trees.

1078 6. Authors contribution

1079 Authors contributed to the study as in the following: S. Casetou-Gustafson: study design, data treatment, analyses,
1080 interpretation and writing. Magnus Simonsson: study design, analysis, interpretation and writing. Johan Stendahl:
1081 study design, analysis, interpretation and writing. B.A. Olsson: study design, data treatment, analysis,
1082 interpretation and writing. S. Hillier: interpretation and writing. Sune Linder: Provided long-term experimental
1083 data, interpretation and writing. Harald Grip: Provided long-term experimental data, interpretation, and writing

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1400 Table X: Shown is a short description of characteristics of three different approaches that are used in thi study to
 1401 estimate base cation release rates at the pedon scale using a harmonized set of input data. The difference
 1402 between methods reflect differences can be expected due to different time scales, conceptual differences,
 1403 assumptions about weathering kinetics and pedogenesis.

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

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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. 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 32. Extractable cC Concentrations of different elements at the reference depths used for calculating historical weathering rate at the Asa and Flakaliden sites.

Site	Plot	Ref. depth (cm)	Ca (%)	Mg(%)	K(%)	Na (%)	Zr (ppm%)	Ti (%)
Asa	K1	80-90	1.41	0.51	0.93	1.06		0.34
	K4	80-90	1.29	0.44	0.88	1.00	288.10.00029	-
	F3	60-70	1.41	0.55	0.87	1.04	282.60.00028	-
	F4	80-90	1.26	0.49	0.85	0.98	293.30.00029	-
Flakaliden	10B	60-70	1.09	0.57	0.88	0.87	243.80.00024	-
	- 14B+1B	60-70	1.59	0.70	0.81	1.03	336.10.00043	—
	- 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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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 _e m ⁻² yr ⁻¹)	Measured data on open field and throughfall deposition available from nearby Swedish ICP Integrated Monitoring Sites	SO ₄ ²⁻ : 27.0 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 ₄ ²⁻ : 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 _e 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 _e 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 _e 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 _e m ⁻² yr ⁻¹)	Literature data from Hellsten et al. (2013)	179.8	47.5
Evapotranspiration (Fraction)	Precipitation data and runoff data. Runoff data calculated based on proportion of runoff to precipitation (R/P) at Gammtratten and Aneboda.	0.3	0.6

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

Parameter	Unit	Source
Exposed mineral surface area	$\text{m}^2 \text{m}^{-3}$	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)

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

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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 _e 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 _e 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 _e 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 _e m ⁻² yr ⁻¹	Literature data from Hellsten et al. (2013)
Nitrogen in litterfall	Site	mmol _e 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 Gamttratten 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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Table 54. 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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Table 5. Judgement of data quality for terms included in the base cation budget estimate of weathering

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

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1473 **Table 6:** Standard errors and standard uncertainties ($\text{mmol}_c \text{m}^{-2} \text{yr}^{-1}$) for the terms in the base cation budget, Eq.
 1474 (4). Combined standard uncertainty, plot average value and confidence interval for the weathering rate of base
 1475 cation i derived from base cation budgets $W_{\text{budget},i}$ ($\text{mmol}_c \text{m}^{-2} \text{yr}^{-1}$). ~~Estimated combined uncertainty ($\text{mmol}_c \text{m}^{-2}$~~
 1476 ~~yr^{-1}) of weathering rates calculated by the BC budget approach. The combined uncertainty is the sum of 95%~~
 1477 ~~confidence intervals of each term in the BC budget (Eq. 4).~~

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	1.0	9.7	0.1	10	37	± 29
	Na	4.0	0.9	0.0	5.1	7	7	± 20
Flakaliden	Ca	0.8	10.5	13.3	0.7	17	28	± 51
	Mg	0.3	1.1	1.5	0.3	2	12	± 6
	K	0.2	0.6	6.7	0.2	7	19	± 20
	Na	0.7	1.2	0.0	0.8	2	2	± 5

1479
 1480

Site	Element	Deposition	Soil change	Biomass accum.	Leaching	Combined uncertainty
Asa	Ca	3.4	25.3	58.5	6.3	93.5
	Mg	3.2	1.2	7.4	3.1	14.9
	K	0.9	2.0	29.2	0.1	32.3
	Na	11.9	1.73	0.0	10.0	23.6
Flakaliden	Ca	2.5	20.6	40.0	1.4	64.4
	Mg	0.9	2.2	4.6	0.6	8.3
	K	0.5	1.2	20.2	0.4	22.2
	Na	2.2	2.4	0.0	1.6	6.1

1481
 1482
 1483
 1484

1485 **Figure captions**

1486 **Figure 1.** Titanium (Ti) to zirconium (Zr) ratio (by concentration) used as an indicator of uniform parent material
1487 in all soil layers at Asa (F3, F4, K1, K4) and Flakaliden (10B, 11B, 14B, 15A).

1488 **Figure 25.** Zirconium (Zr) gradient in the soil at Asa (K1, K4, F3, F4) and Flakaliden (10B, 11B, 14B, 15A)

1489 **Figure 32.** (Left) Historical weathering rate of base cations ($\text{mmol}_e \text{ m}^{-2} \text{ yr}^{-1}$) estimated by the depletion method
1490 and (right) steady-state weathering rate estimated by the PROFILE model in different soil layers at Asa and
1491 Flakaliden.

1492 **Figure 43.** Comparison of weathering rates ($\text{mmol}_e \text{ m}^{-2} \text{ yr}^{-1}$) for Ca, Mg, Na and K determined with the depletion
1493 method, the PROFILE model and the [base cation budgetmass-balance](#) method for the 0-50 cm layer at Asa and
1494 Flakaliden. [For the weathering rates based on the depletion method and the PROFILE model](#), error bars represent
1495 the standard error calculated based on four soil profiles at each study site, [except for Flakaliden, where the](#)
1496 [depletion method was only applied in two soil profiles](#). For weathering rates based on the [base cation budget](#)
1497 [approach](#), error bars represent combined standard uncertainties, which are based on standard errors derived from
1498 [plot-wise replicated data of the present experiments \(for leaching and changes in exchangeable soil pools\) and on](#)
1499 [standard uncertainties derived from Simonsson et al. 2015, where replicated data were missing in the present study](#)
1500 [\(for accumulation in biomass and total deposition\)](#).

1501 **Figure 54.** (Left) [Sink](#) and (right) [source](#) of base cations in ecosystem net fluxes at Asa and
1502 Flakaliden. The soil is a net source if soil base cation stocks decrease and a net sink if they increase. 'BC
1503 [budgetMass-balance](#)' = current base cation weathering rate (W_{budgetBC}) estimated with the [base cation budgetmass](#)
1504 [balance](#) method, including measured changes in soil extractable base cation stocks; 'PROFILE' = soil extractable
1505 pools estimated from [base cation budgetmass-balance](#) using PROFILE estimates of steady-state weathering rate;
1506 'Historical' = soil extractable pools estimated from [base cation budgetmass-balance](#) using estimates of historical
1507 weathering rate by the depletion method. 'Measured soil change' and '[Base cation budgetMass-balance](#) estimated
1508 soil change' indicates that equation 43 was used to estimate weathering rate or the soil change, respectively.

1509 **Figure 5.** Zirconium (Zr) gradient in the soil at Asa (K1, K4, F3, F4) and Flakaliden (10B, 11B, 14B, 15A)

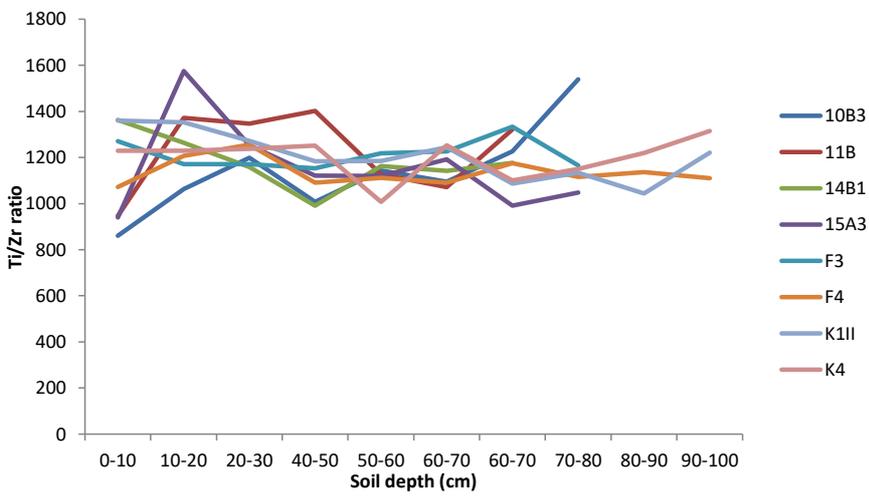
1510 **Figure 6.** Time (years) required to achieve the measured historical element loss in different soil layers with
1511 maximum or minimum PROFILE weathering rates at (a) Flakaliden and (b) Asa.

1512

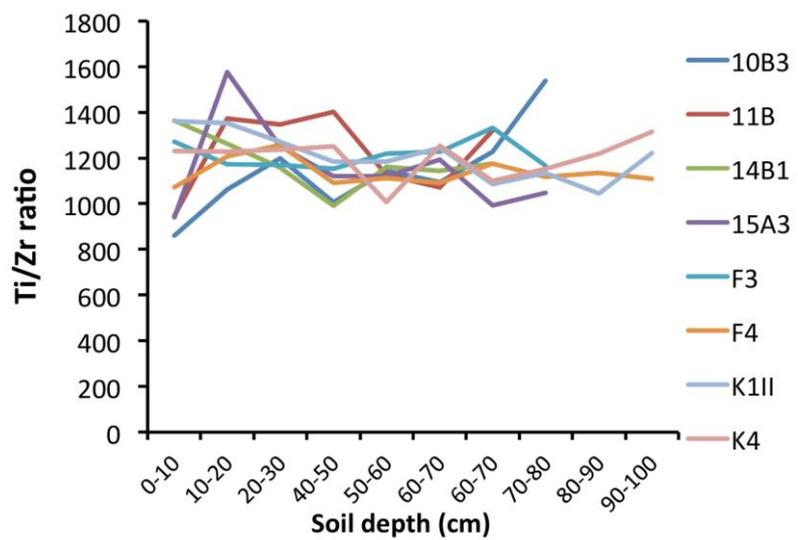
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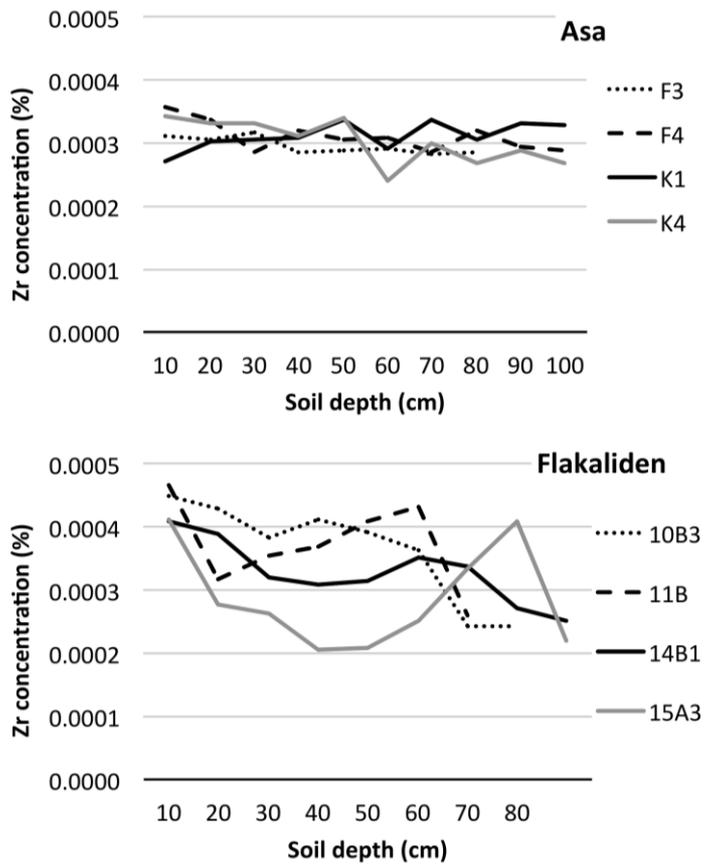


1524

1525 Figure 1.

1526

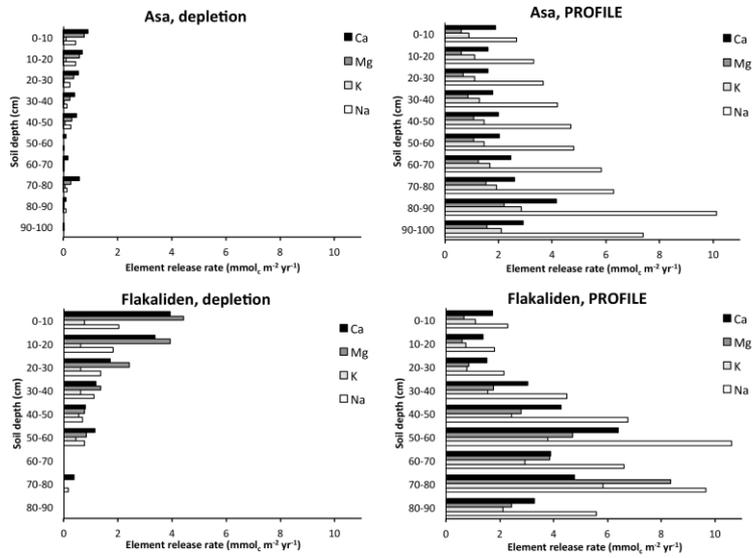
1527



1528

1529 **Figure 2.**

1530



1531

1532 **Figure 32.**

1533

1534

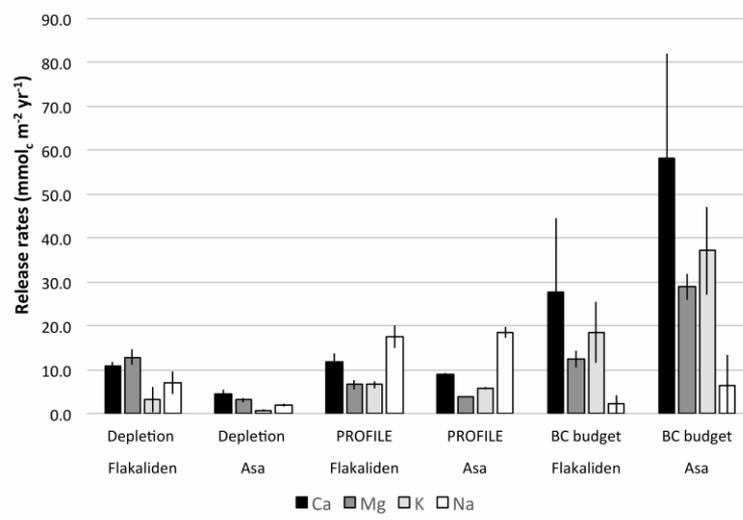
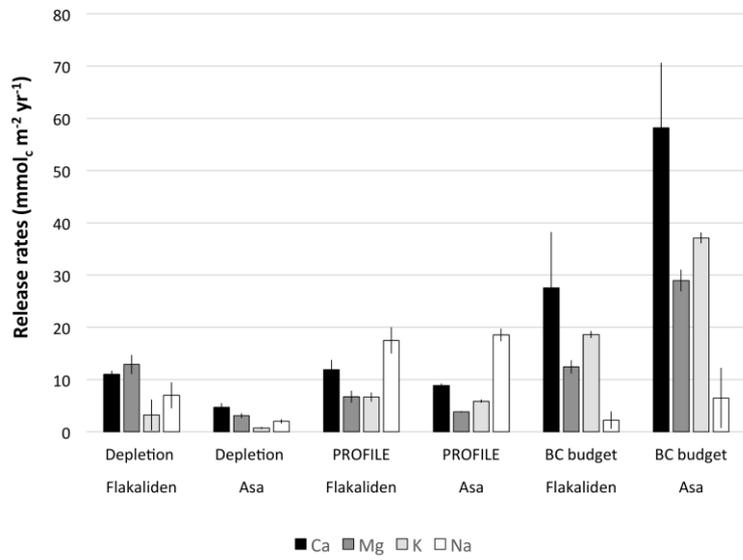
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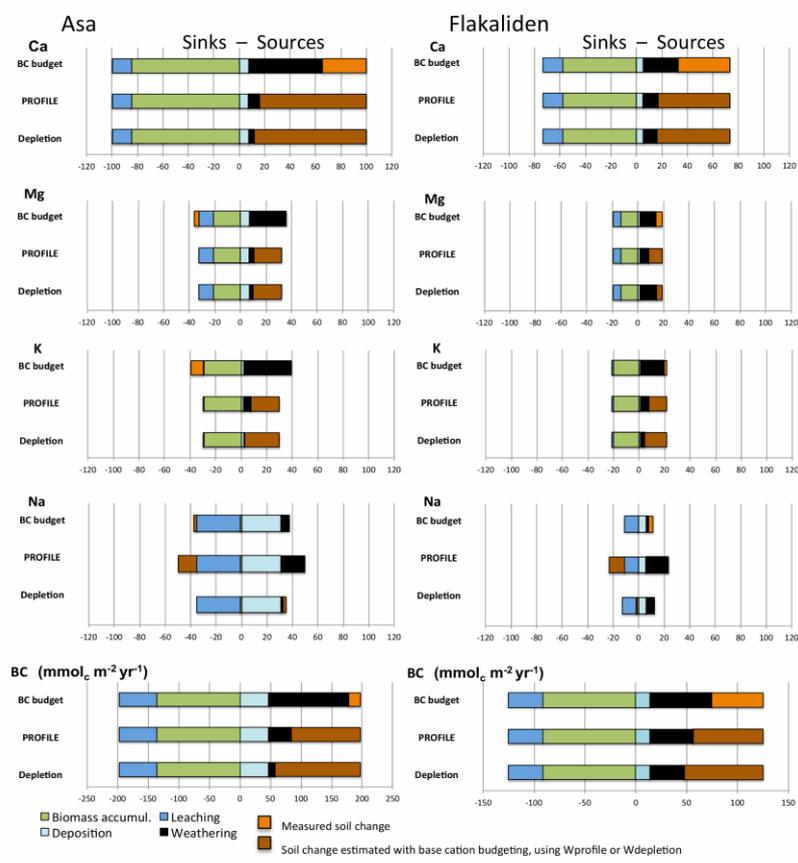


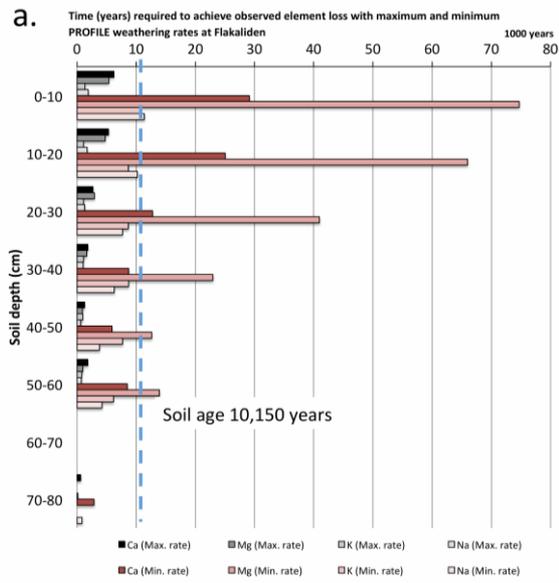
1540

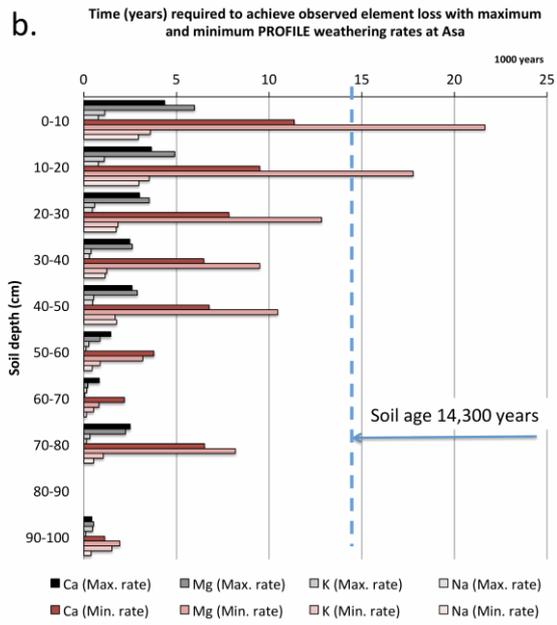
1541

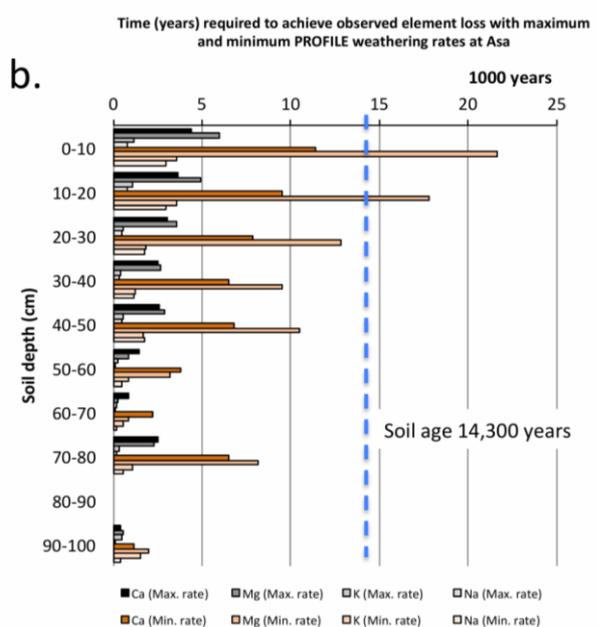
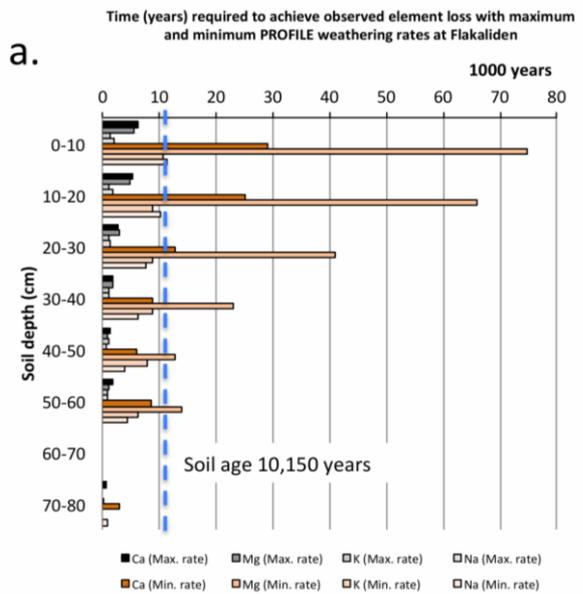
1542

Figure 43.









1548
1549

Figure 6.

1550 [Resubmission letter](#)

1551

1552 [Dear Prof. Andersson,](#)

1553 -

1554 [Thank you for providing the reviews and for your editorial comments on our manuscript and the](#)
1555 [opportunity to submit a revised version. Your suggestions \(marked in grey color\) were:](#)

1556

1557 [Original comments:](#)

1558

1559 [Associate Editor Decision: Publish subject to minor revisions \(review by editor\) \(12 Apr 2019\)](#)
1560 [changed to major revision \(review by editor\) \(15 Apr 2019\) by Suzanne Anderson Comments](#)
1561 [to the Author:](#)

1562 [I have received three reviews of the manuscript, of which two were quite positive and one was](#)
1563 [extremely negative. My own reading lies somewhere between these poles. I think with](#)
1564 [attention to the comments of the reviewers the authors will be able to produce an acceptable](#)
1565 [contribution.](#)

1566

1567 [The goal of the manuscript is to assess different methods to determine current mineral](#)
1568 [weathering rates in soils. The question is of more than academic importance, as mineral](#)
1569 [weathering must in the long run replace cation loss resulting from forest harvesting and](#)
1570 [consequent soil acidification. The work is conducted in the context of a Swedish environmental](#)
1571 [goal of managing sustainable forestry. Three established methods of assessing weathering](#)
1572 [rates are tested in two well-characterized forest soils in Sweden. While the work is clearly](#)
1573 [important from this perspective, the question and the methods used are not an approach that](#)
1574 [is likely to bring about a paradigm shift or blinding insight.](#)

1575

1576 [Reviewer #1 offered the very negative appraisal, based mostly on two points—first that the](#)
1577 [methods and models used have been compared in other sites before, and therefore there is](#)
1578 [nothing new. The second complaint was that little data was used from the two study sites. I](#)
1579 [sympathize with the authors response that this study is distinguished from others by the quality](#)
1580 [of the data available for the method comparison \(a key being uniformity of collection and](#)
1581 [analysis methods\). Both negative points can be addressed with nearly the same antidote:](#)
1582 [providing a much clearer description of how the data used is generated. I suggest the authors](#)
1583 [come up with a way to highlight responses to this reviewer very early and with some panache](#)
1584 [in the text. The text is rather long overall, and while methodical in its presentation, it is easy to](#)
1585 [miss the point amidst some of the details.](#)

1586

1587 [General points to attend from Reviewers 2 & 3:](#)

1588 [1\) Terminology: Reviewer #2 found the manuscript very interesting, but also offers some](#)
1589 [helpful guidance on improving clarity. I concur with this reviewer that the terminology naming](#)
1590 [the methods was hard to keep straight. In short, these are "depletion method", the "steady-](#)
1591 [state method", and the "mass balance method". For instance, the depletion method \(based on](#)
1592 [the assumption of Zr immobility\) is in essence a mass balance calculation. I wonder if the](#)
1593 [authors could come up with a small table that would summarize the 3 methods? It would be](#)
1594

1595 [helpful to have these briefly outlined and set apart from the text in a way that the reader can](#)
1596 [circle back quickly when confusion sets in.](#)

1597
1598 [I believe some terminological confusion arises because the goals of this study are narrowly](#)
1599 [focused on determining the weathering rate going on in Swedish forests now, to address the](#)
1600 [needs of forest management now. Some of the methods employed \(depletion method in](#)
1601 [particular\) are averaged over much longer timescale than the present \(more on this below\).](#)
1602 [Moreover, choices such as focusing only on the top 50 cm are driven by interest in weathering](#)
1603 [in the rooting zone. I think the authors might rewrite the introduction and parts of the discussion](#)
1604 [to highlight how their motivations might differ from those of a pedologist, interested in the full](#)
1605 [history and depth of soil development, or from a geochemist interested in weathering rates](#)
1606 [over long time scales.](#)

1607
1608 [2\) Soil age: I disagree with Reviewer #2 on soil age changing with depth in the soil profile. It](#)
1609 [is standard soil science to use soil age in the manner used by the authors. However, the](#)
1610 [authors need to correct an error in their reporting of soil ages. Asa is reported to be 143 000](#)
1611 [thousand years old \(or \$1.43 \times 10^8\$ years.... Cretaceous!\), while Flakaliden is reported as 10](#)
1612 [150 thousand \(\$1.015 \times 10^7\$ years\). I'm pretty sure the authors mean 143 ka and 10.15 ka,](#)
1613 [respectively. These ages are significantly different. Asa has been exposed and weathering](#)
1614 [since the last interglacial, while Flakaliden is only Holocene. The significant difference in](#)
1615 [weathering \(disintegration of boulders, accumulations of clay and organic matter, etc\) in till](#)
1616 [from different glaciations is an important tool in determining relative ages. I am surprised that](#)
1617 [the influence of the much longer pedogenesis at the Asa site is not addressed in the](#)
1618 [manuscript. Since Asa was apparently not glaciated in the last glaciation, I would guess it was](#)
1619 [instead subjected to periglacial processes for ~100 ka of its age. I also wonder about any](#)
1620 [eolian \(e.g. loess\) deposition during the last glaciation? In any case, I would like the authors](#)
1621 [to address the very different history of weathering at these sites and how this impacts the](#)
1622 [weathering rates they assess. \(In line 218-219, the soils are described as similar in B horizon](#)
1623 [thickness-- quite surprising given the 1000 fold difference in age of these soils that the B](#)
1624 [horizons are similar in thickness. You will need to explain why-- it's striking that the very old](#)
1625 [soil in the warmer climate seems to be quite similar to the very young soil in the colder climate.\)](#)

1626
1627 [3\) Table 4 "quality of term quantification". Several reviewers were unimpressed with a vague](#)
1628 [and subjective description of the quality of quantification of different terms in the mass balance](#)
1629 [method. Is there a better way to do this?](#)

1630
1631 [Reviewer #2 offers a number of useful comments on minor points in the manuscript, please](#)
1632 [address these.](#)

1633
1634 [4\) I found the Conclusions section to be unsatisfying. As the 11th group to compare different](#)
1635 [weathering rate computation methods, is our knowledge of weathering rates improved? Did](#)
1636 [using more carefully collected data and uniform sampling methods improve these numbers? I](#)
1637 [am not sure from reading the conclusions. Nor am I sure what recommendation would be](#)
1638 [made to land managers on the basis of this work for how to measure weathering rates. I](#)
1639 [suggest pulling back out to the big picture, and addressing the reader who has skipped from](#)
1640 [introduction straight to conclusions in rewriting this section.](#)

1641
1642 [My own minor comments:](#)
1643 [Line 65: The definition of "weathering rate" given does not define a rate \(dimensionally\).](#)
1644 [Line 182: I'm surprised at lack of attention to till mineralogy: does this differ between sites?](#)
1645 [Line 200: Describe the solid fertilizer used.](#)
1646 [Line 218: "sandy loam till" is not a texture. "sandy loam" is.](#)

1647 [Line 607-608: Pinus is conifer, not deciduous. What was the vegetation at Asa during the last](#)
1648 [glaciation?](#)

1649

1650

1651 [Response:](#)

1652

1653

1654 [We have carefully read through all the comments and have critically discussed possible changes. We](#)
1655 [hope that you will find all major points sufficiently addressed and that the manuscript is acceptable](#)
1656 [to you in revised form.](#)

1657

1658 [In terms of changes we have focused mainly on your principal suggestions, i.e. to "describe very early](#)
1659 [and with panache" that three methods are required to cover three very different conceptual views on](#)
1660 [weathering \(i.e. steady-state, historical and dynamic weathering\). To our knowledge this has not been](#)
1661 [done to the same extent previously based on harmonized implementation of all methods for the same](#)
1662 [sites. Kolka et al. \(1996\) is the only group that used a similar approach, however, that study was based](#)
1663 [on less detailed data. We hope that our discussion of these different estimates in a mass balance](#)
1664 [perspective adds further novel insights into how these methods relate to other ecosystem sources](#)
1665 [and sinks of base cations in an aggrading forest ecosystem.](#)

1666

1667 [Details of the changes in the manuscript are as follows :](#)

1668

1669 [1. Terminology:](#)

1670 [- Throughout the manuscript: We have changed the name of the third method used to estimate](#)
1671 [weathering from "mass balance approach" to "base cation budget". We have also added a new table](#)
1672 [\(Table 2\) that summarizes major differences \(conceptual, scales etc.\) between the methods.](#)

1673 [- Additionally, we have rewritten parts of the introduction and discussion to highlight our rationale](#)
1674 [behind the use of the perspective of historical versus present-day weathering estimates.](#)

1675

1676 [2. Soil age \(Line 284\): The soil age at Asa should be 14,300 years, not 143,000 years. This was an](#)
1677 [unfortunate typo in the text \(but the correct age was given in Figure 6\). The soil age at Flakliden is](#)
1678 [younger, but both soils were formed during the end of the latest \(Wechselian\) ice age, and there is no](#)
1679 [eolian loess deposition at either site \(Fréden 2009\).](#)

1680

1681 [3. Former Table 4 \(Now table 5: We have now attempted to give an additional description of the](#)
1682 [quality and uncertainty of different terms in the base cation budget \(former "mass balance method"\)](#)
1683 [by estimating combined uncertainty, which is given in a separate Table \(Table 6\). The combined](#)
1684 [uncertainty provides a better picture of the uncertainty of weathering estimates by the base cation](#)
1685 [budget approach. New text describing the method of calculation, material and methods, results and](#)
1686 [discussion is now inserted at appropriate places in the manuscript, i.e., at Lines 582-595, 700-706 and](#)
1687 [945-946.](#)

1688
1689 [4. Conclusions: We have made a new improved version of the conclusions that we hope is clear and](#)
1690 [informative with respect to the novelty of our study, and has more obvious links with the context and](#)
1691 [rational given in the Introduction. We stress that a contribution of new knowledge is gained from](#)
1692 [using a harmonized study design, i.e. \(1\) where similarities and dissimilarities of methods occur with](#)
1693 [regard to different test criteria, and \(2\) in terms of the similarities and dissimilarities of different](#)
1694 [methods with regard to their relative importance in the overall base cation budgets. All of which](#)
1695 [enable us to identify some important issues for future research.](#)

1696
1697 [5. Minor comments:](#)

1698 [-Line 66: We have changed the definition of weathering rate so that dimensions are evident.](#)

1699 [-Line 247-249: We have cited Casetou-Gustafson \(2018\) where all details can be found about soil](#)
1700 [mineralogy at Asa and Flakaliden.](#)

1701 [-Line 267-268: We have added the information about which base cations were contained in the solid](#)
1702 [fertilizer mix.](#)

1703 [-Line 287: We changed soil texture to sandy loam.](#)

1704 [-Lines 899-900: We improved this sentence. Furthermore, we would like to clarify that there was no](#)
1705 [vegetation during the last glaciation as Asa was glaciated.](#)

1706
1707

1708 [Additional changes:](#)

1709
1710 [- We found an unfortunate error in the calculation of fine-root biomass which is now corrected \(Line](#)
1711 [505\). The change has no effect on how the calculation is described in the Materials and Methods](#)
1712 [section, but the consequences is a reduced fine root biomass leading to ca 5% lower BC uptake in](#)
1713 [biomass for Ca, Mg and K. This had no impact on the conclusions and the general picture, but the](#)
1714 [substantial discrepancies between present-day weathering rates produced by the base cation budget](#)

1715 [and PROFILE are now slightly less pronounced. The new calculations are now included in the revised](#)
1716 [Figures 4 and 5 \(former Fig. 3 and 4\).](#)

1717
1718 [- The description of how base cation budgets were calculated is now expanded with detailed](#)
1719 [information about sampling procedures and sampling sizes \(section 2.5\), as was requested by several](#)
1720 [reviewers. Additional graphs showing temporal changes in soil water chemistry and runoff are](#)
1721 [included in the Supplementary material \(Figure S4-S5; see also below\). Apparently, reviewer 1 in](#)
1722 [particular got the impression that the base cation budgets were based on a quite limited sampling.](#)
1723 [We hope the present text will change that view.](#)

1724
1725 [-By mistake error bars in Figure 3 \(now Fig 4\) have been switched between K and Na and we have](#)
1726 [corrected for this.](#)

1727
1728 [-We have revisited our results that we obtained from applying the depletion method and came to the](#)
1729 [conclusion that the relatively low values given by the historical weathering losses is due to](#)
1730 [complicated Zr gradients observed in two soil profiles at the Flakaliden site \(i.e. 11B and 15A; Fig.5\).](#)
1731 [By removing these profiles from the calculations \(described now in Lines 363-367 and Line 904-917\),](#)
1732 [predictions of historical weathering losses for Ca and Mg are more in line with the general view of](#)
1733 [declining rates over time. It makes more sense to observe Ca and Mg losses that are of similar](#)
1734 [magnitude, since both elements are contained to a similar extent in the easily weatherable mineral](#)
1735 [hornblende, which is an important mineral in the Svecofennian granitic bedrock. An editorial](#)
1736 [consequence of this was that we also moved former Fig. 5 to Fig. 2.](#)

1737
1738 **[Referee 1:](#)**

1739 [-In order to strengthen our study we have attempted to be clear about the novelty from the beginning](#)
1740 [of the manuscript \(i.e. Introduction\). Furthermore, as described above, we have added an additional](#)
1741 [assessment of uncertainty of the data that are used to construct the base cation budget \(Table 6\).](#)

1742 **[Referee 2:](#)**

1743 [Historical weathering:](#)

- 1744 [- We have corrected for the wrong unit used for Zr in former Table 2 \(now Table 3\).](#)
- 1745 [- We have added an equation \(1\) to the manuscript in the method section which describes the](#)
- 1746 [calculation by the depletion method \(Line 327\).](#)
- 1747 [- We have added estimated volume change \(strain calculations according to a formula in White](#)
- 1748 [et al.1996\) in the Supplements \(Table S5\) and a mentioning in Lines 348-352.](#)

1749 [Steady-state weathering:](#)

1750 - [We included a short mentioning of the steady-state concept in the introduction \(Line 148\) and](#)
1751 [in Table 2.](#)

1752 - [We have enlarged former Table 3 \(now Table 4\) and added a column that contains general](#)
1753 [information for each site. Layer-specific information is given in Supplementary Table S3-S4.](#)

1754 [Base cation budget:](#)

1755 - [We have added a more detailed description of how total deposition was calculated. The same](#)
1756 [deposition data was used for parameter setting of PROFILE and in the base cation budget.](#)

1757 - [We have added two supplementary figures \(Figure S4-S5\) to illustrate monthly mean and](#)
1758 [standard deviation of drainage \(mm\) in soil water at 50 cm depth in the soil of the four control](#)
1759 [plots at Asa and Flakaliden \(Figure S5\) and mean and standard error of BC ions \(mg/l\) in soil](#)
1760 [water sampled at 50 cm depth in the soil of four control plots at Asa and Flakaliden \(Figure](#)
1761 [S4\).](#)

1762 - [We have added a new table to the manuscript \(Table 6\) that contains estimated uncertainty](#)
1763 [ranges for the different terms in the base cation budget and their combined uncertainty.](#)
1764 [These uncertainties are based on standard errors derived from plot-wise replicated data of](#)
1765 [the present experiments \(for leaching and changes in exchangeable soil pools\) and on](#)
1766 [standard uncertainties derived from Simonsson et al. 2015, where replicated data were](#)
1767 [missing in the present study \(for accumulation in biomass and total deposition\). A detailed](#)
1768 [description of the statistical procedure is given in Lines 582-595.](#)

1769

1770 [Discussion:](#)

1771 [We have improved section 4.2.](#)

1772 [Figures:](#)

1773 - [We have inserted an explanation of error bars in Line 1494-1500 and in Lines 582-595.](#)

1774

1775 [Referee 3](#)

1776

1777 - [We have removed site names in figure 4 \(now figure 5\).](#)

1778 - [Apart from issues that were already raised by the other referees, we have corrected](#)
1779 [for minor errors, such as misspellings and we have changed to “extractable](#)
1780 [concentrations” instead of “concentrations” in the table description of former Table](#)
1781 [2 \(Now Table 3\).](#)

1782

1783 [In addition to the revised manuscript we have also provided a corresponding version with tracked](#)
1784 [changes on, so that the revisions are clearly visible. We have also been carefully through the whole](#)
1785 [text and made some additional minor revisions which we believe aid clarity.](#)

1786

1787 [We hope you will find our revised manuscript acceptable for publication in Biogeosciences and look](#)
1788 [forward to hearing from you in due course.](#)

1789

1790

1791 [On behalf of all authors, yours sincerely,](#)

1792 -

1793 [Sophie Casetou-Gustafson,](#)

1794

1795 [Corresponding author](#)

1796

1797