

## Authors response to reviewers

We have only achieved the detailed review report by Prof Velbel, why we have based our revision on his comments and suggestions for improving the manuscript, beside the editors note. In addition to that, we have made additional corrections of flaws and poor design in the text, figures and tables when necessary. We thank the reviewer (Velbel) for having scrutinized the manuscript and providing a comprehensive, well structured and useful report that has helped us to improve the paper. The reviewer emphasizes three major points, which were also stressed by the Editor: (1) to strengthen the connection between problem definition, aims and conclusions, aims should be defined in a clearer way and novelty in approach and results clearly stated, (2) it should be written in a globally relevant perspective to attract the international scientific community, (3) it lacks important references (is under-referenced). Besides remarks on terminology, language and some flaws, as well as recommendations (include a map etc.), we notice that these critical remarks mostly concerns the Abstract, Introduction, Discussion, and Conclusions, but not the Material and methods, and Results sections.

This is in brief our response to the major critique: In the Introduction, we initially stress that the demands for more accurate estimate of base cation weathering rates emerged from soil and water acidification, and the useful concept of critical loads of acidity. This is a more logical entry and explains for example the development of the PROFILE model and the wide application of this model in e.g. Europe and North America. The rationale for the study is now expressed more clearly, leading to the new formulation of the aims, which is "to analyse the causes of discrepancies in estimations of weathering rates, with focus on conceptual versus random sources of discrepancies, between the depletion method, the PROFILE model and the balanced base cation budget approach." We think that an analysis of conceptual and random sources of discrepancies between methods is useful and novel in a general sense that can attract wider groups of the scientific community, although our approach may not be entirely new. In the Discussion, the subsections follow the three criteria and is updated to follow the aims. The introductory part of the Discussion is now deleted because the new Introduction made it redundant. The Conclusion is changed to make a stronger connection to the aims. A consequence of the revision is also that a number of references have been added, and a few have been deleted.

The changes listed below are numbered as by the reviewer (bg-2019-47-referee-report-3.pdf), and refer to line numbers in the revised manuscript.

1. This is a summary of the reviewers comments that we response to in detail below.
2. We deleted the sentence about MAGIC, because we deemed it not necessary in this background description. However, the MAGIC model has been used as an approach to estimate weathering rates based on measured and modelled ion fluxes. Weathering rate of different base cations is a parameter in MAGIC that can be set to achieve a balance between sources and sinks, and in this meaning it contains a budget approach. Some new references include important pioneering works on the budget method.

The sensitivy of PROFILE with respect to dissolution kinetics is considered and acknowledged in the Discussion and Conclusion. We have added a sentence about this

on line 179-182 in the Introduction to make the connection between Introduction and later sections stronger.

4. OK, we can see the problem, but as the reviewer also acknowledge, we address this issue in detail later in the manuscript. The problems associated with the application of the depletion method are indeed important, and we stress this point further in the revised manuscript by introducing the concepts of conceptual and random sources to causes of discrepancies between method outputs. We think this is one nobelty of the paper.

5. Yes, BD was measured for a majority of soil samples.

6. Thanks, we appreciate this note.

7. OK, we admit that this might be a problem, but we have also given fair rationales to why this was made, on Lines 489-494 in the revised manuscript (no changes made).

8. OK, the Figure 4 caption can be misleading, so we have reformulated it. It now states that all error bars are SE, or the equivalent. Line 1097, Figure caption.

9. We agree. Previous work that shows closest resemblance for Na weathering, between depletion and budget calculations, are now referred to in the Discussion on line 706-711.

10. We think this comment is much included the abovementioned note (#9).

11. We appreciate this comment

12. We appreciate this comment.

13. We agree that Zr mobility and corrosion can be an issue for the depletion method, but we decided to not stress this question further in the Discussion due to lack of relevant data.

14. Thanks.

15. Thanks. See our comment to #9. We have also added some additional (new) references (Rosenstock 2019a, b, Callesen et al 2016) in support of our conclusions about the budget method: last paragraph of Discussion.

16. This comment of the contribution of the study to the scientific community is a very general statement. Our ambition with the revised manuscript is to overcome this critique, described elsewhere in our response. See the first paragraph of this report for a general answer.

17. This is compliment we take to our hearts.

18. This comment is a summary of recommended changes. Our changes to meet these requirements have been explained elsewhere in this response.

19. We agree fully! As described in the introductory part (2nd# paragraph) of this response letter, we have made major changes particularly in the Introduction to give a more clear background, explicit rationale of study (Line 125-141), and aims (L204-209), that we hope will be of significant for a wider group of readers. In particular, we introduce the concept of conceptual versus random causes to discrepancies between different methods to estimate weathering rates, and link these concepts to our ambition to make a harmonised comparison of methods. We have also made a number of changes in the Discussion to make a clearer connection to questions raised in the Introduction. Furthermore, we believe that one of the major strengths of our study is the focus on weathering and nutrient uptake by forest trees. Abstract and Conclusions have been changed in accordance with these changes.

20. The comment touches upon similar aspects (on regional vs global interest) as previous points made by the reviewer: Taken literally, a regional (local) study may be of local interest only, but it may also mean that it is of no general interest, in the sense of importance to scientific abstractions and theory, which by definition are rarely 'local'. However, most studies in this field of science are literally local as they are based on data from a limited number of sites, but can nevertheless be of general, theoretical value. The present study of course remains as a case study based on two forest sites about 1000 km apart, but we hope that the revised version will add more general value to the scientific community. This was achieved by a small shift in focus and stronger stress on analysing the causes of discrepancies between method, and by separating the conceptual from the random origins of discrepancies. The ideas behind the concepts have been latent, but are now explicit.

21. We hope the present revision of the Introduction, Discussion and Conclusions now meet those expectation. (Similar aspects as for #16, 19, 22)

22. This is not a review paper, but results from previous studies in Sweden using the same methods are referred to, as a way to see if our results are consistent with previous studies. See our answer on #20 to the critique that this study is of local significance only. Also, notice how the aims are formulated in the revised manuscript.

23. We have included a map over Scandinavia, showing the locations of the sites.

24. Thanks, we realized that figures and tables in particularly the supplement were not in correct order, and has corrected that.

25. OK, we have corrected this flaw.

26. The reviewer points out areas of under-referencing, and we have accordingly added a few more references on the specific issue.

27. This is matter for editorial decision, which we will follow. Biogeosciences require that Supplements should be uploaded as pdf. In addition, BG also demands that source data should be available at DOI data repository sites. By the way, we have revised the Supplement with respect to order, legend and figure captions, and table design.

28. OK, corrected throughout the paper.

29. OK, corrected, line 673.

30. OK, corrected.

31. OK, corrected (L452)

32. OK, corrected. We write: 'due to their resistance to weathering'.

33. OK, corrected, we used the term 'constant' (Line 319) and 'uniform at L629, 631.

34. OK, soil layer changed to soil horizon throughout the manuscript, when relevant.

35. OK, corrected (Line 235, 430)

36. OK, corrected on numerous places.

37. OK, we have checked the references to harmonise with the requirements by the journal.

**Below: Velbels comments are in italics.**

*Specific comments:*

*Line 101 – replace “if” with “whether”*

- Whole sentence is changed

*Line 170 – replace “on” with “to”*

- Whole sentence is replaced

*Line 353 – replace “ar” with “is”*

- OK, corrected (Line. 405...)

*Line 416 – Delete close paren.*

- Done.

*Line 481 – Replace “as opposed” with “in contrast”.*

- OK, corrected (Line 537)

*Line 580 – Replace “were possible to reconcile” with “could be reconciled”*

- OK, corrected (Line 663)

*Line 648 – delete the duplicate period.*

- OK, corrected (Line 700)

*Line 832 – “Sedimentologists” is plural.*

- OK, corrected (Line 884)

*Line 864 – Journal title should be in title case (all major words capitalized).*

- OK, corrected (Line 932)

*Figure axis labels should be in the format “Label (units)”. The experienced reader presumes that elemental “concentration (%)” in Figure 2 means weight %, but, because it could be atomic or molar %, (“wt. %”) would eliminate the possibility of misunderstanding by non-specialists and novice readers. The labeling of axes for all other Figures is excellent.*

- OK, corrected, new Figure # is Fig.3.

*Tables S1 and S2 are not useful as formatted. Graphical representation of the sensitivity analysis is required if it is intended to be understood by readers.*

- OK, we have made new graphs based on the tables, Figures S4-S5

*Tables S3 and S1b contain similar data for the two field areas; the numbering of these tables does not make sense.*

- Agree, the Supplement is revised.

*Table S4 – Reporting model-input soil bulk densities and exposed mineral surface areas to 15 significant figures is not justified by anything explicitly stated in the text.*

- Agree, that Supplement table has been trimmed.

*These comments, above and below, are intended to help improve the effective presentation of the work done and the scientific impact of the revised manuscript.*

Thank you!

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

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27 **Abstract**

28 Reliable and accurate methods for estimating soil mineral weathering rates are required tools in  
29 evaluating the sustainability of increased harvesting of forest biomass and assessments of critical loads of  
30 acidity. A variety of methods that differ in concept, temporal and spatial scale and data requirements are  
31 available for measuring weathering rates. In this study, causes of discrepancies in weathering rates between  
32 methods were analyzed and were classified as being either conceptual (inevitable) or random. The release rates  
33 of base cations (BC; Ca, Mg, K, Na) by weathering were estimated in podsolised glacial tills at two experimental  
34 forest sites, Asa and Flakaliden, in southern and northern Sweden, respectively. Three different methods were  
35 used: (i) historical weathering since deglaciation estimated by the depletion method, using Zr as assumed inert  
36 reference; (ii) steady-state weathering rate estimated with the PROFILE model, based on quantitative analysis of  
37 soil mineralogy; and (iii) BC budget at stand scale, using measured deposition, leaching and changes in base  
38 cation stocks in biomass and soil over a period of 12 years. In the 0–50 cm soil horizon historical weathering of  
39 BC were 10.6 and 34.1 mmol<sub>c</sub> m<sup>-2</sup> yr<sup>-1</sup> at Asa and Flakaliden, respectively. Corresponding values of PROFILE  
40 weathering rates were 37.1 and 42.7 mmol<sub>c</sub> m<sup>-2</sup> yr<sup>-1</sup>. The PROFILE results indicated that steady-state weathering  
41 rate increased with soil depth as a function of exposed mineral surface area, reaching a maximum rate at 80 cm  
42 (Asa) and 60 cm (Flakaliden). In contrast, the depletion method indicated that the largest postglacial losses were  
43 in upper soil horizons, particularly at Flakaliden.

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

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

Bengt Olsson 2019-10-19 16:03

Borttagen: through ...y weathering v ... [1]

Bengt Olsson 2019-10-17 22:06

Formaterat: Inte Färgöverstrykning

Bengt Olsson 2019-10-2 11:29

Borttagen: layers...orizons, PROFIL ... [2]

Bengt Olsson 2019-10-2 11:29

Borttagen: layers

104 **Definitions and abbreviations**

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

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

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

110  
111  $W_{\text{depletion}}$  = Historical weathering rate based on calculation of loss of mobile elements since last deglaciation

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

113  $W_{\text{budget}}$  = Current weathering rate based on base cation budget calculations

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115

116

Bengt Olsson 2019-10-19 16:06

Borttagen: a

Bengt Olsson 2019-10-2 11:31

Borttagen: Definitions -

119 **1. Introduction**

120 Silicate weathering is the major long-term source of base cations in forest ecosystems (Sverdrup and Warfvinge,  
121 1988) and is therefore crucial for sustainable plant production and for proton consumption, counteracting soil  
122 and water acidification (Nilsson et al., 1982; Hedin et al., 1994; Likens et al., 1998; Bailey et al., 2003). These  
123 effects of weathering are important in areas where in the past high sulphur (S) deposition has caused severe  
124 acidification of forest soils and waters (Reuss and Johnson, 1986), for example in southern Scandinavia,  
125 northeastern USA and southeastern Canada, regions where felsic igneous bedrock and less readily weatherable  
126 soils are abundant (Likens and Bormann, 1974; Nilsson and Tyler, 1995). To aid the multi-lateral negotiations  
127 on reducing emissions of acidifying air pollution, the effect-based concept of critical loads of acidity was  
128 developed in the late 1980s (Lidskog and Sundqvist, 2002). One advantage of the concept was that the critical  
129 loads could be calculated and mapped for different regions at various scales. Because weathering is a key  
130 component in estimates of critical loads, reliable applications of the critical load concept required that  
131 weathering rates could be estimated with sufficient accuracy at regional scale (Sverdrup and de Vries, 1994).  
132

133 By 1990 in most European countries, the trend of increasing S emissions since the 1950s started to abate  
134 (Grennfelt and Hov, 2005) with a simultaneous decrease in atmospheric deposition of base cations (Hedin et al.  
135 1994). In Sweden, forest growth has at the same time gradually become a relatively more important source to  
136 soil acidity (Iwald et al., 2013). Besides the reduction in S deposition, this change has partly been driven by  
137 increased use of logging residues for energy production (i.e. whole-tree harvesting), and probably also by a  
138 general higher forest production over recent decades in Sweden (Binkley and Högberg 2016). Soil acidification  
139 by forest growth is principally caused by accumulation of base cations in tree biomass in excess of anion uptake  
140 (Nilsson et al., 1982). The return of base cations in remaining biomass and residues following harvesting  
141 determines to what extent the acid load can be neutralised. The soil acidification effect of whole-tree compared  
142 to stem-only harvesting has been demonstrated in long-term field experiments (Olsson et al., 1996; Zetterberg et  
143 al., 2013). The combined effects can therefore impede recovery from acidification and place increasing demands  
144 on nutrient supply.

145  
146 The sustainability of increased harvest intensity of forest biomass has been questioned and analysed in many  
147 studies from various viewpoints and criteria with focus on Europe and North America (e.g. Boyle et al., 1973;  
148 Paré et al., 2002; Thiffault et al., 2011, Achat et al. 2015; De Jong et al., 2017; Ranius et al., 2018), where the  
149 role of weathering in maintaining base cation balance being one criterion. The impact of increased use of logging  
150 residues on base cation balances in Swedish forest soils has been examined in several previous studies (Sverdrup  
151 and Rosén, 1998; Akselsson et al., 2007). A regional-scale study on Swedish forest soils found that, in parts of  
152 Sweden, base cation losses can occur at rates that lead to very low base saturation of the soils, possibly leading  
153 to negative effects on e.g. soil fertility and runoff water quality within just one forest rotation (Akselsson et al.,  
154 2007). In their study, base cation depletion in the soil was found to be more common after whole-tree harvesting  
155 than stem-only harvesting, especially for Norway spruce, with deficits being more common in southern than in  
156 northern (boreal) Sweden.  
157

Bengt Olsson 2019-10-2 13:54

**Borttagen:** and forest and accumulation of base cations in tree biomass in excess of anion uptake has become a more important source of acidity to the soil (Nilsson et al., 1982). Whole-tree harvesting can thus result in more acid, base cation-depleted soils than stem-only harvesting (Olsson et al., 1996; Zetterberg et al., 2013).

Bengt Olsson 2019-10-17 21:01

**Borttagen:** of increased productivity of forests in Sweden, resulting in increased stocks of forest biomass, and increased use of whole-tree harvesting for energy purposes

Bengt Olsson 2019-10-2 13:56

**Borttagen:** In society there is a need to know if current forestry practices are sustainable, that is if current weathering provides enough base cations to at least balance their export by forestry. The role of weathering in maintaining b

Bengt Olsson 2019-10-17 21:01

**Borttagen:** B

Bengt Olsson 2019-10-2 11:31

**Borttagen:** frequent



178 In regional assessments of the sustainability of different harvesting regimes, the estimated weathering rate has a  
179 strong influence on the base cation balance. Klaminder et al. (2011) found that different approaches to estimating  
180 weathering rates for a forested catchment in northern Sweden yielded results that differed substantially, and that  
181 uncertainties in the methods had a great influence on the predicted sustainability of different harvesting  
182 practices. Futter et al. (2012) compiled weathering rates estimated at 82 sites on three continents, using different  
183 methods, and found both large between-site as well as within-site differences in the values. Differences in input  
184 data can be attributed to different time scales used when acquiring different input data, challenges determining  
185 accurate mineralogical compositions and the use of field data compared with laboratory data (Van der Salm,  
186 2001; Futter et al., 2012). Thus, they recommend that at least three different approaches be applied per study site  
187 to evaluate the precision in weathering estimates.

188  
189 Different approaches to estimate weathering rates are likely to produce different estimates due to their  
190 conceptual differences, but additional sources to discrepancies of more random nature will also appear. The  
191 latter may be due to e.g. misfits in spatial scales, measurement errors or uncertainties in model parametrisation.  
192 A number of studies comparing different approaches to estimate weathering rates have been published (e.g.  
193 Kolka et al., 1996; Sverdrup et al., 1998; Van der Salm et al., 2001; Ouimet and Dechesne, 2005; Whitfield et al.,  
194 2006, 2011; Koseva et al., 2010; Klaminder et al., 2011; Stendahl et al., 2013; Futter et al., 2012; Augustin et al.,  
195 2016) such that additional studies on this issue may seem redundant. However, several of these comparison  
196 studies can be criticized for poor harmonisation with respect to the spatial scale, or that nutrient uptake in  
197 biomass and soil change have been neglected, or poorly quantified in approaches where these processes are  
198 relevant for the estimates. Poor harmonisation makes it difficult to separate conceptual from random sources of  
199 discrepancies. We therefore see a need for improved comparisons, performed with a spatially constrained and  
200 refined harmonisation in the sense of Futter et al. (2012), and combined with a focus on forest soils, tree  
201 nutrition and growth. Starting from the viewpoint that no method provides the 'true' estimate of weathering, and  
202 acknowledging that different approaches are conceptually different and use different input data, in the present  
203 paper we examined three approaches in the present paper: (1) 'historical weathering' based on geochemical  
204 investigation of the soil profile, (2) modelled present weathering rate and (3) present weathering rate based on  
205 cation balances at the ecosystem level.

206  
207 The choice of methods was primarily based on the fact that rates of weathering may (do) vary over time  
208 (Klaminder et al., 2011; Stendahl et al., 2013). The average weathering under long-term environmental change,  
209 i.e. 'historical weathering', is thus different from the weathering potential under present-day environmental  
210 conditions, i.e. 'present-day weathering', which is why we need to be able to consider historical weathering  
211 when assessing current/present-day weathering rates. Moreover, present-day weathering rates estimated by  
212 models based on the steady-state concept, which lacks the dimension of time, may differ from dynamic estimates  
213 of weathering rates derived from measured base cation budgets. These three different concepts of estimating  
214 weathering cannot be covered by a single method (Klaminder et al., 2011; Futter et al., 2012). Indeed,  
215 wweathering estimates based on these concepts have often differed grossly from pedon to catchment scale,  
216 whereas truly harmonised comparisons of methods require that methods are tested uniformly at the same spatial  
217 scale. This spatial scale can be the pedon, which also contains the major part of the mineral nutrient sources in

Bengt Olsson 2019-10-2 14:01

**Borttagen:** The approaches examined

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**Borttagen:** include

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**Borttagen:** is

Bengt Olsson 2019-10-11 10:23

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Bengt Olsson 2019-10-19 16:15

**Borttagen:** W

Bengt Olsson 2019-10-19 16:16

**Borttagen:** largely

Bengt Olsson 2019-10-16 13:47

**Borttagen:** z

225 the soil available for forest growth. To our knowledge, Kolka et al. (1996) is the only study to have previously  
 226 used this [multiple](#) approach.  
 227  
 228 The first approach, the depletion method, makes use of soil profile based mass balances (Chadwick et al., 1990;  
 229 Brimhall et al., 1991) to estimate total base cation losses in the soil above a reference soil depth. An element in a  
 230 weathering-resistant mineral is used as a standard, most commonly zirconium (Zr, present in e.g. zircon) or  
 231 titanium (Ti, present in e.g. rutile) (Sudom and St. Arnaud, 1971; Harden, 1987; Chadwick et al., 1990; Bain et  
 232 al., 1994), due to their [resistance to weathering](#) at low temperatures (Schützel et al., 1963). To yield an annual  
 233 average weathering rate (mmol<sub>c</sub> m<sup>-2</sup>), calculated element losses are commonly divided by an estimated soil age.  
 234 In Nordic glacial tills situated above the marine limit, soil age is conventionally considered to be the number of  
 235 years lapsed since the site of interest was finally deglaciated at the end of the Weichselian. [Because](#) the rate of  
 236 weathering may vary over time (Klaminder et al., 2011; Stendahl et al., 2013), the average ‘historical  
 237 weathering’ rate may differ from the present-day weathering rate.  
 238  
 239 The second approach commonly involves the [process-based PROFILE model, which has been used widely as a](#)  
 240 [tool to estimate critical loads of acidity in the Nordic countries \(e.g. Sverdrup et al., 1992\) and North America](#)  
 241 [\(Whitfield and Watmough, 2012; Phelan et al., 2014\). In PROFILE,](#) release rates of base cations are estimated  
 242 based on [built in assessments of the](#) the dissolution kinetics of a user-defined set of minerals present in the soil,  
 243 and the physical and chemical conditions that drive the dissolution of [those](#) minerals. [Because](#) it is a mechanistic  
 244 model, its strength is its transparency, while its main weakness is the difficulty in setting values of model  
 245 parameters and input variables to which it may have high sensitivity. Akselsson et al. (2019) concluded that the  
 246 most important way to reduce uncertainties in modelled weathering rates is to reduce input data uncertainties,  
 247 e.g. regarding soil texture, although there is still a need to improve process descriptions of e.g. biological  
 248 weathering and weathering brakes (e.g. Erlandsson Lampa et al., this issue). The sensitivity of PROFILE to  
 249 variations in soil physical parameters (e.g. soil texture, soil bulk density) and mineral composition was discussed  
 250 by Jönsson et al. (1995) and Hodson et al. (1996). [The](#) importance of the ability to determine the precise identity  
 251 and quantity of the minerals was analysed by Casetou-Gustafson et al. (2019). [They \(ibid.\) also suggested that](#)  
 252 [the dissolution kinetics of minerals used in the PROFILE model should be revised and the uncertainties assessed](#)  
 253 [to improve the accuracy in model predictions.](#)  
 254  
 255 The third approach to estimating weathering rate is the [balanced](#) base cation budget approach. [This](#) method has  
 256 been applied to estimate current weathering rates at various temporal and spatial scales, [mostly the catchment](#)  
 257 [scale \(Velbel, 1985; Likens et al., 1998\). In one way of using the approach, mean weathering rates of individual](#)  
 258 [minerals can be estimated at the catchment scale based on data for the mineralogical composition of soils along](#)  
 259 [with element inputs in deposition and outputs in stream water and biomass uptake \(e.g. Garrels and Mackenzie,](#)  
 260 [1967; Velbel 1985, Velbel and Price, 2007\). Others have estimated weathering as an unknown source from the](#)  
 261 [missing balance between known sources \(deposition, soil depletion\) and known sinks \(uptake, leaching, increase](#)  
 262 [in soil BC stocks\) \(e.g. Sverdrup et al. 1998; Simonsson et al., 2015\). The method requires measurements of](#)  
 263 [known fluxes within a system with defined boundaries. The high data demand restricts the application of the](#)  
 264 [base cation budget approach to a limited number of sites, essentially catchments with long-term monitoring of](#)

Bengt Olsson 2019-10-18 09:34  
**Borttagen:** et al.

Bengt Olsson 2019-10-2 11:32  
**Borttagen:** stability

Bengt Olsson 2019-10-2 11:32  
**Borttagen:** Since

Bengt Olsson 2019-10-3 13:41  
**Borttagen:** The depletion method is most widely used in Sweden to estimate weathering rates, specifically at the regional scale (Olsson et al., 1993).

Bengt Olsson 2019-10-2 14:02  
**Borttagen:** mechanistic

Bengt Olsson 2019-10-3 13:40  
**Borttagen:** by which

Bengt Olsson 2019-10-2 11:33  
**Borttagen:** Since

Bengt Olsson 2019-10-16 13:47  
**Borttagen:** this issue

Bengt Olsson 2019-10-2 14:03  
**Borttagen:** , while the

Bengt Olsson 2019-10-16 13:48  
**Borttagen:** this issue

Bengt Olsson 2019-10-11 10:24  
**Borttagen:** (Velbel, 1985; Likens et al., 1998).

280 | fluxes and well-defined boundaries. However, even then estimated weathering rates may suffer from large  
281 | uncertainties, as errors in the sinks and sources accumulate in the mass balance equation (Simonsson et al.,  
282 | 2015). Furthermore, the base cation budget approach has mostly been applied under conditions where  
283 | accumulation in biomass were not directly measured but estimated to be small, or base cation stocks in the soil  
284 | were assumed to be at steady-state (e.g. Kolka et al., 1996; Sverdrup et al., 1998; Whitfield et al., 2006).

285 | However, the nutrient demand is particularly large during the aggrading phase of a stand development where the  
286 | foliage biomass is increasing rapidly. Hence, due to difficulties in application of the budget method to regional  
287 | scale, the PROFILE model and the depletion method are the most commonly used methods in Sweden to  
288 | estimate weathering rates.

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

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

## 309 | 2. Materials and methods

### 310 | 2.1 Study sites

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

315 | The experiment at Flakaliden was established in 1986 in a 23-year-old Norway spruce stand, planted in 1963  
316 | with four-year-old seedlings of local provenance after prescribed burning and soil scarification (Bergh et al.,  
317 | 1999). The experiment at Asa was established one year later (1987), in a 12-year-old Norway spruce stand  
318 |

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**Borttagen:** and components of the budget approach have been used in different ways in some models, e.g. MAGIC (Cosby et al., 1985). The weathering rate is estimated indirectly as the difference between other sinks and sources of base cations, which are measured within a system with defined boundaries. The missing source in the mass balance equation is assumed to represent the weathering. The base cation budget approach is most reliable when based on long-term data from well-defined systems, although

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In this study, we applied the three conceptually different methods of estimating weathering on two well-defined forest ecosystems, Asa and Flakaliden in southern and northern Sweden, to allow a harmonized comparison of methods, and to place weathering in the context of other base cation fluxes in aggrading Norway spruce forests. The base cation budgets were estimated at the period of stand development when nutrient demand was expected to peak. In combination with access to highly accurate data on biomass production, these conditions also provided opportunities to relate weathering to base cation accumulation in biomass at high nutrient uptake rates, and possible simultaneous depletions of extractable base cation stocks in the soil. Furthermore, input data to PROFILE were characterised by high quality quantitative mineralogical data, measured directly by X-ray powder diffraction (XRPD), as previously discussed by Casetou-Gustafson et al. (2018). ... [3]

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**Borttagen:** In this study, we applied the three conceptually different methods of estimating weathering on two well-defined forest ecosystems, Asa and Flakaliden in southern and northern Sweden, to allow a harmonized comparison of methods, and to place weathering in the context of other base cation fluxes in aggrading Norway spruce forests. The base cation budgets were estimated at the period of stand development when nutrient demand was expected to peak. In combination with access to highly accurate data on biomass production, these conditions also provided opportunities to relate ... [4]

399 planted in 1975 with two-year-old seedlings after clear-felling and soil scarification. The experimental design  
400 was similar at both sites and included control, irrigation and two nutrient optimisation treatments (Bergh et al.,  
401 1999). All treatments were replicated in 50 m × 50 m plots, arranged in a randomised block design. Only two of  
402 the four treatments were used in the present study; the control (C) and plots receiving an annual dose of an  
403 optimised mix of solid fertiliser (F), which among other elements per year contained about 10 kg ha<sup>-1</sup> Ca, 8 kg  
404 ha<sup>-1</sup> Mg and 45 kg ha<sup>-1</sup> K (Linder, 1995).

405  
406 Flakaliden is located in the central boreal sub-zone with a harsh climate, with long cool days in summer and  
407 short cold days in winter. Mean annual temperature for the period 1990-2009 was 2.5 °C, and mean monthly  
408 temperature varied from -7.5 °C in February to 14.5 °C in July. Mean annual precipitation in the period was  
409 ~650 mm, with approximately one-third falling as snow, which usually covers the frozen ground from mid-  
410 October to early May. Mean length of the growing season (daily mean temperature ≥ 5 °C) was 148 days, but  
411 with large between-year variations (cf. Table 1 in Sigurdsson et al., 2013).

412  
413 Asa is located in the hemi-boreal zone, where the climate is milder than at Flakaliden, which is reflected in a  
414 longer growing season (193 days). Mean annual temperature (1990-2009) was 6.3 °C, mean monthly  
415 temperature varied from -1.9 °C in February to 16.0 °C in July and mean annual precipitation was ~750 mm.  
416 The soil is periodically frozen in winter. The difference in climate is reflected in differences in site productivity,  
417 which broadly follows climate gradients in Sweden (Bergh et al., 2005).

418  
419 The soils at Asa and Flakaliden differ in age due to differences in the time since deglaciation (Table 1), from  
420 approximately 14,300 years at Asa and 10,150 years at Flakaliden (estimated from Fredén, 2009). The soil type  
421 at both sites is an Udic Spodosol, with a mor humus layer overlying glacial till derived from felsic bedrock. The  
422 soil texture is classified as sandy loam. The transition between the B- and C-horizons is mostly located at 50 cm  
423 depth at Flakaliden and 50-60 cm depth at Asa. The natural ground vegetation at Flakaliden is dominated by  
424 *Vaccinium myrtillus* (L.) and *V. vitis-idaea* (L.) dwarf-shrubs, lichens and mosses (Kellner, 1993; Strengbom et  
425 al., 2011). The ground vegetation at Asa is dominated by *Deschampsia flexuosa*, (L.) and mosses (Strengbom et  
426 al., 2011; Hedwall et al., 2013).

## 427 2.2. Soil sampling and analyses of geochemistry and mineralogy

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

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

441  
442 Soil samples were taken from each 10-cm soil layer. Prior to chemical analysis, these samples were dried at 30-  
443 40 °C and sieved to <2 mm. Analysis of particle size distribution was performed by wet sieving and  
444 sedimentation (pipette method) in accordance with ISO 11277. Geochemical analyses were conducted by ALS  
445 Scandinavia AB and comprised inductively coupled plasma-mass spectrometry (ICP-MS) on HNO<sub>3</sub> extracts of  
446 fused samples that were milled and ignited (1000 °C) prior to fusion with LiBO<sub>2</sub>.

447  
448 Quantitative soil mineralogy was determined with the X-ray powder diffraction (XRPD) technique (Hillier 1999,  
449 2003). Samples for measurement of XRPD patterns were prepared by spray drying slurries of soil samples (<2  
450 mm) micronised in ethanol. A full pattern fitting approach was used for quantitative mineralogical analysis of  
451 the diffraction data (Omotoso et al., 2006). This fitting process involved the modelling of the measured  
452 diffraction pattern as a weighted sum of previously measured and verified standard reference patterns of the  
453 identified mineral components. The determination of chemical compositions of various minerals present in the  
454 soils was conducted by electron microprobe analysis (EMPA) of mineral grains subsampled from the sifted (< 2  
455 mm) soil samples. [Mineralogical composition of the soils is given in the Supplement \(Table S1\).](#)

## 456 2.3 Historical weathering determined with the depletion method

### 457 2.3.1 Method description

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

$$463 W_{\text{depletion},i} = \frac{d \cdot \rho}{100} \cdot \frac{X_c \cdot Zr_{w,i}}{Zr_c} - X_{w,i}$$

Eq. 1

464 where  $W$  denotes loss of the  $i$ th element ( $\text{g m}^{-2}$ ),  $X$  denotes mobile element concentrations (%),  $Zr$  denotes  
465 immobile element concentrations (%),  $w$  and  $c$  denote a weathered soil horizon and the assumed unweathered  
466 reference horizon, respectively,  $d$  is horizon thickness (m), and  $\rho$  is bulk density ( $\text{g m}^{-3}$ ). Zirconium is  
467 commonly used as the immobile element due to the inert nature of the mineral zircon ( $\text{ZrSiO}_4$ ), although Ti is  
468 sometimes used due to the resistance of the Ti-containing minerals anatase and rutile ( $\text{TiO}_2$ ) to weathering  
469 (Olsson and Melkerud, 1989). The unweathered reference horizon is located in the C horizon, and has X to Zr  
470 ratios that are assumed to represent pristine conditions of the presently weathered horizons above it. In the  
471 weathered horizons, X to Zr ratios are smaller; that is, Zr is enriched compared with the mobile elements (i.e. the  
472 base cations). The method is based on the assumptions that Zr, hosted in zircon, was uniformly distributed  
473 throughout the soil profile at the time of deglaciation, that weathering only occurs above the reference horizon  
474 and that zircon does not weather. The latter implies that Zr concentrations and Zr/base cation ratios are constant  
475 below the reference horizon. The reference depths for different base cations compared with Zr, which were used  
476 as the depths of immobile element concentrations, are shown in Table 3. The Zr/base cation ratio (Fig. S1) was

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

### 495 2.3.2. Application

496 Prior to calculating base cation weathering rates with the depletion method, fractional volume change  $V_p$  was  
497 calculated according to White et al. (1996) in order to assess if there were any large volume changes (collapse)  
498 in the mineral soil with implications for which depth the weathering should be calculated to. Similar to White et  
499 al. (1996), it was assumed that values close to zero indicate no volumetric change, which was the case below 30-  
500 40 cm of soil depth at both sites (Table S2). The homogeneity of the parent material was also evaluated (Fig. 2)  
501 using the criterion that the ratio of Ti to Zr should be more or less constant with depth in an originally  
502 homogeneous material. Use of the ratio of two immobile elements to establish uniformity of parent material has  
503 been suggested previously (Sudom and St. Arnaud, 1971; Starr et al., 2014). The homogeneity criterion was not  
504 met using Zr in plot K1 at Asa (i.e. the Zr concentrations decreased towards the soil surface; Fig. 2); here Ti was  
505 used as the immobile element instead. Furthermore, the plots 15A and 11B at Flakaliden had to be eliminated  
506 from the calculations, because relatively large variability in both the Zr and Ti gradients was observed. These  
507 large heterogeneities led to an overall gain of base cations in the rooting zone, which is opposite to what would  
508 be expected (i.e. that losses and gains can occur at specific soil depths due to eluviation and illuviation processes  
509 in podzolic soils). For this reason, soil profiles 15A and 11B were eliminated from further consideration in  
510 calculations of historical weathering rates using the depletion method. Thus, apart from heterogeneities,  
511 transportation processes (eluviation and illuviation) and/or erratic Zr or Ti gradients could lead to “negative”  
512 weathering, i.e. leading to a calculated relative accumulation of elements. Such negative values were not  
513 considered in the calculation of historical weathering losses.

514  
515 Bulk density was estimated for each soil layer except in some plots where density measurements could not be  
516 made below a certain soil depth. Bulk density in these cases was estimated using an exponential model for total  
517 organic carbon (TOC) and bulk density (BD,  $\text{g cm}^{-3}$ ) based on our own data. For Asa (soil horizons F3: 70-90  
518 cm; F4: 0-10, 30-40, 50-60, 60-70, 70-80, 80-90, 90-100 cm; and K4: 70-80, 80-90, 90-100 cm), the following  
519 function was used:

$$520 \rho = 1.3 e^{-0.1 x}$$

521 where  $x$  is TOC content (% of dry matter). For Flakaliden (soil layers 14B: 80-90cm; 10B: 60-70 cm; and 11B:  
522 40-70 cm), the function used was:

$$523 \rho = 1.8 e^{-0.2 x}$$

### 524 2.4.1 The PROFILE model

#### 525 2.4.1 Model description

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Borttagen: where weathering of the  $i$ th base cation ( $W_{\text{profile},i}$ ) is described by long-term mineral dissolution kinetics at the interface of wetted mineral surfaces and the soil solution. PROFILE is a multilayer model, where parameters are specified for each soil layer based on field measurements and estimation methods (Warfvinge and Sverdrup, 1995).

544 The steady state weathering of soil profiles was estimated using the biogeochemical PROFILE model (Table 2),  
545 where weathering of the  $i$ th base cation ( $W_{\text{profile},i}$ ) is described by long-term mineral dissolution kinetics at the  
546 interface of wetted mineral surfaces and the soil solution. PROFILE is a multilayer model, where parameters are  
547 specified for each soil layer based on field measurements and estimation methods (Warfvinge and Sverdrup,  
548 1995).

#### 549 2.4.2 PROFILE parameter estimation

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

552  
553 Exposed mineral surface areas were estimated from soil bulk density and texture data using the algorithm  
554 specified in Warfvinge and Sverdrup (1995). Volumetric soil water content for each soil profile in Flakaliden  
555 and Asa was estimated to be  $0.25 \text{ m}^3 \text{ m}^{-3}$  according to the moisture classification scheme described in Warfvinge  
556 and Sverdrup (1995) (Table S3).

557  
558 The aluminium (Al) solubility coefficient, a soil chemical parameter needed for solution equilibrium reactions,  
559 was defined as  $\log\{\text{Al}^{3+}\}+3\text{pH}$ . It was estimated by applying a function developed from previously published  
560 data (Simonsson and Berggren, 1998) and existing total carbon and oxalate-extractable Al measurements for the  
561 sites (Casetou-Gustafson et al., 2018) (Table S3). For partial  $\text{CO}_2$  pressure in the soil, the default value of  
562 Warfvinge and Sverdrup (1995) was used. Data on measured dissolved organic carbon (DOC) in the soil  
563 solution at 50 cm depth were available for plots K4 and K1 at Asa and plots 10B and 14B at Flakaliden, and  
564 these values were also applied for deeper soil horizons. Shallower horizons (0-50 cm) were characterised by  
565 higher DOC values, based on previous findings (Fröberg et al., 2006, 2013) and the DOC classification scheme  
566 in Warfvinge and Sverdrup (1995) (Table S3).

567  
568 Site-specific parameters used were evapotranspiration, temperature, atmospheric deposition, precipitation, runoff  
569 and nutrient uptake in biomass (Table 4a). Mean evapotranspiration per site was estimated from mean annual  
570 precipitation and runoff data, using a general water balance equation.

571  
572 Total deposition was calculated using deposition data from two sites of the Swedish ICP Integrated Monitoring  
573 catchments, Aneboda (for Asa) and Gammtratten (for Flakaliden) (Löfgren et al., 2011). Na was used as a tracer  
574 ion in order to distinguish canopy exchange from dry deposition for Ca, Mg and K. Dry deposition for Na and Cl  
575 was calculated as the difference between wet and throughfall deposition. As outlined in Zetterberg et al. (2016),  
576 wet deposition for all elements was calculated by correcting bulk deposition for dry deposition using wet-only to  
577 bulk deposition ratio. Wet deposition was estimated based on the contribution of dry deposition to bulk  
578 deposition, both for base cations and anions, using dry deposition factors from Karlsson et al. (2011, 2013).  
579 Finally, total deposition for all elements was calculated from the sum of dry and wet deposition.

580  
581 Net base cation and nitrogen uptake in aboveground tree biomass (i.e. bark, stemwood, living and dead branches,  
582 needles) was estimated as mean accumulation rate over a 100-year rotation period in Flakaliden and a 73-year

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589 rotation period in Asa. These calculations were based on Heureka simulations using the StandWise application  
590 (Wikström et al., 2011) for biomass estimates, in combination with measured nutrient concentrations in  
591 aboveground biomass as described in section 2.5.4 below (Linder, unpubl. data).

### 592 2.4.3 PROFILE sensitivity analysis

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

## 604 2.5 The base cation budget approach

### 605 2.5.1. General concepts of the base cation budget approach

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

$$613 W_{\text{budget}, i} = L_i + \Delta B_i + \Delta S_i - TD_i$$

Eq. 4

### 614 2.5.2 Atmospheric deposition, $TD_i$

615 The same estimates of total atmospheric deposition as used in parameter setting of the PROFILE model (section  
616 2.4.2) were used in the base cation budget, Eq. (4).

### 617 2.5.3. Changes in exchangeable soil pools, $\Delta S_i$

618 Changes in extractable base cation stocks in the soil were calculated from the difference between two soil  
619 samplings, performed in 1986 and 1998 at Flakaliden, and in 1988 and 2004 at Asa. The organic layer was  
620 sampled with a 5.6 cm diameter corer, whereas a 2.5 cm diameter corer was used to sample 10 cm sections to 40  
621 cm depth in the mineral soil. For each plot and layer, 25 cores were combined into one sample.  
622

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625 | Exchangeable base cation content in the soil (<2 mm) for all Flakaliden samples and in Asa for samples from  
626 | 1988 was determined by extraction of dry samples with 1 M NH<sub>4</sub>Cl using a percolation method, where 2.5 g of  
627 | sample was leached with 100 mL of extractant at a rate of 20 mL h<sup>-1</sup>. The base cations were analysed by atomic  
628 | absorption spectrophotometry (AAS). For the Asa samples from 2004, batch extraction was performed using the  
629 | same extractant, and the base cations were determined with ICP. A separate test was made to compare the yield  
630 | of the percolation and batch extraction methods. No consistent difference between the methods was observed.  
631 |

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

#### 638 | **2.5.4 Net uptake in biomass, $\Delta B_i$**

639 | Accumulation of base cations in tree biomass, i.e. net uptake of base cations, was calculated as a mean value of  
640 | control plots over the period 1989-2003, based on increments in aboveground biomass at Asa and Flakaliden for  
641 | this period and on the concentrations of elements in different tree parts. The increment in aboveground biomass  
642 | was based on measurements of stem diameter at breast height (DBH) of all individual trees in the plots, and  
643 | applying DBH data to allometric functions developed for Norway spruce at the sites (Albaugh et al., 2009,  
644 | 2012). The allometric functions were based on destructive samplings (1987 - 2003) of 93 and 180 trees at Asa  
645 | and Flakaliden respectively. The increment in belowground biomass was estimated from general allometric  
646 | functions for Norway spruce stumps and roots in Sweden (Marklund, 1988). Since Marklund's functions (1988)  
647 | underestimate belowground biomass by 11 %, a factor to correct for this was included (Petersson and Ståhl,  
648 | 2006). Furthermore, the finest root fraction ( $\leq 2$  mm), which is not included in the functions of Marklund (1988)  
649 | and Petersson and Ståhl (2006), was assumed to be 20% of needle biomass at Asa and 33% at Flakaliden,  
650 | respectively, based on data from Helmisaari et al. (2007).

651 |  
652 | Data on element concentrations in biomass were available from measurements on harvested trees (S. Linder,  
653 | unpublished data). At Flakaliden, total element concentrations were analysed in trees sampled for  
654 | biomassdetermination in 1992 and 1997. Analyses of needles and branches (dead and live) were conducted on  
655 | the same tree parts in the biomass sampled in 1993 and 1998. Base cation concentrations in biomass were  
656 | determined from acid wet digestion in HNO<sub>3</sub> and HClO<sub>4</sub>, followed by determination of elements by ICP-atomic  
657 | emission spectrophotometry (ICP-AES) (Jobin Yvon JY-70 Plus).

658 |  
659 | Data on element concentrations in belowground biomass fractions were taken from literature from the Nordic  
660 | countries (Hellsten et al., 2013). Specifically, data on stump and root biomass of Norway spruce were available  
661 | for Asa and data from Svartberget was used for Flakaliden (Table 7 in Hellsten et al., 2013).

#### 662 | **2.5.5. Leaching, $L_i$**

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665 Base cation leaching was quantified in six-month intervals from modelled daily runoff multiplied by average  
666 element concentrations in soil water collected with tension lysimeters at 50 cm soil depth.  
667  
668 Soil water was collected from five ceramic tension lysimeters (P80) installed at 50 cm depth in each  
669 experimental plot. Soil water was collected during frost-free seasons, applying an initial tension of 70 kPa in 250  
670 mL sampling bottles, and left overnight. These soil water samples were pooled by plot. The base cation  
671 concentration in the soil solution was determined with ICP-AES. Soil water sampling was performed twice  
672 every year, i.e. in the spring and in the autumn, which are the periods of highest water flux, so that the most  
673 important leaching events were covered. The spring samples were collected soon after the snowmelt and  
674 depending on the weather in a specific year this meant that the yearly spring sampling date varied between the  
675 last week of April and the last week of May. The autumn samples were collected when frost risk increased. That  
676 meant that the autumn sampling dates varied from year to year, i.e. from the first week in September to mid-  
677 November. The seasonal variation in soil water chemistry is shown in Fig. S2.

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678  
679 The drainage flux out of the profile was calculated by the CoupModel (Jansson, 2012). The model was  
680 parameterised based on hydraulic soil properties measured at the sites. The model was run with hourly mean  
681 values of locally measured climate variables (precipitation, global radiation, wind speed, air temperature and  
682 humidity) and model outcomes were tested against tensiometer data, i.e. bi-weekly tensiometer readings at 15,  
683 30 and 45 cm depth were used for model calibration. The parameters were then adjusted slightly to obtain good  
684 agreement between measured and calculated soil water content. Annual precipitation varied considerably during  
685 the period 1990-2002, ranging from 906 to 504 mm at Flakaliden (mean 649 mm) and from 888 to 575 mm at  
686 Asa (mean 736 mm). Annual evapotranspiration increased by about 50 mm at both sites, during the period 1987-  
687 2003 at Flakaliden and 1990-2002 at Asa, due to the increment in tree leaf area. Monthly means and standard  
688 deviation of drainage (mm) at 50 cm depth in the soil of control plots at Asa during 1990 – 2004 and at  
689 Flakaliden during 1988-2004 are shown in Fig. S3.

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#### 690 2.5.6. Assessment of data quality in base cation budget

691 The precision and accuracy of a base cation budget estimate of  $W_{\text{budget}, i}$  was determined by the quality of  
692 estimates of each individual term in Eq. (3), in proportion to the magnitude of each term (Simonsson et al.,  
693 2015). Significant uncertainty in the estimate of a quantitatively important term will therefore dominate the  
694 overall uncertainty in estimates of  $W_{\text{budget}}$ . Firstly, the quality of data for each term in Eq. (3) was assessed based  
695 on the spatial and temporal scales of measurements and the quality of measurements (Table 5). Using these  
696 criteria, we consider the estimates of deposition, leaching and accumulation in biomass to be of moderate to high  
697 quality. The measurements of changes in extractable soil pools were of lower quality because extraction methods  
698 were not identical for samples collected 1986/1988 and 1998/2004, which would cause significant uncertainty if  
699 soil changes were an important part of the element budget. To partly overcome this uncertainty, we used the  
700 estimates obtained by the PROFILE ( $W_{\text{profile}, i}$ ) and depletion method ( $W_{\text{depletion}, i}$ ) in additional base cation  
701 budget calculations where the change in soil was determined from the base cation budget. These additional base  
702 cation budget estimates, which are conceptually analogous to the regional mass balances presented by Akse

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706 et al. (2007), were also used to place the PROFILE and depletion method estimates of  $W_i$  in the context of other  
707 base cation fluxes at the ecosystem scale.

## 708 2.6 Statistical analyses

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

$$720 \quad u_c(W_{\text{budget}, i}) = \sqrt{(SE(L_i))^2 + (u(\Delta B_i))^2 + (SE(\Delta S_i))^2 + (u(TD_i))^2} \quad \text{Eq. 4}$$

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

## 723 3. Results

### 724 3.1 Depletion method estimates of historical weathering rates

725 At both Asa and Flakaliden, historical weathering rates estimated with the depletion method ( $W_{\text{depletion}}$ ) were  
726 highest in the upper soil layers and showed a gradual decrease down to the reference depth, which was defined at  
727 60-70 cm at Flakaliden and for most plots at 80-90 cm at Asa (Fig. 3). Flakaliden had a higher historical annual  
728 weathering rate to 90 cm soil depth,  $37.8 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$ , than Asa,  $12.8 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$ ; the corresponding value  
729 for 0-50 cm depth was  $34.1 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$  at Flakaliden and  $10.5 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$  at Asa. The gradients with depth  
730 showed that  $W_{\text{depletion}}$  increased towards the surface, although this trend was more pronounced at Flakaliden than  
731 at Asa. At Flakaliden,  $W_{\text{depletion}}$  was highest for Mg, followed by Ca, Na and K (Figs. 3 and 4); at Asa, it was  
732 highest for Ca, closely followed by Mg, Na and K (Figs. 3 and 4).

### 733 3.2 PROFILE model estimates of steady state weathering rates

734 The steady state weathering rate estimated by the PROFILE model ( $W_{\text{profile}}$ ) differed from the historical rate with  
735 respect to all three test criteria, i.e. (1) total weathering rate in the 0-50 cm soil layer, (2) variation in weathering  
736 with depth and (3) ranking order of base cations (Figs. 3 and 4). Firstly, regarding base cation weathering rate in  
737 the upper 50 cm of the mineral soil,  $W_{\text{profile}}$  estimates for Asa and Flakaliden (Asa:  $37.1 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$ ,  
738 Flakaliden:  $42.7 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$ ) were around 3.5 and 1.3-fold higher than  $W_{\text{depletion}}$  estimates, respectively.  
739 Secondly, the total modelled base cation weathering rate for the soil profile down to 90 cm was around 7-fold  
740 higher than the rate estimated using the depletion method at Asa ( $89.4 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$ ), and 3.4-fold higher at

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744 Flakaliden ( $127.6 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$ ). Unlike the historical weathering based on the depletion method, PROFILE  
745 predicted that weathering rates increased with soil depth at both sites. At Flakaliden, high contents of K- and  
746 Mg-bearing tri-octahedral mica (Casetou-Gustafson et al., 2018) gave rise to particularly high weathering rates  
747 at 70-80 cm. Thirdly, as opposed to  $W_{\text{depletion}}$ ,  $W_{\text{profile}}$  was largest for Na at both sites, followed by Ca. However,  
748  $W_{\text{profile}}$  was larger for K than for Mg at Asa, while the reverse was true at Flakaliden.

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

### 760 3.3 Base cation budget estimates of current weathering rates

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

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

780 By using the weathering estimates obtained with PROFILE and the depletion method in the base cation budget  
781 equation, Eq. (4), in combination with measured estimates of deposition, leaching and uptake in biomass,  
782 alternative soil balances were estimated (Fig. 6). Since the base cation budget method predicted much higher

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803 weathering rates than the other methods, a balance of sources and sinks consequently required more marked  
804 decreases in exchangeable soil stocks for K, Ca and Mg when weathering rates were based on PROFILE or the  
805 depletion method. Furthermore, as a consequence of the substantially higher  $W_{\text{profile}}$  for Na, the PROFILE based  
806 base cation budget suggested substantial increases in exchangeable Na stocks.

#### 807 4. Discussion

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

#### 814 4.1 First test: Lower weathering rates by the depletion method compared to PROFILE

815 Modelled ( $W_{\text{profile}}$ ) and historical ( $W_{\text{depletion}}$ ) base cation weathering rates were within the range of recently  
816 published data for similar forest sites on podzolised glacial till (Stendahl et al., 2013). However, the historical  
817 weathering rates at Asa were similar to the lowest historical weathering rate observed by Stendahl et al. (2013)  
818 and the historical weathering rates for Flakaliden were similar to their highest rates, at least with regard to Ca  
819 and Mg. The overall  $W_{\text{profile}}$  in the 0–50 cm depth was higher than  $W_{\text{depletion}}$  for Na and K. Similarly, high ratios of  
820  $W_{\text{profile}}/W_{\text{depletion}}$  were found at catchment scale by Augustin et al. (2016). At the pedon scale, Stendahl et al.  
821 (2013) found  $W_{\text{profile}}/W_{\text{depletion}}$  ratios of on average 2.7 for 16 Swedish study sites (with average max. and min.  
822 ratios of 7.9 and 0.4, respectively); this ratio was larger than the one found for Flakaliden in our study (1.5) and  
823 lower than the one found for Asa (5.1). Similar to Flakaliden, low ratios have been reported for the Lake  
824 Gårdsjön site situated in south-western Sweden (Sverdrup et al., 1998; Stendahl et al., 2013). An exception to  
825 the general trend of higher steady-state PROFILE weathering rates compared to historical rates calculated by the  
826 depletion method, was found for Mg at the Flakaliden site, where  $W_{\text{depletion}}$  was 1.9-fold greater than  $W_{\text{profile}}$  in the  
827 upper mineral soil, but only at Flakaliden. This exception with regard to Mg was also found by Stendahl et al.  
828 (2013) for all of their 16 study sites.

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

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**Kommentar [2]:** Perhaps this makes it more clear

Magnus Simonsson 2019-10-19 16:46

**Kommentar [3]:** I'm not sure what this means.

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**Borttagen:** Our comparison of three approaches to estimate weathering rates showed significant discrepancies in spite of the fact that the study was well harmonised at the spatial scale and originated from analyses of the same soil material.

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**Borttagen:** 4.1 Comparison of conceptually different methods . . . [6]

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**Borttagen:** However, the estimated weathering rates are relevant for different temporal scales. S

864 The particularly low  $W_{\text{depletion}}$  at Asa was largely attributed to a weakly developed depth gradient of Zr in the soil  
865 (Fig. 3). This observation has probably a random rather than a conceptual origin, because it might have been the  
866 result of soil mixing by different means. Mechanical soil scarification was carried out at both Asa and Flakaliden  
867 prior to planting of the present stand, which would at least have caused partial mixing or inversion of surficial  
868 soil layers. In addition, clearance cairns of unknown age were found in the experimental area at Asa, indicating  
869 small-scale agriculture in the past. Moreover, if burrowing earthworms have been abundant in the past, they  
870 might have produced soil mixing in the upper soil horizons (Taylor et al., 2019), resulting in a disturbed Zr  
871 gradient and in low estimates of historical weathering in the rooting zone (Whitfield et al. 2011). High or near-  
872 neutral soil pH and deciduous litter can promote high population densities of burrowing earthworms following  
873 forest clearing and agriculture; and we note that partly deciduous vegetation dominated at Asa until only 1000-  
874 2000 years BP, with species such as *Corvus avellana* (L.), *Betula* spp., *Quercus* spp. and *Tilia* spp. (Greisman et  
875 al., 2009).

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

893 Regardless of errors in the Zr gradients, both  $W_{\text{depletion}}$  and  $W_{\text{profile}}$  showed more marked gradients with soil depth  
894 at Flakaliden compared to Asa. This could be expected based on the more well-developed podzol profile at  
895 Flakaliden. It has been postulated that the formation of podzols is enhanced by long duration and great depth of  
896 snow cover (Jauhiainen, 1973; Schaetzl and Isard, 1996), which would imply that soil formation had progressed  
897 further at Flakaliden than at Asa (Lundström et al., 2000). At Flakaliden, the average mass loss of Ca and Mg  
898 was 4.0-fold larger in the E-horizon than in the B-horizon, which is similar to findings by Olsson and Melkerud  
899 (2000) of a 5-fold higher ratio between losses of base cations in the E- compared with the B-horizon.

#### 900 4.2 Second test: PROFILE and depletion method produce different weathering gradients in the soil

901 Our second test, postulating similarity between  $W_{\text{depletion}}$  and  $W_{\text{profile}}$ , concerning the weathering rate gradient with  
902 soil depth, was not fulfilled. This discrepancy was basically of conceptual nature. We may imagine a front of

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Borttagen: As to possible bias in the historical weathering rates, underestimates are possible at Asa, where the low values of  $W_{\text{depletion}}$  can be attributed to the low gradient of Zr in the soil (Fig. 5). This might, in turn, be the result of soil mixing by different means.

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Borttagen: Apart from disturbances, natural variability in weathering rates can likely be attributed to differences in soil texture (i.e. exposed mineral surface area), climate (i.e. temperature and water percolation rate) and mineralogy.

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922 intense weathering moving downward through the soil profile over the millennia. Each horizon would undergo  
923 an episode, limited in time, of intense weathering followed by slower weathering in the ageing material. The  
924 sensitivity test performed with PROFILE revealed that the model output was only little affected by the  
925 differences in mineralogy between horizons. Therefore, if processes are correctly modelled with PROFILE, the  
926 notion of a weathering front should primarily be associated with changes in bulk density and exposed mineral  
927 surface area, as also suggested by the positive correlation between  $W_{profile}$  and exposed mineral surface area and  
928 bulk density (Figs. S6-S7) and by the findings of Jönsson et al. (1995).

930 The increase in weathering rate with soil depth simulated by PROFILE is obviously in contrast with the classic  
931 notion of weathering rates being highest in the A- or E-horizon of podzolised soils (Tamm, 1931). To test  
932 whether the high  $W_{profile}$  values could be reconciled with the observed historical weathering, the hypothetical  
933 time needed for the PROFILE weathering rates to accomplish the element losses determined with the depletion  
934 method was calculated. This showed that the highest weathering rate, presently prevailing at approximately  
935 80 cm (Asa) or 60 cm (Flakaliden) depth according to PROFILE (Fig. 4), would cause the observed depletion  
936 losses within less than half of the soil age ('max rates' in Fig. 7), potentially in concert with the concept of a  
937 weathering front. However, the calculation also showed that the present minimum weathering rate, presently  
938 simulated for the topmost 1-3 horizons (Fig. 4), would often result in a more severe base cation depletion within  
939 less than the postglacial period than observed by the depletion method ('min rates' in Fig. 7), particularly at  
940 Flakaliden, and for K and Na also at Asa. Hence, even considering the concept of a possible weathering front,  
941 there appears to be a positive bias in  $W_{profile}$  at the investigated sites.

#### 942 4.3 Third test: Depletion method and PROFILE resulted in different element rank-order

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

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- Bengt Olsson 2019-10-3 10:30  
**Borttagen:** If this is not accounted for,
- Magnus Simonsson 2019-10-15 18:00  
**Borttagen:** d it would originate from
- Magnus Simonsson 2019-10-15 18:00  
**Borttagen:** both
- Bengt Olsson 2019-10-17 13:33  
**Borttagen:** at
- Bengt Olsson 2019-10-3 14:00  
**Borttagen:** .

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988  
989

990 **4.4 Weathering in a base cation budget perspective**

991 The base cation budget approach consistently resulted in much higher weathering rates than PROFILE and the  
992 depletion method for all base cations except Na. However, as was shown by the large combined uncertainties  
993 given in Table 6, base cation budget estimates of weathering are associated with substantial uncertainties from  
994 different sources. **In general, significant uncertainties in the element budget of ecosystems are common (Yanai et**  
995 **al., 2010), and similarly** large uncertainties associated with estimates of  $W_{\text{budget}}$  were observed by Simonsson et  
996 al. (2015) for the Skogaby site in south-western Sweden, a Norway spruce site of similar stand age and soil  
997 condition as Asa. Accounting for all sources of uncertainty, they found that the 95% confidence interval in  
998 estimates of base cation weathering was 2.6 times the mean ( $33 \text{ mmol}_c \text{ m}^{-2} \text{ yr}^{-1}$ ).  
999

1000 Despite the considerable uncertainties in  $W_{\text{budget}}$  estimates, the base cation budget approach **showed that**  
1001 accumulation in biomass was a dominant sink for all base cation elements except Na, **in line with findings of**  
1002 Nykvist (2000) for two Norway spruce sites in Sweden and **the findings of** Simonsson et al. (2015). However,  
1003 **this contrasts to other studies, which assumed** no change in soil and tree biomass stocks of base cations **over time**  
1004 (e.g. Sverdrup et al., 1998). The higher estimated weathering rate at Asa reflected the higher productivity and  
1005 nutrient demand of the stand at this site (Bergh et al., 1999), which has resulted in 1.4-fold greater accumulation  
1006 of base cations in biomass than at Flakaliden.  
1007

1008 Calcium and Mg uptake in forest trees is considered to be more or less passive flow driven by transpiration  
1009 fluxes, whereas K uptake is an energy-demanding active process (Nieves-Cordones et al., 2014). Considering  
1010 that Na was the dominant base cation in the soil solution at 50 cm soil depth (Fig. 4), the negligible  
1011 accumulation of Na in tree biomass suggests that Na uptake in trees is physiologically blocked. Low  
1012 concentrations of Na seem to be a general feature of terrestrial plants in boreal forests, in contrast to aquatic  
1013 plants, which explains why the latter are considered important Na sources for large herbivores like moose  
1014 (Ohlson and Staaland, 2001). Thus, **as in agreement with findings by e.g. Taylor and Velbel (1991) and Velbel**  
1015 **(1995) the negligible Na accumulation in tree biomass and the particularly low deposition at Flakaliden simplify**  
1016 **the Na budget to include** only three major counterbalancing fluxes: weathering, deposition and leaching. **Because**  
1017  $W_{\text{depletion}}$  and  $W_{\text{budget}}$  of Na were fairly similar, and were much lower than  $W_{\text{profile}}$ , our results provide additional  
1018 support for the claim that the PROFILE model produced consistently too high Na weathering.  
1019

1020 **Accumulation in biomass was the dominant sink for Ca, Mg and K, and this term in the BC budget was**  
1021 **considered to be of moderate to high quality (Table 5). The changes observed in extractable Ca stocks in the soil**  
1022 **was considered more uncertain (Table 5), but they are consistent with observations over 22 years of aggrading**  
1023 **Norway spruce forests by Zetterberg et al. (2016), who reported exchangeable Ca depletion rates of 5-11 and 23-**

Bengt Olsson 2019-10-3 10:28

**Flyttad uppåt [1]:** As to possible bias in the historical weathering rates, underestimates are possible at Asa, where the low values of  $W_{\text{depletion}}$  can be attributed to the low gradient of Zr in the soil (Fig. 5). This might, in turn, be the result of soil mixing by different means. Mechanical soil scarification was carried out at both Asa and Flakaliden prior to planting of the present stand, which would at least have caused partial mixing or inversion of surficial soil layers. In addition, clearance cairns of unknown age were found in the experimental area at Asa, indicating small-scale agriculture in the past. Moreover, if burrowing earthworms have been abundant in the past, they might have produced soil mixing in the upper soil horizons (Taylor et al., 2019, ... [9])

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**Borttagen: 3**

Bengt Olsson 2019-10-11 10:29

**Borttagen: S**

Bengt Olsson 2019-10-16 14:04

**Borttagen:**

Bengt Olsson 2019-10-16 14:04

**Borttagen:**

Magnus Simonsson 2019-10-15 18:03

**Borttagen:** illustrated

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Bengt Olsson 2019-10-17 13:35

**Borttagen:** The Na fluxes differed f (... [10])

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**Formaterat:** Inte Färgöverstrykning

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**Borttagen:** 5

Magnus Simonsson 2019-10-15 18:25

**Kommentar [4]:**

Bengt Olsson 2019-10-17 13:35

**Borttagen:** Since



1141 39 mmol<sub>c</sub> m<sup>-2</sup> yr<sup>-1</sup> for sites in south-western and northern Sweden, respectively. The higher value for the northern  
1142 site reflected higher Ca saturation in the soil. The corresponding values for Asa and Flakaliden were larger, but  
1143 of similar magnitude (34.5 and 40.5 mmol<sub>c</sub> m<sup>-2</sup> yr<sup>-1</sup>, respectively). Brandtberg and Olsson (2012) studied the  
1144 same sites as Zetterberg et al. (2016) over a 10-year period and found a general minor increase in exchangeable  
1145 K soil stocks and a substantial decrease in the Ca stocks, a result much similar to the findings of the present  
1146 study.

1147  
1148 When an independent estimate of current weathering rate ( $W_{\text{profile}}$ ) is introduced in the budget (Fig. 6) the high  
1149 rate of accumulation in biomass is not explained by the combination of measured ( $TD$ ,  $\Delta S$ ) or modelled ( $W_{\text{profile}}$ )  
1150 sources or sinks ( $L$ ). This result suggests that forest trees have access to additional sources of Ca, Mg and K, not  
1151 measured or captured by our study. We can only speculate about the nature of such sources: It is possible that  
1152 depletion of ammonium-chloride-exchangeable base cations underestimates the plant-available phases of BC in  
1153 the soil. Using other extract media than  $\text{NH}_4\text{Cl}$  may have revealed additional sources from e.g. oxalates  
1154 (Rosenstock et al., 2019b). Additional BC release from decomposing roots, stumps and residues from the felling  
1155 of the former stand was probably neglected because of difficulties to include coarse wood in soil sampling. It is  
1156 also possible that the assumption made that no base cation uptake takes place below 50 cm in the soil was  
1157 wrong. If trees can take up base cations from deeper soil horizons (e.g. Callesen et al., 2016; Brantley et al.,  
1158 2017), the discrepancy in weathering rates between the two methods would be reduced since PROFILE predicted  
1159 higher weathering rates with increasing depth. Furthermore, although biological processes are represented in  
1160 PROFILE, the model fail to capture biological feedback mechanisms in their entirety, in particular feedbacks  
1161 generated by plant uptake and mycorrhiza (Finlay et al., 2009; Sverdrup, 2009; Smits and Wallander, 2017;  
1162 Akselsson et al., 2019; Finlay et al., this issue; Rosenstock et al. 2019a).

## 1163 **5. Conclusions**

1164 A general observation from our comparison of three conceptually different methods was that weathering rate  
1165 estimates were lower by the depletion method than the PROFILE model for the 0–50 cm soil horizon, and that  
1166 the highest weathering rates were estimated by the BC budget approach. In sharp contrast to the historic  
1167 weathering estimated by the depletion method, the current steady-state weathering by PROFILE increased with  
1168 increasing soil depth.

1169  
1170 The Na weathering rate was an important exception from the general finding as PROFILE estimated much  
1171 higher weathering rate for Na than the other methods, which produced similar weathering rates for Na. This  
1172 indicated that the high weathering rate of Ca, Mg and K by the budget method was at large an effect of high  
1173 nutrient demand and uptake rate of these elements in the aggrading forest stands. Hence, weathering rates of Ca,  
1174 Mg and K by the budget method were in our case most likely overestimated. An implication of this conclusion is  
1175 that forest trees probably have access to additional sources of nutrients base cation, not measured or captured by  
1176 our study.

1177  
1178 Another implication of the higher weathering rate for Na by PROFILE compared to the other methods is that the  
1179 model may have overestimated release rates of Na, and probably also of K. This conclusion was based on

1180 [differences between historical and steady-state estimates regarding the rank-order of elements, and the fact that](#)  
1181 [even the lowest PROFILE weathering rates were too high compared with observed depletions of Na and K. A](#)  
1182 [possible cause to the fact that K weathering rates were overestimated by the PROFILE method was incorrect](#)  
1183 [parameters for the weathering of K-bearing minerals in the model, which should be accounted for in future](#)  
1184 [PROFILE based weathering estimate.](#)

1185  
1186 [The depletion method resulted in generally lower weathering rates at Asa than at Flakaliden, whereas the](#)  
1187 [PROFILE estimates for the sites were more similar, indicating that historical weathering estimated by the](#)  
1188 [depletion method was probably underestimated at Asa. This was an effect of the weakly developed and possibly](#)  
1189 [erratic Zr gradients in the soil at Asa could have been caused by natural and anthropogenic disturbances. Future](#)  
1190 [studies based on the depletion method should ensure that the Zr gradient with depth show a net enrichment of Zr](#)  
1191 [towards the soil surface. This condition was not fulfilled for soil profiles at the Asa site. Another important](#)  
1192 [outcome of the study was to show that within-site variations in Zr gradients can be large, as was the case at](#)  
1193 [Flakaliden for two soil profiles.](#)

#### 1194 **6. Authors contribution**

1195 Authors contributed to the study as in the following: S. Casetou-Gustafson: study design, data treatment,  
1196 analyses, interpretation and writing. Magnus Simonsson: study design, analysis, interpretation and writing. Johan  
1197 Stendahl: study design, analysis, interpretation and writing B.A. Olsson: study design, data treatment, analysis,  
1198 interpretation and writing. S. Hillier: interpretation and writing. Sune Linder: Provided long-term experimental  
1199 data, interpretation and writing. Harald Grip: Provided long-term experimental data, interpretation, and writing.

#### 1200 **7. Acknowledgements**

1201 Financial support from The Swedish research Council for Environment, Agricultural Sciences and Spatial  
1202 Planning (212-2011-1691) (FORMAS) (Strong Research Environment, QWARTS) and the Swedish Energy  
1203 Agency (p36151-1). Stephen Hillier acknowledges support of the Scottish Government's Rural and Environment  
1204 Science and Analytical Services Division (RESAS). We thank Cecilia Akselsson for her contribution to study  
1205 design, PROFILE model development and valuable comments on earlier versions of the manuscript.

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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 <sup>3</sup> )	Soil age (calender years )
Asa	K1	9.49	25.04	45.30	20.18	1.10	14300
	K4	7.65	22.59	39.21	30.48	1.09	14300
	F3	4.95	25.26	40.54	29.25	0.99	14300
	F4	8.64	25.69	40.13	25.54	0.94	14300
Flakaliden	15A	1.92	9.21	68.98	19.68	1.89	10150
	14B	7.71	34.09	33.71	24.17	1.35	10150
	10B	7.75	45.17	37.23	8.90	1.36	10150
	11B	9.56	45.07	33.91	10.72	1.47	10150

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

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

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**Table 3.** Extractable concentrations of different elements at the reference depths used for calculating historical weathering rate at the Asa and Flakaliden sites.

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

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

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

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

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

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

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

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1511 **Table 6:** Standard errors and standard uncertainties ( $\text{mmol}_e \text{m}^{-2} \text{yr}^{-1}$ ) for the terms in the base cation budget,  
 1512 Eq. (4). Combined standard uncertainty, plot average value and confidence interval for the weathering rate of  
 1513 base cation  $i$  derived from base cation budgets  $W_{\text{budget}, i}$  ( $\text{mmol}_e \text{m}^{-2} \text{yr}^{-1}$ ).  
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Site	Element	Deposition	Soil change	Biomass accum.	Leaching	Combined standard uncertainty	$W_{\text{budget}}$	Confidence interval (combined standard uncertainty $\times 3$ )
Asa	Ca	1.1	12.9	19.5	3.2	24	58	$\pm 71$
	Mg	1.1	0.6	2.5	1.6	3	29	$\pm 10$
	K	0.3	1.0	9.7	0.1	10	37	$\pm 29$
	Na	4.0	0.9	0.0	5.1	7	7	$\pm 20$
Flakaliden	Ca	0.8	10.5	13.3	0.7	17	28	$\pm 51$
	Mg	0.3	1.1	1.5	0.3	2	12	$\pm 6$
	K	0.2	0.6	6.7	0.2	7	19	$\pm 20$
	Na	0.7	1.2	0.0	0.8	2	2	$\pm 5$

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**Figure captions**

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

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

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

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

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

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

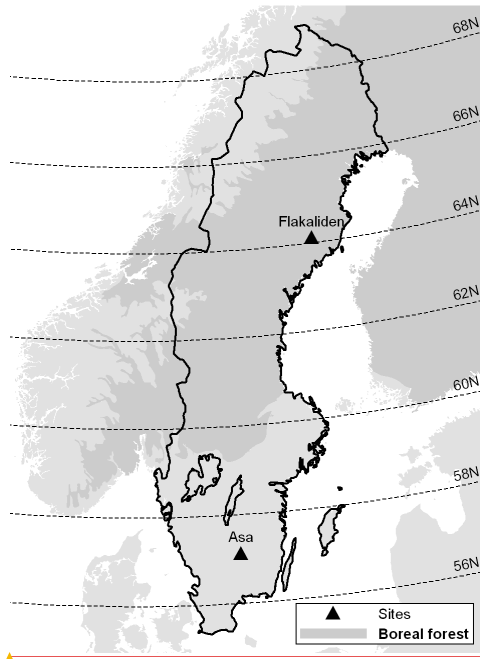
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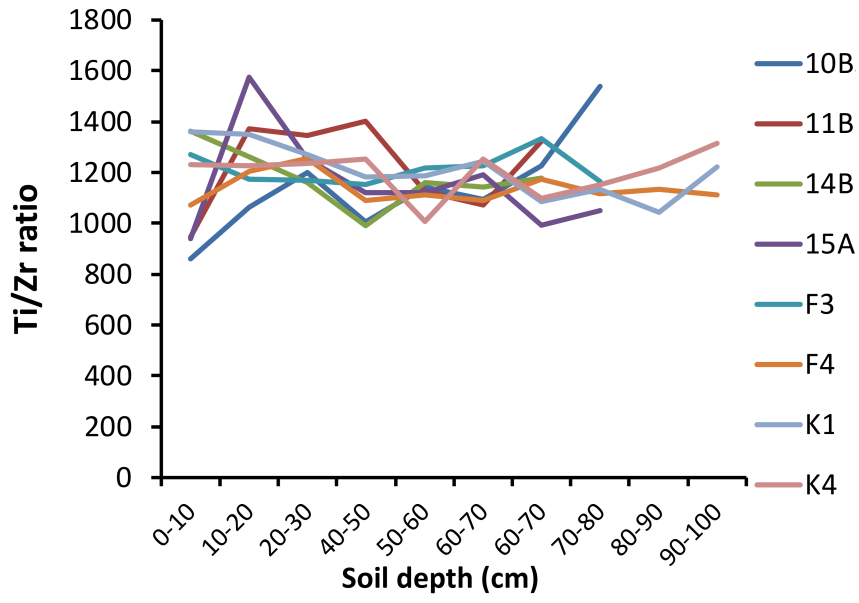


**Figure 1.**

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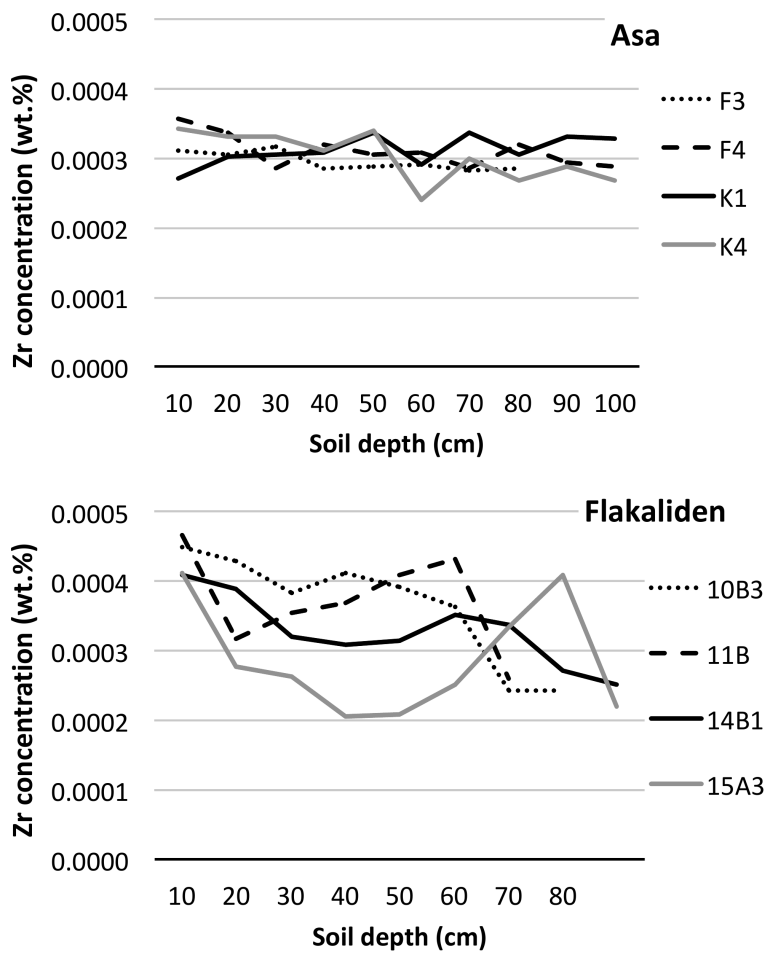
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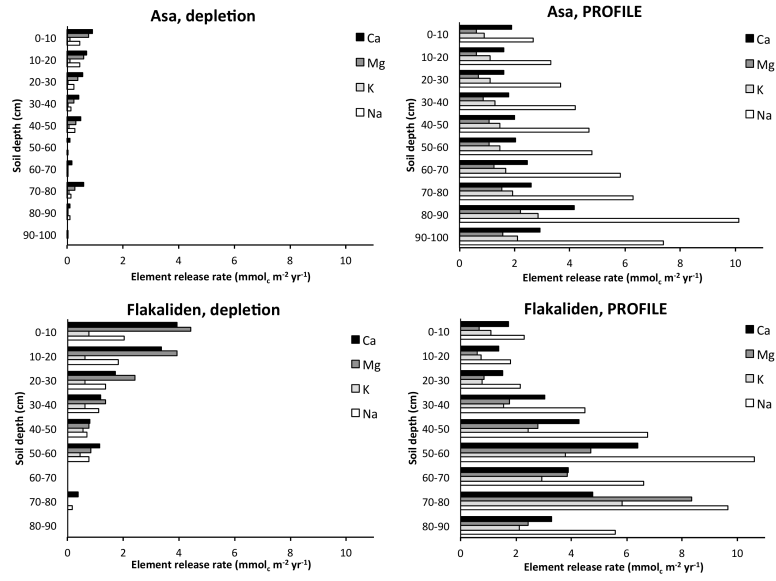
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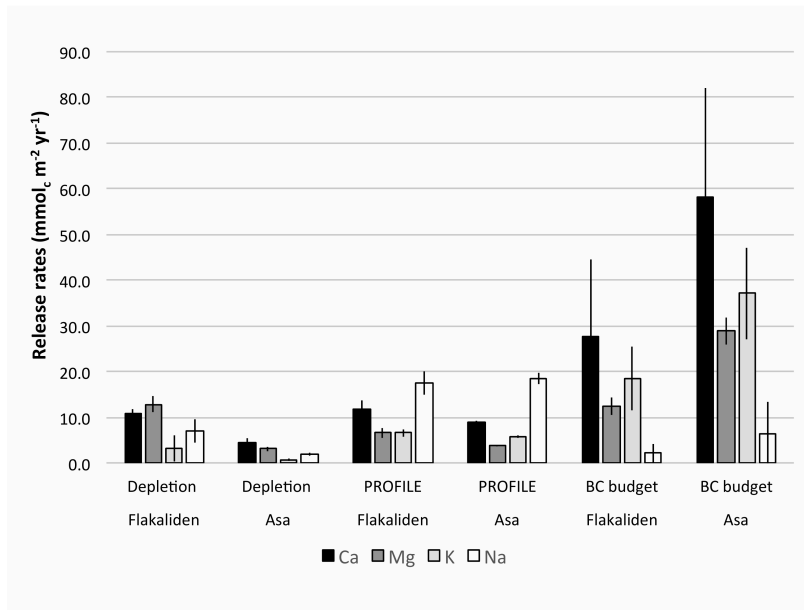
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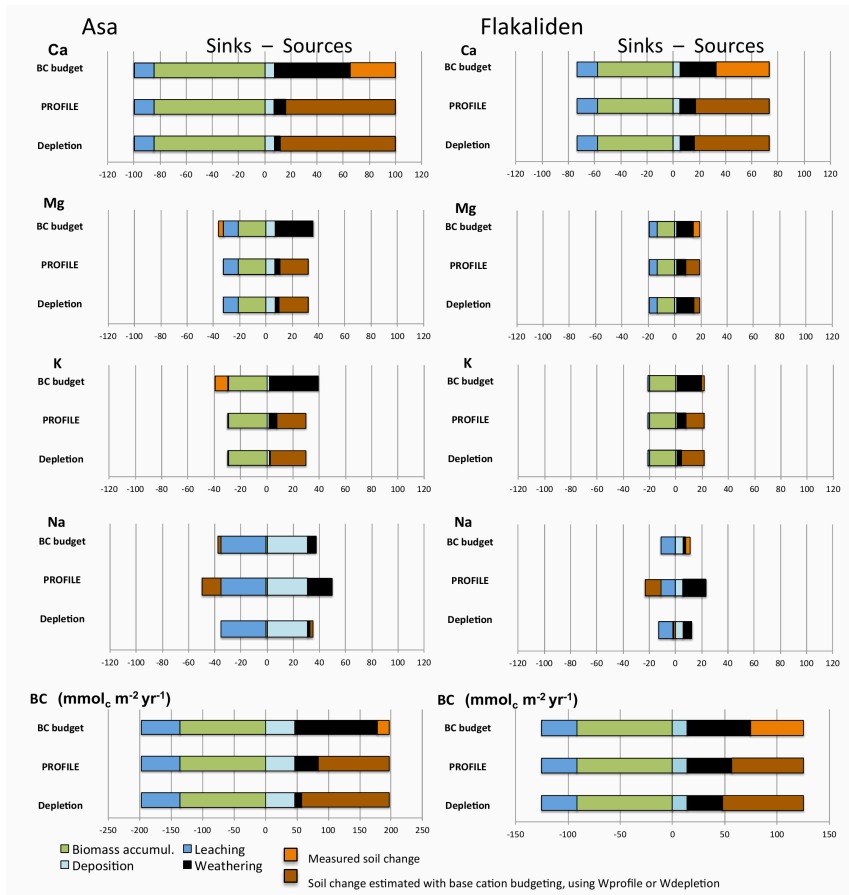
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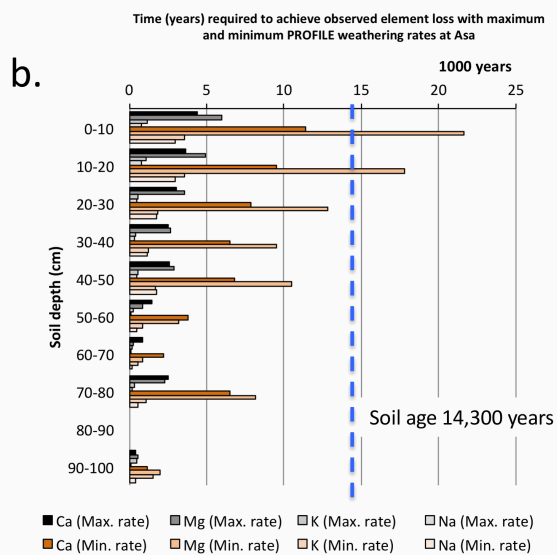
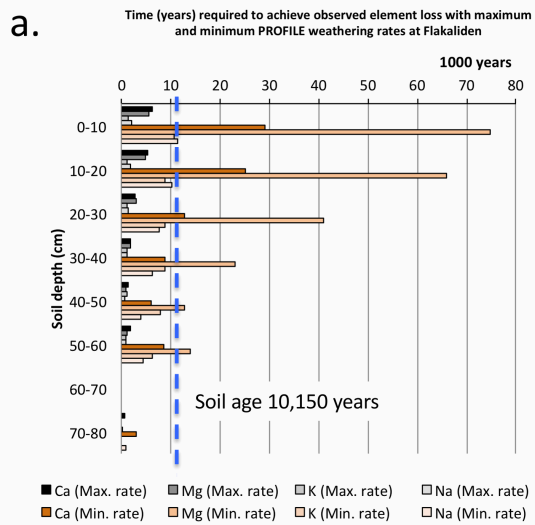
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