

## Review

# Silicate mineral weathering rate estimates: Are they precise enough to be useful when predicting the recovery of nutrient pools after harvesting?

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## ABSTRACT

Are current estimates of silicate minerals weathering rates precise enough to predict whether nutrient pools will recover after forest harvesting? Answering this question seems crucial for sustainable forestry practices on silicate dominated soils. In this paper, we synthesize estimated Ca and K weathering rates (derived using seven different approaches) from a forested area in northern Sweden (the Svartberget–Krycklan catchment) to evaluate the precision of weathering rate estimates. The methods were: mass-balance budgets (catchment and pedon-scale); long-term weathering losses inferred from weathered soil profiles (using zirconium as a conservative tracer); strontium isotopes ( $^{86}\text{Sr}/^{87}\text{Sr}$ ) as proxy for catchment export of geogenic Ca; climate based regressions; a steady-state, process-based weathering model (PROFILE) and a dynamic, conceptual catchment geochemistry model (MAGIC). The different methods predict average weathering rates of  $0.67 \pm 0.71 \text{ g Ca m}^{-2} \text{ year}^{-1}$  (mean  $\pm$  stdev) and  $0.39 \pm 0.38 \text{ g K m}^{-2} \text{ year}^{-1}$ , suggesting a cumulative weathering release during a forest rotation period of 100 years that is the same magnitude as losses induced by forest harvesting at the end of the period. Clearly, forestry practices have the capacity to significantly alter the long-term nutrient status of the soil and cation concentrations in soil–water runoff. However, the precision in weathering estimates are lower than that needed to distinguish between effects on nutrient pools by different forest practices (complete-tree harvesting versus conventional stem only harvest). Therefore, we argue that nutrient budgets, where weathering rates play a crucial role, cannot be used as basis for resolving whether different harvesting techniques will allow nutrient pools to recover within one rotation period. Clearly, this hampers the prerequisite for sound decision making regarding forestry practices on silicate mineral dominated soils.

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## 1. Introduction

On slowly weathering soils dominated by silicate minerals, forest harvesting may reduce nutrient pools and lower the soil buffer capacity which controls the acidity and nutrient balance of surface waters. Complete-tree harvest (stem, branches, needles and stumps)—a method that removes more nutrients and hence is likely to put soil fertility and surface water chemistry under increased stress in comparison with conventional stem-only harvest—has been suggested and to some extent practiced since the 1970s. During recent years, demand for forest biomass has increased dramatically as a result of new energy policies driven by security of energy supply and the conversion of the Swedish energy system towards more renewable energy sources. Techniques for complete-tree harvest have evolved since the 1970s and the use of solid wood fuel in district heating in Sweden has increased dramatically from 1 PJ (~0.15 million m<sup>3</sup> wood) in 1980 to 92 PJ (~13.8 million m<sup>3</sup> wood) in 2008 (Anon, 2009). However, several studies have suggested that more intensive forestry will lower the long-term fertility of forest soils (Boyle et al., 1973; Sverdrup and Rosen, 1998; Kreutzweiser et al., 2008) and may chronically acidify surface waters (Watmough et al., 2003). Yet the increasing demand for forest fuels means decision makers must set policies for complete-tree harvest operations to retain ecosystem processes and structure.

Nutrient budgets are important indicators of forest sustainability. These budgets are based on inputs from soil mineral weathering, atmospheric deposition, and estimates of losses through soil–water leaching and biomass removal. As such, sites may be identified that are suitable for complete-tree harvesting. In nutrient budgets, the dissolution rate of nutrients from soil minerals (driven by biological, chemical and physical processes; hence referred to as “weathering” for simplicity) is of central importance. Despite their potential usefulness, considerable variation exists in weathering estimates. This may limit their application in quantitative determinations of the effects of different harvesting techniques on the recovery of nutrient pools in the soil.

Studies in Canada (Ouimet and Duchesne, 2005; Whitfield et al., 2006), Finland (Starr et al., 1998) and the UK (Hodson and Langan, 1999) have shown that different methods of estimating biogeochemical weathering can give widely differing results and the implications of this has been discussed from a soil acidification perspective. This uncertainty, caused by a lack of precision in estimated weathering rates, has potentially serious implications for calculated nutrient budgets that should provide the basis for decision making regarding forest harvesting techniques. If, for example, the credible range of soil weathering is greater than the difference in the amount of nutrients removed in complete-tree versus conventional harvesting, it will be difficult to predict how these management options will affect the recovery process.

Estimates of weathering rates are particularly important in Fennoscandia, where many forest soils are recovering from the effects of anthropogenic acidification and/or growing on nutrient-poor soils. Both Sweden and Finland have ambitious plans for forest biomass utilization to partly meet climate change goals (Ericsson, 2004). Meeting these goals may include the use of faster growing species, forest fertilization, shorter rotation periods and complete-tree harvesting. In Sweden, Akselsson et al. (2007) suggest that whole-tree harvesting (branches, needles and stem) of spruce forests could lead to rates of Ca and K removal much greater

than can be replenished through mineral weathering. In Finland, whole-tree harvesting on acid-sensitive soils may slow the recovery from acidification, and in some cases, cause lakes to re-acidify (Aherne et al., 2008). In north-eastern North America, greater tree growth, either through the use of faster growing species (Belanger et al., 2004) or as a result of climate change (Huntington, 2005), may cause declines in soil Ca pools which in turn may negatively affect plant growth (Zaccherio and Finzi, 2007). While acidification effects on trees are still debated, it is clear that base cation depletion in soils has chronically acidified surface water runoff in southern Scandinavia (Kirchner and Lydersen, 1995). Reductions in acid deposition have initiated recovery in surface waters but this recovery is far from complete (Skjelkvale et al., 2003).

In this paper we compile Ca and K weathering rates—estimated for a boreal forest catchment in northern Sweden using seven different approaches—and discuss the difficulties in determining weathering rates relevant for plant cycling with sufficient precision so as to predict the long-term base cation status of forest soils under different forestry practices.

## 2. Methods

### 2.1. Study area

The 50 ha Svartberget catchment (64° 14' N, 10° 46' E) is situated within the Vindeln Experimental Forest and the Krycklan catchment study area (Fig. 1). Long before the official establishment of these experimental forests in 1923, this area has been a focal point of forest research on soil and water chemistry in Sweden. Intensive monitoring of atmospheric deposition and stream water since 1980 when the climate reference program was initiated by the Faculty of Forestry at their field stations makes the area highly suitable for mass-balance assessment of element cycles. Weathering rates have been quantified by researchers studying soil formation (Lundstrom et al., 2000; Olsson and Melkerud, 2000), acidification (Köhler, in press), forest nutrient balances (Akselsson et al., 2004) and the Ca biogeochemical cycle (Jacks et al., 1989).

Forest stands in the study area consist of 50–100 year old mixed coniferous forest with Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies* L. (Karst.)), and some Birch (*Betula* spp.). The average annual stem wood production rate is 3.6 m<sup>3</sup> ha<sup>-1</sup> year<sup>-1</sup>. Average annual air temperature in the area is around 2 °C and corrected precipitation about 600 mm year<sup>-1</sup>, of which about half fall as snow. Podzolic soils have developed in glacial till, about 5–10 m thick where granitic and gneissic rocks are the predominant mineral source. Peaty riparian soils are found typically within a distance of 10 m from the stream, where the organic horizon may reach a thickness of up to 50 cm in contrast to a thickness of typically <10 cm in the uphill soils. Dominant minerals, assessed using X-ray diffraction analysis of the material found at depth between 80 and 100 cm, are quartz (45–47%), plagioclase (24–29%), K-feldspar (19–23%), hornblende (7–12%) with low concentration of phyllosilicate minerals such as muscovite (1–4%), biotite (<2%) chlorite (0–3%) and traces of apatite (<0.5%).

Lakes and streams in the study area reveal no signs of being affected by acid deposition (Korsman, 1999; Bishop et al., 2000). Mineral soil pH values also appear to have remained relatively constant in the area between 1920s and 1980s (Tamm and Hallbäck, 1988), further suggesting limited anthropogenic acidification.

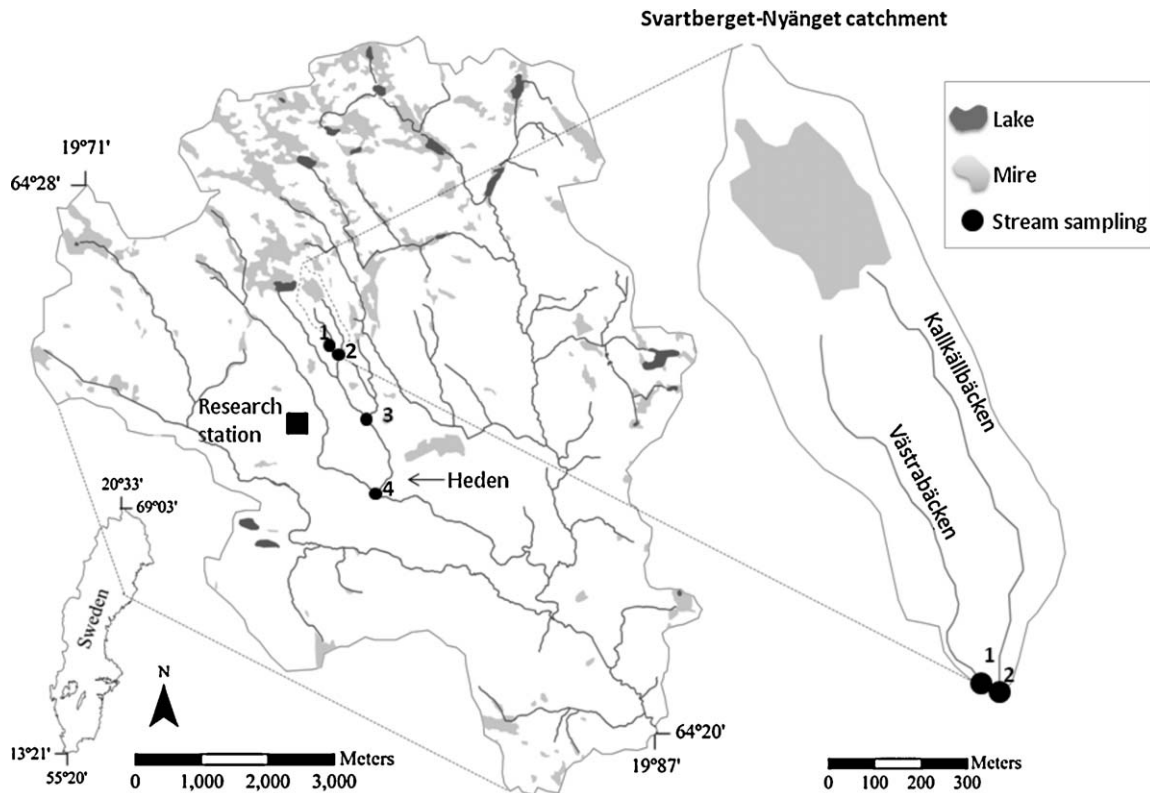


Fig. 1. Map over study area showing both its location in Sweden (left), at local-regional scale (centre) and with the most intensively studied Svartberget catchment in high resolution (right).

## 2.2. Model descriptions

Methods used for estimating weathering rates in the study area and their results are briefly described in the sections below.

### 2.2.1. The soil pedon mass-budget method

Lundström (1990) estimated base cation fluxes *in situ* by sampling soil–solute fluxes of Ca and K using zero-tension lysimeters. Their conceptual model defined the build-up of Ca and K in the soil as the net balance between inputs from weathering and atmospheric fallout, and losses induced by plant accumulation and soil–water leaching. From a mass-balance perspective this is expressed as:

$$\frac{\partial Q_j}{\partial t} = A_j + W_j - U_j - L_j \quad (1)$$

where  $Q$  is the mobile pool of the element  $j$  (i.e. either Ca or K) in the soil ( $\text{g m}^{-2}$ ),  $A$  is the atmospheric input,  $W$  is the weathering rate,  $U$  is the accumulation rate in plant compartments that are not returned to the soil as litter-fall (observe that the accumulation rate is less than the actual plant uptake) and  $L$  is the loss of element with infiltrating soil water. All rates are expressed as in  $\text{g m}^{-2} \text{year}^{-1}$ .

By assuming that the system is near steady-state ( $\partial Q/\partial t \approx 0$ ), Lundström (1990) calculated the chemical weathering rate as

$$W_j = L_j + U_j - A_j \quad (2)$$

Element loss with infiltrating soil water was measured using zero-tension lysimeters in three sets of 10 placed at depths of 20 and 80 cm in the soil. Soil–solution sampling started two years after installation of the lysimeters and was conducted each May, June, August and October 1985–1988. Deposition data were derived from collectors situated 1 km from the sampling site during the same years. Plant accumulation rates were calculated to be  $0.23 \text{ g Ca m}^{-2} \text{year}^{-1}$  and  $0.13 \text{ g K m}^{-2} \text{year}^{-1}$  (accumulation in

root; branches and needles was not included in the estimate). Calculations using Eq. (2) suggested average weathering rates of  $0.85 \text{ g Ca m}^{-2} \text{year}^{-1}$  and  $0.17 \text{ g K m}^{-2} \text{year}^{-1}$ .

### 2.2.2. The strontium isotope method

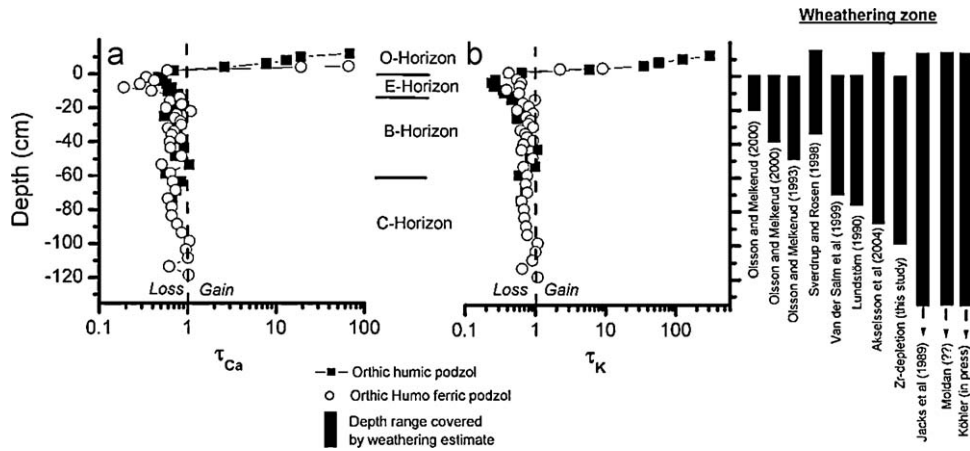
Jacks et al. (1989) used strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) to separate Sr derived from soil weathering from atmospheric inputs in stream water runoff to calculate average weathering rates for the Svartberget catchment over a one year period (1985). A lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of atmospheric aerosols ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.7168;  $n = 7$ ) compared to that of soil minerals found within the catchment ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.7402;  $n = 6$ ) made it possible to calculate the proportion of Sr derived from geogenic sources in the annual runoff based on the  $^{87}\text{Sr}/^{86}\text{Sr}$  signature of the water ( $^{87}\text{Sr}/^{86}\text{Sr}$  0.7398;  $n = 15$ ) using a binary mixing model. Jacks' co-workers calculated that weathering inputs constituted about 98% of the Sr in the stream. By assuming a similar geochemical behaviour of Sr as Ca they calculated a weathering rate of Ca ( $W_{\text{Ca}}$ , unit:  $\text{g m}^{-2} \text{year}^{-1}$ ) as:

$$W_{\text{Ca}} = \frac{A_{\text{Ca}}}{\text{Sr}_p/\text{Sr}_s} \quad (3)$$

where  $A_{\text{Ca}}$  is the deposition rate of Ca ( $\text{g m}^{-2} \text{year}^{-1}$ ),  $\text{Sr}_p$  is the proportion of Sr derived from atmospheric fallout in the stream runoff and  $\text{Sr}_s$  is the proportion of Sr derived from mineral weathering in the stream water. Jacks et al. (1989) measured the wet-deposition of Ca ( $0.054 \text{ g m}^{-2} \text{year}^{-1}$ ) and modelled the dry deposition ( $0.006 \text{ g m}^{-2} \text{year}^{-1}$ ) at the research station (1 km from the catchment) and calculated using Eq. (3) a mineral weathering rate of about  $3 \text{ g Ca m}^{-2} \text{year}^{-1}$ .

### 2.2.3. The zirconium depletion method

Olsson and Melkerud (2000) and van der Salm et al. (1999) applied the method developed by Brimhall and Dietrich (1987) and Brimhall et al. (1991), which is here referred as the Zr-depletion



**Fig. 2.** The enrichment and depletion zones of two soil profiles collected within the study area illustrated by calculated values of a)  $\tau_{Ca}$  and b)  $\tau_K$ , where values below 1 indicates mass-losses of each element while values above one suggests an enrichment (accumulation) of weathering products. In the right panel the weathering zones covered by each individual method are shown, where an arrow indicates that the deeper soil layers may contribute to the weathering estimate.

method. They calculated average weathering rates inferred from soil profiles situated within the Svartberget area. Calculations for this method are based on the assumption that the weathering of soil minerals induces a re-location of mobile elements within a soil profile. Fractional mass gain or losses ( $\tau$ ) of a mobile element ( $j$ ) released from minerals relative to an immobile element ( $i$ ) can be calculated as:

$$\tau_j = \frac{C_{sj}/C_{si}}{C_{pj}/C_{pi}} \quad (4)$$

where  $C_s$  is the concentration of  $j$  and  $i$  in the soil ( $\text{g kg}^{-1}$ ) and  $C_p$  represents the concentration of  $j$  and  $i$  in the un-weathered parent material ( $\text{g kg}^{-1}$ ). Both studies used zirconium as an immobile element when calculating the fractional loss of Ca and K from soil profiles. Absolute weathering losses ( $\delta$ ) of Ca and K relative to the parent material were calculated as:

$$\delta_j = \tau_{C_j,p} p_p V \quad (5)$$

where  $p_p$  is the bulk density of the parent material ( $\text{kg m}^{-3}$ ) and  $V$  is the volume of the weathering zone ( $\text{m}^3$ ). Olsson and Melkerud (2000) defined the weathering zone as the upper 0.2–0.4 m, while van der Salm et al. (1999) integrated weathering losses down to 0.7 m.

These losses were converted to an average weathering rate by dividing integrated loss with the time since the glacial retreat, i.e. Olsson and Melkerud (2000) used 9400 years while van der Salm et al. (1999) used 8800 years. Estimated weathering rates range between  $0.15\text{--}0.37 \text{ g Ca m}^{-2} \text{ year}^{-1}$  and  $0\text{--}0.73 \text{ g K m}^{-2} \text{ year}^{-1}$ .

This method was applied to two additional soil profiles from the catchment where weathering losses were integrated for the upper 1 m and where the vertical variations in  $\tau_{Ca}$  and  $\tau_K$  used for the calculations are shown in Fig. 2. Calculated losses range between  $3.3\text{--}5.7 \text{ kg Ca m}^{-2}$  and  $8\text{--}14 \text{ kg K m}^{-2}$ , corresponding to an average long-term weathering rate of  $0.35\text{--}0.65 \text{ g Ca m}^{-2} \text{ year}^{-1}$  and  $0.9\text{--}1.5 \text{ g K m}^{-2} \text{ year}^{-1}$  assuming a similar soil age as Olsson and Melkerud (2000).

#### 2.2.4. The catchment budget method

Catchment-scale weathering rates can be estimated using an approach similar to that of Lundstrom (1990). Instead of using soil-lysimeters to collect soil–water, annual runoff of Ca and K in the streamwater can be used to estimate the average loss from the catchment soil. In this synthesis, we calculate the weathering rate using Eq. (2) by using export rates of Ca and K during 2003–2006 (annual runoff variation 150–350 mm) in four streams (named 1, 2,

3, 4 in Fig. 1), using previously published stream water data (Buffam et al., 2007) and methods following (Ågren et al., 2007), together with deposition data collected 1983–2007 (annual precipitation 440–850 mm) at the nearby research station (Fig. 1). In contrast to simplified estimate of plant accumulation rates made by Lundstrom (1990), the plant accumulation rates were calculated using empirical data on tree storage where plant biomass variables, as well as K and Ca storage, have been simultaneously measured (Tamm, 1969; Nihlgård, 1972; Nykvist, 1974; Bringmark, 1977; Björkroth and Rosén, 1978; Eriksson and Rosén, 1994; Eriksson et al., 1996; Alriksson and Eriksson, 1998). Plant accumulation rates were calculated using the empirical relationship between plant growth rates (stem volume/ha/stand age;  $\text{m}^3 \text{ ha}^{-1} \text{ year}^{-1}$ ) and the accumulation rate ( $\text{g m}^{-2} \text{ year}^{-1}$ ) compiled from these references (Fig. 3). The accumulation rate ( $A_i$ ) was calculated as:

$$A_i = \frac{\text{Stem}_i + \text{Branch}_i + \text{Root}_i + \text{Stump}_i + \text{Bark}_i}{\text{Stand age}} \quad (6)$$

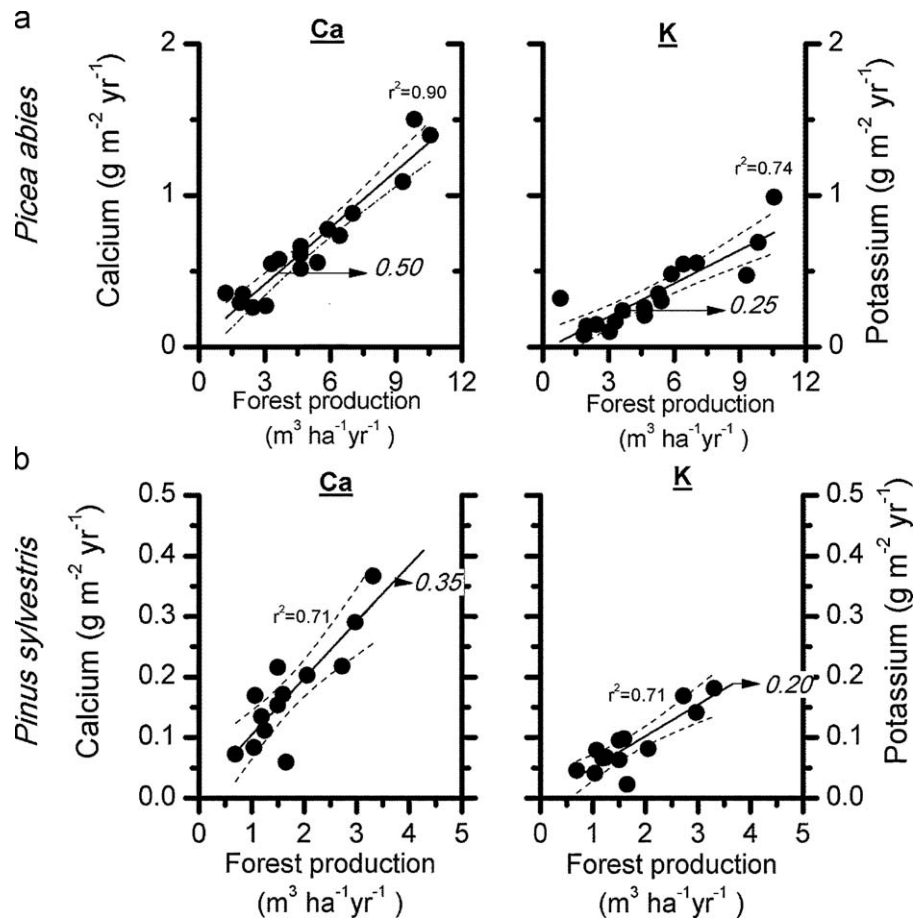
where  $\text{Stem}_i$ ,  $\text{Branch}_i$ , and  $\text{Root}_i$  represent the inventory of element  $i$  ( $\text{g m}^{-2}$ ) in each of these plant components. Stand age is the age of the stand (year). Root and stump biomass was assumed to constitute 40% of the stem-biomass as typically indicated by functions established by Marklund (1988) and assumed to have the same concentration of Ca and K as the stem. Concentrations are, however, often higher for fine roots making this likely to be a conservative estimate. The mass of the bark was assumed to constitute about 6% of the stem biomass as suggested by Marklund (1988) and have a concentration of 1.6% Ca and 0.6% K as found by Isberg (2002). Calculated average plant accumulation rates are indicated with arrows in Fig. 3 while accumulation rates at a catchment scale (50/50 pine and spruce) were estimated to be  $0.425 \text{ g Ca m}^{-2} \text{ year}^{-1}$  and  $0.23 \text{ g K m}^{-2} \text{ year}^{-1}$ . Calculations using these values (Eq. (2)) suggest annual weathering rates of  $0.39\text{--}0.59 \text{ g Ca m}^{-2} \text{ year}^{-1}$  (mean  $\pm$  stdev) and  $0.08\text{--}0.13 \text{ g K m}^{-2} \text{ year}^{-1}$ .

#### 2.2.5. The climate correlation method

Olsson et al. (1993) found a strong correlation ( $r^2 \geq 0.81$ ) between weathering losses of Ca and K calculated through the Zr-depletion method applied to 0.5 m deep soil profiles distributed over Sweden ( $n = 11$ ; including one profile from Svartberget) and geoclimatic conditions at the sites. They developed a regression that has been applied to calculate weathering rates at 1508 sites across Sweden, which is expressed as:

$$W_{Ca} = -111.16 + 0.260(X_{Ca}) \quad (7a)$$





**Fig. 3.** Regressions used to estimate the plant accumulation rate of Ca and K as a function of the volumetric stem growth used in the catchment budget approach. The underlying original data have previously been published (Tamm, 1969; Nihlgård, 1972; Nykvist, 1974; Bringmark, 1977; Björkroth and Rosén, 1978; Eriksson and Rosén, 1994; Eriksson et al., 1996; Alriksson and Eriksson, 1998).

$$W_K = -311.89 + 0.208(X_K) \quad (7b)$$

where  $W_{Ca}$  and  $W_K$  are expressed in  $\text{mg m}^{-2} \text{year}^{-1}$  and  $X_{Ca}$  and  $X_K$  are the products of the temperature sum and the concentration of Ca and K at 0.5 m depth, respectively. Climate correlations are currently the foundation for regional weathering maps used to interpret nutrient balances in forested sites in Sweden (Olsson et al., 1993). Weathering rates in Svartberget calculated using Eqs. (7a) and (7b) are  $0.08 \text{ g Ca m}^{-2} \text{year}^{-1}$  and  $0.14 \text{ g K m}^{-2} \text{year}^{-1}$ .

#### 2.2.6. The PROFILE model

PROFILE is a steady-state soil chemical model that generates weathering rates for cations using soil properties such as estimated exposed mineral surfaces, weathering rates of individual soil minerals (determined through controlled laboratory experiments), soil moisture and depth of the weathering zone (Sverdrup and Warfvinge, 1993). Mineral weathering reactions governing the rate of weathering into the liquid phase includes organic acids, carboxylic acid, water and their dissociated acid/base forms. PROFILE is the base for two sets of regional weathering maps used to interpret nutrient balances within the boreal forest in Sweden, from which estimates of the mineral weathering rate at the Svartberget region were derived (Sverdrup and Rosen, 1998; Akselsson et al., 2004). Estimated ranges of weathering using PROFILE are  $0.20\text{--}0.32 \text{ g Ca m}^{-2} \text{year}^{-1}$  and  $0.08\text{--}0.27 \text{ g K m}^{-2} \text{year}^{-1}$ , where the weathering zone has been constrained to either 0.5 m (Sverdrup and Rosen, 1998) or 1 m (Akselsson et al., 2004).

#### 2.2.7. The MAGIC model

MAGIC is a lumped-parameter, soil acidification model that uses deposition, plant accumulation, retention, cation exchange, carbonic acid and its dissociated acid forms, and solubility/mobilization of aluminium to estimate soil and surface water chemistry (Cosby et al., 2001). MAGIC estimates an average weathering rate for the catchment based on soil parameters, atmospheric deposition and hydrology by optimizing simulated soil chemistry variables to match surface water chemistry data, and an assumed pre-industrial steady state condition between the soil store and stream export. The model has been applied to the Svartberget catchment where stream water chemistry in the Västrabäcken sub-catchment and at the outlet has been used for model calibration (Köhler, in press). Köhler estimated weathering rates in the range between  $0.52\text{--}0.55 \text{ g Ca m}^{-2} \text{year}^{-1}$  and  $0.27\text{--}0.28 \text{ g K m}^{-2} \text{year}^{-1}$  and net release rates (i.e. modelled weathering – modelled plant accumulation) are  $0.32\text{--}0.35 \text{ g Ca m}^{-2} \text{year}^{-1}$  and  $0.07\text{--}0.08 \text{ g K m}^{-2} \text{year}^{-1}$ .

### 3. Method evaluations

#### 3.1. Precision of the weathering rate estimates

Average weathering rates of Ca and K from the Svartberget soils suggested by all methods combined are  $0.66 \pm 0.73 \text{ g Ca m}^{-2} \text{year}^{-1}$  (mean  $\pm$  stdev) and  $0.40 \pm 0.39 \text{ g K m}^{-2} \text{year}^{-1}$ . The large spread in estimated weathering rates, and thus the low precision, is not surprising given that each method is based on different assumptions

**Table 1**  
Summary of synthesized references and constrains regarding depth of the weathering zone, driving weathering processes, time frame covered by the estimate and the average weathering rate estimated by each method.

References	Method	Spatial-scale	Depth of the weathering zone (m)	Time-frame	Weathering g Ca m <sup>-2</sup> year <sup>-1</sup>	Weathering g K m <sup>-2</sup> year <sup>-1</sup>
Lundstrom, 1990	Soil budget	Pedon	0.8	Recent	0.85	0.17
Olsson and Melkerud, 2000	Zr-depletion	Pedon	0.2; 0.4	Historic	0.15;0.16	0.16;0.24
van der Salm et al., 1999	Zr-depletion	Pedon	0.7	Historic	0.37	0.73
This study <sup>a</sup>	Zr-depletion	Pedon	1	Historic	0.31;0.53	0.75;1.26
Jacks et al., 1989	Sr isotopes	Catchment	Flow path constrained	Recent	3.0	N.D.
Köhler, in press	MAGIC	Catchment	Flow path constrained	Recent	0.60	0.28
This study <sup>a</sup>	Catchment budget	Catchment	Flow path constrained	Recent	0.73;0.81;0.85;0.93	0.25;0.25;0.29;0.30
Sverdrup and Rosen, 1998	PROFILE	Pedon to Regional	0.5	Recent	0.20	0.08
Akselsson et al., 2004	PROFILE	Pedon to Regional	1	Recent	0.32	0.27
Olsson et al., 1993	Climate-regression model	Pedon to Regional	0.5	Historic	0.08	0.14

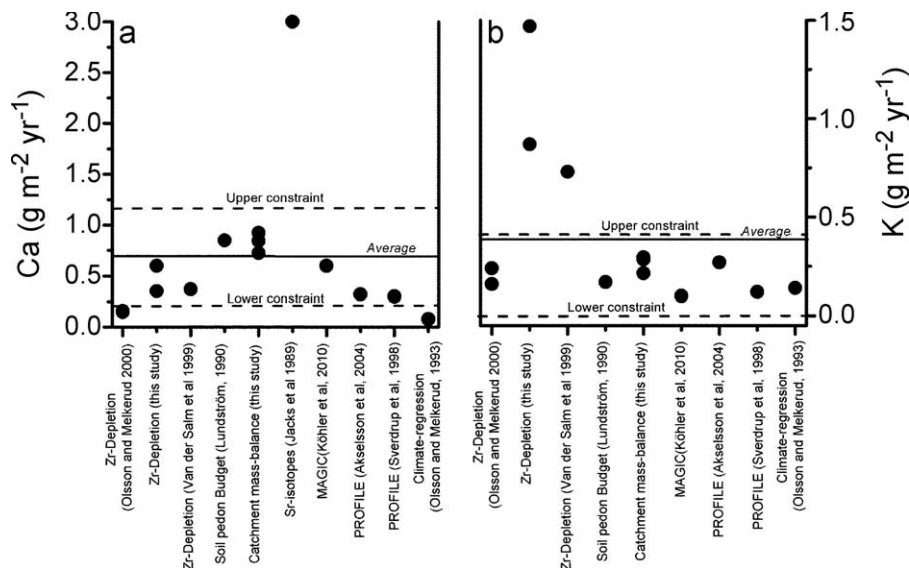
<sup>a</sup> See text for method description.

and has constrained the weathering zone to different soil depths (Table 1). For example, Olsson and Melkerud (2000) constrained weathering to the upper 0.2–0.4 m of the mineral soil (E- and Bs-horizon) and excluded the O-horizon from their weathering budget, whereas the O-horizon is included in the PROFILE model where mineral weathering rates were intergraded down to approximately 0.45 m in the mineral soil. In contrast, the other methods integrate weathering losses over ≥0.7 m of the mineral soil.

Methods integrating weathering over a depth of ≥0.7 m seem to provide systematically higher weathering rates than those constraining weathering to the upper ~0.5 m of the soil (Fig. 4), suggesting significant weathering below ~this depth in the soil. Lundstrom (1990) suggests that about 53–68% of the Ca and K released through weathering in the upper 0.8 m occurs below a depth of at least 0.2 m in the soil. This supports the conclusion that significant weathering takes place at deeper soil depths. A progressive build-up of silicate weathering products during lateral groundwater transport in deep mineral soil layers (at 0.5–4 m depth) has also been observed in the catchment (Klaminder et al., submitted for publication), further supporting a hypothesis of significant weathering in deep mineral soil layers. Using soil solution charge balance calculations, this latter study suggests that deep mineral soil weathering of silicate minerals is driven by the combined influence of carbonic acid derived from soil mineralized carbon and sulphuric acid generated from pyrite oxidation.

It is self-evident that the different boundary conditions for the weathering zone are likely to generate differences in weathering rates and that normalization of the weathering rates to a common soil depth would have reduced the variations in weathering rate estimates. The latter is indicated by Ca weathering rates being fairly similar when integrated for the upper 0.7–1 m (Fig. 4a). However, limited knowledge about the weathering zone most relevant for plant cycling and steam water quality makes a sound normalization of the weathering rates to a common depth difficult. Therefore, we chose to interpret the effects of different weathering depths as part of the total uncertainty generated by competing conceptual views of the weathering system in Svartberget.

We note that estimates derived for the upper 0.7–1 m of the soil should likely be comparable with the flow-path constrained methods applied at the headwater streams, because previous isotope tracer studies have found that most of the runoff traverses the upper 1 m of the soil (Laudon et al., 2004). From the perspective of plant cycling of Ca and K the estimates derived for the upper 0.5 m might be more relevant than estimates including weathering in deeper soil layers, considering that roots are mainly found in the upper part of the soil. On the other hand, roots can take nutrients from deeper in the profile (Plamboeck et al., 1999) and weathering products released below the rooting zone may become accessible for plants downslope where lateral groundwater flow paths come closer to the soil surface.



**Fig. 4.** Comparison of the estimated weathering rate of a) calcium and b) potassium in the Svartberget catchment. For the catchment budget estimate (see text), each circle represents a three-year average value for a stream (streams 1, 2, 3 and 4) within the Svartberget catchment. Average value for all estimates is indicated with a solid line. Upper and lower constrains calculated using Eq. (2) (see text for explanation) are indicated with dashed lines.

Adding further complication to constraining the weathering zone based on root occurrence are mycorrhizal fungi, which serve as a continuation of plant roots (Jongmans et al., 1997). In a boreal forest podzol, two thirds of the total number of mycorrhizal root tips were found in the mineral soil from 18 to 52 cm in contrast to plant roots that occur mainly in upper 10 cm of the soil (Rosling et al., 2003). Clearly, weathering rate uncertainties could be largely reduced if methods to better determine the weathering zone most relevant for plant cycling and stream water quality could be improved.

It is well known that weathering rates may vary at a small spatial scale depending on topography, plants and geological substrates (Jenny, 1943). Early soil formation studies in our study area showed that soils developing down-slope appeared more strongly weathered than up-slope soils (Malmström and Tamm, 1926). A recent study from the catchment has also shown that weathering driven by carbonic acid and sulphuric acid in groundwater are likely to be more profound downslope (Klaminder et al., submitted for publication). Within-catchment variability in weathering rates should therefore be expected and might also be indicated by the large (up to 80%) difference in weathering rates estimated for the 0.7–1 m using the Zr-depletion method (Fig. 4a and b). None of these estimates have been corrected for the soil volume taken up by stones and boulders, typically taking up about 30% of the till in the area (Stendahl et al., 2009), which might explain some of the variability. Still, within-catchment variation in weathering rate estimates is rarely considered when scaling-up weathering rates to regional scale but the large observed variation stress that regional weathering rates inferred from a single soil profile should be treated with caution.

### 3.2. Accuracy of the weathering rate estimates from Svartberget

The accuracy of the weathering rate estimates is often difficult to evaluate because reference values are lacking. In Svartberget, we do not know the 'true' weathering rate, but a likely upper and lower constraint can be estimated using Eq. (2). Here the highest and lowest weathering rate (Eq. (2)) that can be generated from the highest measured variation during an hydrological year regarding runoff ( $0.31\text{--}0.70\text{ g Ca m}^{-2}\text{ year}^{-1}$  and  $0.04\text{--}0.17\text{ g K m}^{-2}\text{ year}^{-1}$ ), precipitation ( $0.03\text{--}0.34\text{ g Ca m}^{-2}\text{ year}^{-1}$  and  $0.01\text{--}0.17\text{ g K m}^{-2}\text{ year}^{-1}$ ) and estimated range in plant accumulation rates ( $0.23\text{--}0.50\text{ g Ca m}^{-2}\text{ year}^{-1}$  and  $0.13\text{--}0.25\text{ g K m}^{-2}\text{ year}^{-1}$ ). This calculation suggests that recent weathering rate is likely to be within the range of  $0.2\text{--}1.2\text{ g Ca m}^{-2}\text{ year}^{-1}$  and  $0\text{--}0.4\text{ g K m}^{-2}\text{ year}^{-1}$ .

As shown in Fig. 4, integrated weathering losses down to a depth of 0.2–0.4 m using the Zr-depletion method alone (Olsson and Melkerud, 2000), or coupled to climatic variables (Olsson et al., 1993), fall below the lower constraint for the weathering rate of Ca. The most obvious reason for this underestimation is that a significant part of the weathering zone contributing to the annual runoff is not included. Additionally, the Zr-depletion method uses soil age to convert the mass-loss of elements into a weathering rate instead of the more appropriate and often significantly shorter mineral residence time in the weathering front (Yoo and Mudd, 2008). Furthermore, weathered minerals and weathering products are transported down the slope through wind-throw action, surface soil erosion and soil leaching. Weathering rates on eroding soil estimated using the Zr-depletion method can be underestimated by as much as 40% if this lateral flux is not taken into account (Yoo et al., 2007). It is notable that the Zr-depletion method, when integrating weathering losses down to a depth of 0.8 m, generates weathering rates for K higher than the upper weathering constraint. This is likely a result of historical weathering rates of K-containing minerals being higher than the more recent rate or simply due to an overestimation by this method. The Ca weathering rate estimated

using Sr-isotopes also appears unrealistically high. The most likely reason for this is the large uncertainty in the Sr-isotope mixing model, i.e. the inferred weathering rate can vary by an order of magnitude by simply letting the measured variables vary within one standard deviation around the average values used in the estimate.

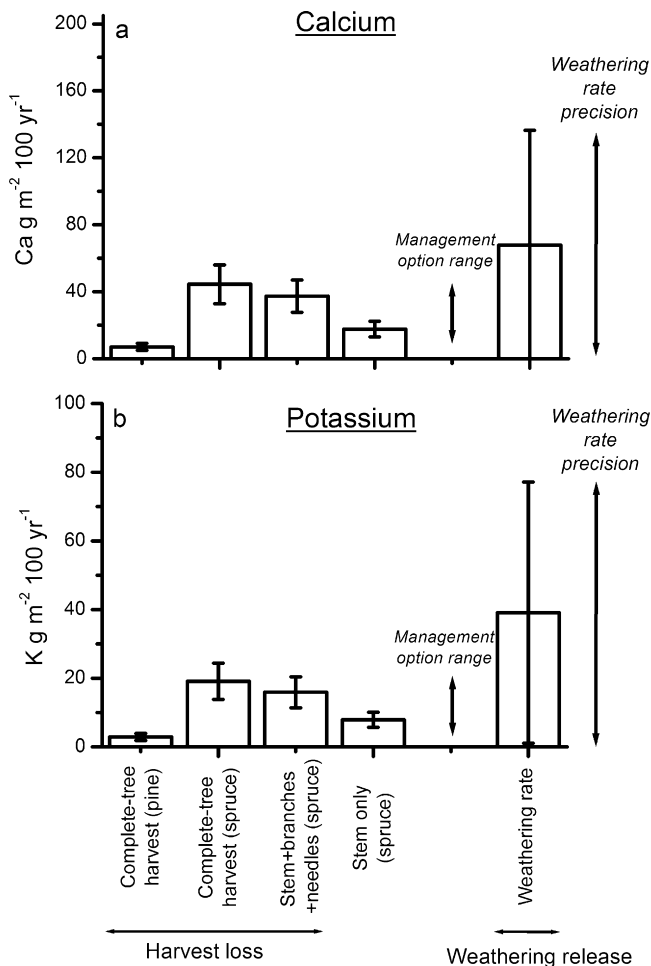
Input–output mass-balance calculations are also subject to uncertainty. For example, K released from dissolved minerals might become trapped within the mineral lattice of secondary clay minerals (Sawhney, 1972), making it less straight forward to assume that soil–water and runoff fluxes represent all K released through weathering. Furthermore, the steady-state assumption underlying Eq. (2), is rarely observed in nature. For example, findings in North America show declines in the exchangeable Ca pool and soil acidification, especially at sites subject to anthropogenic acidification (Watmough et al., 2003). Declines in the soil base cation pool in northern Sweden have also been suggested from PROFILE modelling (Sverdrup et al., 2005). Yet the relatively constant pH values in the mineral soil in the area between 1920s and 1980s (Tamm and Hallbäck, 1988) indicate that fairly stable conditions prevail at the study site.

Importantly, none of the studied methods are able to separate out and quantify the biologically driven weathering process. Biological processes are strongly coupled to mineral weathering rates, driving the acid strength of the soil solution by generating organic acids and increasing the concentration of carbonic acid in the soil through soil respiration (Moulton et al., 2000; Andrews and Schlesinger, 2001). In addition, rooted vascular plants and their mycorrhizal fungal partners have the capacity to mine minerals for nutrients as evident from microscopic analysis of mineral grains from the study area (Jongmans et al., 1997). It seems, therefore, evident that forestry operations and their impact on biological processes will have an effect on the weathering rate, which remains to be quantified.

### 4. Management implications

Currently, the debate about sustainable forest practices has focused on choice of tree species, how much of the stand biomass that can be harvested and if components (twigs, needles, stumps) have to be left or compensated for (ash recycling) to make the soil recover following harvest losses. There is an extensive literature suggesting that whole-tree harvesting is not sustainable on slowly weathering Precambrian substrates (Boyle et al., 1973; Sverdrup and Rosen, 1998; Akselsson et al., 2007; Aherne et al., 2008; Kreutzweiser et al., 2008). Losses of base cations may contribute to reduced tree growth and to surface water acidification.

Fig. 5 shows losses induced by different harvest trees (pine or spruce) and forestry practices (complete-tree harvest, harvest where only the stump is left or stem only harvesting) reported for >100-year old forest within the same region as Svartberget (Nykqvist, 1974; Björkroth and Rosén, 1978). Also shown in this figure are the estimated cumulative flux of Ca and K dissolved from soil minerals in the Svartberget during the same period. In our study, Ca and K pools lost through biomass removal following all forest harvesting options are less than modelled average weathering inputs during the rotation period, suggesting that the soil has the capacity to recover after complete-tree harvesting—especially because additional precipitation inputs are expected. This finding is in line with results from previously glaciated soils in Maine, USA where base cation pools recovered 15 years after whole tree harvests (McLaughlin and Phillips, 2006). However, Ca pools in many Maine soils are clearly susceptible to Ca depletion due to the combined effect from acid deposition, biomass outtake and shifting from softwood- to hardwood-dominated forests (Huntington, 2005). In that perspective it is important to stress that our study



**Fig. 5.** Comparison of Ca and K pools lost after harvesting of ca >100-year old spruce and pine forest reported for sites from the same region as Svartberget (Nykqvist, 1974; Björkroth and Rosén, 1978) and the estimated cumulative pool of Ca and K released through weathering during the same rotation period. Error bars indicate one standard deviation. Uncertainties estimated for harvest losses of Ca (spruce  $\pm 26\%$ ; pine  $\pm 30\%$ ) and K (spruce  $\pm 28\%$ ; pine  $\pm 35\%$ ) has been estimated using the observed variation in harvest losses of boreal forest stands (spruce  $n = 11$ ; pine  $n = 4$ ) previously reported (Tamm, 1969; Nykvist, 1974; Björkroth and Rosén, 1978; Eriksson and Rosén, 1994). These forest stands represent sites with different geologies and where the biomass outtake has varied largely (89–395 m<sup>3</sup>); hence, calculated uncertainties are likely larger than would be expected at an individual stand-level.

site has not been substantially affected by acid deposition and that our mass-balance might be less relevant for soil having a long-term history of acid fallout.

What is evident in the comparison between losses and weathering inputs is that the uncertainty in the average weathering estimate—representing the combined effects from methods uncertainties, within catchment variability in weathering rates and uncertainties when defining the weathering zone relevant for plant cycling—are much larger than the difference induced by alternative forestry practices. In other words, the weathering rates included in nutrient budgets that we use to scrutinize effects of biomass harvests are not sufficiently precise to determine whether alternatives to complete-tree harvests, such as leaving twigs or stumps, will be enough or necessary for maintaining Ca and K pools in managed forest soils. Therefore, we argue that long-term nutrient budgets cannot alone be used to evaluate nutrient balances of forestry practices and should be backed up with long-term monitoring of cation pools and stream water chemistry before such predictions are used as a basis for forest management decisions.

It has been argued using weathering rates modelled using the PROFILE model that conventional forestry practices are already depleting the pool of exchangeable base cations in northern Swedish soils (Sverdrup and Rosen, 1998). Even though this finding is difficult to validate given the previously discussed uncertainty, it is clear that more intensive forestry generates accelerated losses of cations. Nutrient application, potentially through ash recycling, may permit sustained forest growth. Still, ash addition experiments on mineral soils in Scandinavia reveal no positive effect on forest production (Augusto et al., 2008) and the ability of ash recycling to maintain runoff buffering capacity remains unclear. This former finding is not surprising given that the boreal forest production is N-limited (Tamm, 1991), which implies that the long-term sustainability of complete-tree harvest needs to be evaluated from both harvest induced losses of cations as well as losses of N and P.

## 5. Conclusion

Currently available maps of weathering rates in Scandinavia, derived using the climate-regression model (Olsson et al., 1993) or the PROFILE model (Sverdrup and Rosen, 1998; Akselsson et al., 2004), serve as important first steps towards an integration of weathering rates into forest nutrient balances and active management plans. However, weathering rates occurring on these maps should be used with caution in quantitative nutrient budgets adopted to evaluate forestry practices strategies at a stand- to regional-scale. Importantly, these estimates still provide relevant information of regional trends in weathering rates, but placing too much confidence in the absolute rates when developing policies for sustainable forestry practices may generate unforeseen results. Before our understanding about the weathering processes and its coupling to plant cation-uptake and surface water quality has improved, the decisions of future forestry practices should preferably rely on empirical data of cation change in soil and water from field experiments rather than nutrient budgets.

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