



Estimating weathering rates using base cation budgets in a Norway spruce stand on podzolised soil: Analysis of fluxes and uncertainties



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ABSTRACT

Since forestry is often allocated to soils with a low weathering capacity, reliable estimates of weathering rates are crucial in analyses of sustainability, e.g. of whole-tree and stump harvesting. In the present study, weathering rates ($\text{kg ha}^{-1} \text{yr}^{-1}$) for base cations were estimated using cation budgets in a replicated ($n = 4$) experimental Norway spruce (*Picea abies* (L.) Karst.) plantation situated on a nutrient-poor glacial till in south-west Sweden and aged 25–39 years during the study period. Weathering rates (central values) were 2.4, 1.4, 0.3 and 2.3 $\text{kg ha}^{-1} \text{yr}^{-1}$ for Ca, Mg, K and Na, respectively. However, weathering was a minor flux in the overall cycling of these cations in the ecosystem, and the confidence intervals of the weathering estimates had amplitudes that generally were greater than the central values. The overall uncertainties were divided into (i) regular standard errors of the mean, expressing spatial variability, sampling errors and random method-related errors in data from measurements replicated over the experimental plots ('Type A' uncertainties), and (ii) estimated standard uncertainties accounting for systematic errors of methods, and of uncertainties in variables, functions and factors not replicated over the plots ('Type B' uncertainties). For Ca and K, bioaccumulation dominated the overall uncertainty. Most (>90%) of this uncertainty, in turn, was of Type A (between-plot variability in measured stem diameters and cation concentrations); the remainder resulted from Type B uncertainties in allometric functions etc. Hence, regular standard errors over plots yielded a correct level of uncertainty of weathering estimates for these ions at the studied site. For Mg and Na, however, deposition and leaching were large terms in the cation budget. Whereas the uncertainty in deposition was mostly taken into account by plot-wise replicated measurements of throughfall (Type A uncertainty), Type B uncertainties were crucial to the estimates of leaching. Due to the fact that uncertainties accumulate when terms are added and subtracted in a cation budget, it is difficult to predict the sustainability of the pools of exchangeable cations from estimated weathering rates; it may be better to measure them directly in the soil. However, in the studied ecosystem these had a rapid turnover (mean residence time, 1–4 years), and underwent abrupt fluctuations over only a few years. A study performed during a limited time may therefore suffer from considerable temporal uncertainties, if the results are to be generalised for a longer period.

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1. Introduction

Weathering is a key process in the cycling of base cations, phosphorus and other elements in terrestrial ecosystems. Reliable esti-

mates of weathering rates are crucial in analyses of the long-term sustainability of forest practices, and when assessing trends in soil and water quality under various scenarios of harvesting and deposition of air pollutants (e.g., Akselsson et al., 2007). For instance, estimates of weathering rates have been of fundamental importance in the calculation of critical loads of acidity to soils (e.g., Hodson and Langan, 1999). Forestry is often allocated to soils with low weathering rates, where negative base cation balances may impede long-term productivity. In particular, the introduction of more intensive harvesting practices in forestry, such as whole-tree

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and stump harvesting, may reduce the availability of plant nutrients at sites with a moderate or low inherent soil fertility (Thiffault et al., 2011). For instance, the study of Olsson et al. (1996) found it likely that whole-tree harvesting depletes base cations substantially in the forest floor of certain sites. This emphasises the importance of mineral weathering and stresses the requirement for an improved accuracy of weathering estimates (Klaminder et al., 2011). There is therefore a need to include base cation weathering in the planning of sustainable forest management. Biogeochemical simulation models, e.g. the PROFILE steady state model (Sverdrup and Warfvinge, 1993; Holmqvist et al., 2003), may be useful for estimating weathering rates over large areas. However, the quality of output data may be hampered by the often limited information regarding soil mineralogy, specific surface area and soil humidity. Furthermore, available versions have neglected the effects on surface reactivity of precipitates of secondary minerals and organic matter, and have failed to take account of micro-scale effects on weathering by exudates of roots and mycorrhiza ('biological weathering'). Hence, there is a need to improve existing modelling tools by validation against model-independent weathering estimates based on data from more or less intensively studied forest ecosystems.

Relevant methods include 'historical weathering' and ecosystem cation budgets (mass balances). In the former method, an element residing in highly weathering-resistant minerals, such as zirconium, is used as an internal standard for calculating mass losses of the more mobile elements in the soil profile (Olsson and Melkerud, 1989, 2000; Bain et al., 1993; Stendahl et al., 2013). In the cation budget method, weathering rates of base cations over a certain period are quantified from leaching, accumulation or losses in biomass and soil pools, inputs from atmospheric deposition and any application of fertiliser (as explained in Section 2.2.1). Hodson and Langan (1999) examined weathering rates for a Scottish moorland catchment, estimated by various methods, and concluded that reported and guesstimated uncertainties of the tested methods severely hampered the assessment of a critical load. Similar conclusions were reached by Klaminder et al. (2011) in a review of estimated calcium (Ca) and potassium (K) weathering rates for a forested catchment in northern Sweden: inconsistencies between estimates derived from different methods made them unreliable for predicting the effects of different harvesting intensities on soil nutrient pools.

It can be argued that all methods have their particular uncertainties, and possibly also biases, and cannot be expected to converge on a common weathering rate for a particular soil. Whereas historical weathering rates are interesting from a pedological viewpoint, because they yield an estimate of cumulative weathering since the onset of soil formation, cation budgets yield an estimate of the current weathering rate that may be more relevant for characterising the present flows in an ecosystem. Stendahl et al. (2013) pointed out that that millennial historical weathering rates should deviate substantially from current ones if weathering itself has altered the mineralogy of the soil. It therefore seems justified to analyse the precision within the methods, rather than across several ones. With these uncertainties known, it may be possible to draw conclusions from comparative studies on weathering rates in contrasting soils and/or land-use systems using a single method.

Cation budgets have been calculated at the scale of catchments (e.g., Koseva et al., 2010) as well as experimental plots (e.g., Andrist-Rangel et al., 2007; Simonsson et al., 2007; Öborn et al., 2010). In a soil cation budget, weathering is estimated by the difference from other independently measured element fluxes. Measurements of all these fluxes in forest ecosystems require substantial resources, time and patience. Sufficient data for estimating weathering rates are therefore available only for a limited

number of study sites, where the original objectives were not necessarily to assess weathering. As weathering rates are estimated from the sum of several fluxes that are measured independently, the uncertainties of these will add up into the uncertainties of the weathering estimate (see Simonsson et al., 2007). For each process in the cation budget, there is a natural spatial and temporal variation in the environment, as well as errors that originate from sampling, sample preparation and chemical analyses etc. The influence of several of the many sources of uncertainty in an element budget have been addressed previously (Laclau et al., 2005; Yanai et al., 2010). However, there is currently a lack of any critical evaluation of the influence of the different terms and factors in cation budgets.

The aims of this study were: (i) to estimate weathering rates of calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) in an experimental forest using the cation budget method, and (ii) to analyse the sources of uncertainty in these estimates. The method took account of fluxes of deposition and leaching and accumulation in the growing biomass. In forest floor and mineral soil, changes in exchangeable cations were considered, but not of non-exchangeable cations. Special attention was paid to the partitioning of uncertainties on spatial variability and method errors expressed in standard errors over the experimental plots ('Type A' uncertainties), and the uncertainty of factors and functions that were generalised for all plots ('Type B' uncertainties), e.g. allometric biomass functions and systematic error when calculating the content of stones and boulders in the soil.

2. Materials and methods

2.1. Site characteristics

The study was conducted in the Skogaby forest experiment, which was an intensely studied field experiment designed to test the effect of deposition and nutritional conditions on the vitality and growth of trees. In 1913, the former *Calluna* moorland was planted with Scots pine (*Pinus sylvestris* (L.)). This stand was replaced by Norway spruce (*Picea abies* (L.) Karst.) in 1966. The site is located in southwest Sweden (56°33'20"N, 13°13'05"E) at 95–125 m above sea level and 17 km from the coast. The annual mean precipitation is 1100 mm and the annual mean temperature 7.6 °C. The area is exposed to deposition of anthropogenic sulphur (S) and nitrogen (N), as well as elements from a sea origin (Na, Mg, Cl, S, etc.), although the input of anthropogenic S and atmospheric acidity declined dramatically during the 1990s (Bergholm et al., 2003). The yearly mean open-field deposition of S and N for the period 1989–2001 was 11 and 17 kg ha⁻¹ respectively.

The soil is a Haplic Podzol (FAO, 1990) developed on a loamy sandy till with approximately 4% clay (Table 1). The clay mineralogy, as described by Courchesne and Gobran (1997), is mainly vermiculitic and therefore poor in K-bearing phyllosilicates. The quantitative bulk mineralogy of the fine earth (<2 mm) shown in Table 1 was assessed in four plots (two of the control plots and two plots receiving ammonium sulphate applications) by spray drying of random powders according to Hillier (1999, 2003) and full-pattern fitting of X-ray diffraction patterns, similarly to participant 18 in Omotoso et al. (2006). Soil pH (H₂O) prior to the experimental treatments was 3.9 in the Oa-horizon, 4.1 in the upper 10 cm of the mineral soil, and 4.5 at 50 cm depth. The effective base saturation was 30 % in the Oa-horizon and varied from 8% to 12% in the top 50 cm of the mineral soil. Further physical and chemical characteristics of the soil were described by Bergholm et al. (1995). Organic matter constitutes virtually the entire humus layer and declines from 36 g kg⁻¹ in the upper mineral soil, to 10 g kg⁻¹ at 50 cm depth.

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