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Weathering rates of Ca and Mg related to granitic and gabbro mineralogy in boreal forest soils and the effect of mechanical soil disturbance on weathering release


Highlights
• Weathering rates were higher in the gabbro than the granitic areas.
• Weathering was an important Ca and Mg source to forest trees, and it increased after mechanical soil disturbance.

Abstract
This study’s aim was to calculate the weathering rates of Ca and Mg for five boreal forest soils in southern Finland on granitic and gabbro containing bedrock. The effect of mineralogy on the total concentrations of Ca and Mg in soil and weathering rates was evaluated. The aim was also to estimate the effect of mechanical soil disturbance related to ploughing on the weathering in the gabbro area. The total concentrations of SiO₂, CaO, MgO, and Zr were determined by XRF, and weathering rates of Ca and Mg were determined based on the changes in the CaO, MgO, and Zr concentrations. The weathering rates of Ca+Mg varied 5–38 mmol m⁻² year⁻¹ in the E+B/BC horizons among the plots. Soil disturbance related to ploughing increased the weathering of Ca and Mg largely in the disturbed part of the topmost mineral soil as indicated by the decreasing concentrations of Ca and Mg after mechanical soil disturbance. The weathering input of Ca in the undisturbed soil did not fully replace the Ca output in final whole-tree cutting. The weathering input of Mg in the undisturbed soil was sufficient to replace the lost Mg in stemwood harvesting but not on all the plots the lost Mg in whole-tree harvesting. Weathering rates were higher in the gabbro than the granitic areas.

Keywords base cations; ploughing; mineral soil weathering; rotation period

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1 Introduction

The elemental cycling of base cations (Ca, Mg, K, Na) in forest ecosystems depends strongly on the weathering fluxes of these elements from silicate minerals (Carey et al. 2005; Starr et al. 2014). It has been shown that the weathering flux of base cations can be one of the most important fluxes in size compared with those in atmospheric deposition, litterfall and percolation water in forested catchments, and the weathering processes are therefore essential to the sustainability of site productivity (Starr et al. 2014). As part of the soil development of podzolic soils in boreal forests, the topmost part of the mineral soil is weathered leading to the relative enrichment of minerals being resistant to chemical weathering (e.g. zircon) and depletion of minerals (e.g. mafic minerals) susceptible to weathering (Olsson and Melkerud 2000; Starr and Lindroos 2006). Base cations liberated in the weathering process are available for nutrient uptake, exchange on soil cation exchange sites, or leaching with water moving through the vadose zone. The weathering rate has been reported to depend on acidity (Sverdrup and Warfvinge 1988, 1993; Alveteg et al. 1995), dissolved organic compounds (Pohlman and McColl 1988; Lundström 1991, 1993; Raulund-Rasmussen et al. 1998), and forest soil management practices such as ploughing after a clear-cut as part of the regeneration of the forest stand (Lindroos et al. 2016a) as well as temperature, water availability and mineralogy. The mineralogy of the soil material is important in weathering processes, and material containing mafic minerals such as gabbro is more susceptible to weathering release than more acidic (felsic) material that is dominated by less-weathered quartz and K-feldspars such as granite (Bazilevskaya et al. 2013; Starr et al. 2014).

There are several methods for estimating the weathering rates of base cations (Clayton 1979; Jacks 1990; Langan et al. 1995; White 1995; Klaminder et al. 2011). Long-term weathering rates can be determined based on the mass transfer coefficient (Nesbitt 1979; Brimhall and Dietrich 1987; Anderson et al. 2002). The determination is based on minerals being resistant to chemical weathering and their elements (e.g. zirconium, Zr) which can be used as an internal standard against the depletion of base cations from the soil. The long-term weathering rates and linear regression equations based on the rates have been widely used in the Nordic countries (Olsson and Melkerud 1991; Olsson et al. 1993; Johansson and Tarvainen 1997; Starr et al. 1998; Starr et al. 2014). Although the method based on elemental depletion is theoretically relatively easy to apply, it is important that the soil material is originally formed from the same parent material. If weathering and enrichment processes in the soil profile are non-consistent due to variable moisture conditions or non-homogenous soil material, the method may produce even negative weathering rates as was the case in Canadian study (Whitfield et al. 2011). Thermodynamic modelling (e.g. PROFILE, Warfvinge and Sverdrup 1992, 1995; Akselsson et al. 2006) is also widely used to calculate weathering rates. The PROFILE model requires detailed input data for many parameters, and if unavailable, these must be estimated, which increases risks of inaccurate estimates. The PROFILE model has been used successfully for example in British Columbia (Mongeon et al. 2010) and Ontario in Canada (Koseva et al. 2010), as well as for Swedish forest soils (Akselsson et al. 2004). The catchment mass balance method can also be used if the input of base cations through deposition and the output of base cations in stream water are known (Forsius et al. 1995; Starr et al. 1998). The catchment mass balance method can, however, also produce inaccurate estimates in some conditions (Uhlig et al. 2017). However, a caution must be exercised when different approaches are compared, because studies related to the use of Zr in estimating long-term weathering rates and PROFILE can reflect weathering rates of the topmost part of the soil, while the catchment mass balance method includes the weathering of soil in a watershed scale. The method based on the use of Zr integrates chemical weathering rates over kilo year timescales (long-term), while the PROFILE model integrates chemical weathering over days to year timescales.
Starr et al. (2014) reported the estimated values of long-term weathering rates for podzol soils (10,200 years old), and the results indicated that Ca and Mg fluxes released in soil weathering were higher than those entering the soil from atmospheric deposition in the remote catchment in eastern Finland. This example highlights the importance of the weathering release of base cations for the elemental cycling in forest ecosystems. Weathering rates of these base cations near the coastline of Finland were even higher than in the older inland podzols due to the land uplift from the sea, because less-weathered soil material is exposed to weathering, and more rapid soil forming processes in young soils (300–400 years old) (Starr and Lindroos 2006).

Mechanical site preparation, such as ploughing, as part of the forest management practices after a clear-cut and when regenerating forests, exposes mineral soil material to the soil surface (Tanskanen et al. 2004; Tanskanen and Ilvesniemi 2004; Tanskanen 2006; Lindroos et al. 2016a). Mechanical site preparation is widely used in Finland, nearly always in relation to planting new trees in a clear-cut area. There are several methods for mechanical soil preparation, and ploughing is the method that has been widely used previously in Finland. The purpose of ploughing is to form tilts and furrows in a clear-cut area, and seedlings are placed on top of the tilts (Laine et al. 2019). Ploughing aims also to expose mineral soil, because this facilitates development of planted seedlings. Ploughing is a method in which the B and BC horizons are exposed to the surface of the mineral soil in tilts and furrows (Tanskanen et al. 2004; Tanskanen and Ilvesniemi 2004; Lindroos et al. 2016a).

The aim of this study was to calculate weathering rates for five boreal forest soils in southern Finland on granitic and gabbro-containing bedrock. The weathering loss of Ca and Mg in E+B/BC horizons (E – eluvial horizon, B – illuvial horizon, BC – transition horizon between B and C, C – parent material) were determined for the soil formation time of c. 10,000 years, and long-term weathering rates were calculated based on the time of soil formation. The effect of mineralogy on the total concentrations and weathering rates was evaluated. The second aim was to estimate the effect of mechanical soil disturbance (ploughing) on the total concentrations of Ca and Mg in the gabbro containing area. We hypothesized that weathering rates are higher in the gabbro bedrock area than in the granitic bedrock area. It was also hypothesised that mechanical soil disturbance (ploughing) will result in increased weathering rates which is reflected in the decreased total concentrations of Ca and Mg.

2 Material and methods

2.1 Weathering rates in undisturbed soils

The long-term weathering rates (c. 10,000 years) were calculated based on the data from five boreal forest soils in southern Finland. The basic characteristics of the plots are shown in Table 1. The plots were located on either granitic or gabbro bedrock areas. All the plots located in a flat area without sloping landscapes. All the soils showed podzolic features, in which the E, B (BC), and C horizons could be identified. On four of the plots, the soil type was Arenosol/Podzol, and on one plot, it was Podzol (IUSS Working Group WRB 2006). The soils have been subjected to soil forming processes between 10,000 and 11,500 years after the most recent deglaciation. The sites have previously been described in Lindroos et al. (2016a) for Karkkila, Lindroos et al. (2008) for Tammela, Lindroos et al. (2016b) for Evo and Lapinjärvi, and Adamczyk et al. (2016) for Utti (Anjalankoski).

The soil samples for the analysis of geochemical total elemental concentrations by X-ray fluorescence (XRF) were taken from five sample plots (30 m × 30 m) from the steel auger samples
(Karkkila), soil pit samples from the 6-m long wall of the pit (Lapinjärvi, Utti), and four separate soil pit profiles (Tammela, Utti). In all cases, one composite sample for each horizon (E, B, BC, C) was taken by combining four subsamples covering the whole length of the wall of the 6 m long soil pit (Lindroos et al. 2016b), from the four separate soil profile pits or 8 –11 subsamples for the auger points (Lindroos et al. 2016a). The sampled soil horizons with their depths are shown in Table 2. We decided to use composite samples for each horizon per sample plot, because previous

Table 2. Basic characteristics of the study plots. Soil samples were taken from the plots for element analysis and weathering rate estimations. Tree species: Scots pine (Pinus sylvestris), Norway spruce (Picea abies).

<table>
<thead>
<tr>
<th>Plot/ location</th>
<th>Forest site type</th>
<th>Tree species</th>
<th>Soil type</th>
<th>Mafic minerals (%)</th>
<th>Bedrock</th>
<th>Bulk density (g/cm$^3$)</th>
<th>Stoniness (%)</th>
<th>Age of soil formation (yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karkkila/ 60°N, 24°E</td>
<td>Oxalis-Myrtillus type</td>
<td>spruce</td>
<td>Cambic podzol</td>
<td>Glacial till</td>
<td>25</td>
<td>Gabbro, diorite</td>
<td>1.0 (0.6)</td>
<td>30</td>
</tr>
<tr>
<td>Tammela/ 60°N, 23°E</td>
<td>Vaccinium type</td>
<td>pine</td>
<td>Albic arenosol/ Haplic podzol</td>
<td>Sand</td>
<td>12</td>
<td>Granitic</td>
<td>0.87</td>
<td>6</td>
</tr>
<tr>
<td>Utti/ 60°N, 26°E</td>
<td>Myrtillus type</td>
<td>spruce</td>
<td>Haplic arenosol/ podzol</td>
<td>Sand</td>
<td>7</td>
<td>Granitic</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>Lapinjärvi/ 60°N, 26°E</td>
<td>Myrtillus type</td>
<td>spruce</td>
<td>Haplic arenosol/ podzol</td>
<td>Sand</td>
<td>9</td>
<td>Granitic, gneiss</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>Evo/ 61°N, 25°E</td>
<td>Myrtillus type</td>
<td>spruce</td>
<td>Haplic arenosol/ podzol</td>
<td>Sand</td>
<td>17</td>
<td>Granitic, gneiss</td>
<td>0.89</td>
<td>0</td>
</tr>
</tbody>
</table>

1 Cajander (1949)
3 According to Tanskanen and Ilvesniemi (2004); Korhonen (2008); Törmänen (2016)
4 Mechanically disturbed soil (ploughing)

Table 2. Soil sample depths and soil horizons on the sample plots. Soil samples were taken from the soil horizons of the plots for element analysis and weathering rate estimations. Horizons sampled: E – eluvial horizon, B – illuvial horizon, BC – transition horizon between B and C, C – parent material.

<table>
<thead>
<tr>
<th>Plot</th>
<th>Horizon</th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karkkila</td>
<td>E</td>
<td>0–4</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4–10</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>10–20</td>
</tr>
<tr>
<td></td>
<td>BC</td>
<td>20–40+</td>
</tr>
<tr>
<td>Tammela</td>
<td>E</td>
<td>0–3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3–6</td>
</tr>
<tr>
<td></td>
<td>BC</td>
<td>6–36</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>36+</td>
</tr>
<tr>
<td>Utti</td>
<td>E</td>
<td>0–6</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>6–22</td>
</tr>
<tr>
<td></td>
<td>BC</td>
<td>22–44</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>44+</td>
</tr>
<tr>
<td>Lapinjärvi</td>
<td>E</td>
<td>0–4</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4–35</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>35+</td>
</tr>
<tr>
<td>Evo</td>
<td>E</td>
<td>0–3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>3–24</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>24+</td>
</tr>
</tbody>
</table>
studies have shown they satisfactorily reflect the changes in total geochemical concentrations with a depth at plot level requiring the number of horizon samples to cover all the horizons down to the parent material (C horizon) (Starr et al. 1998, 2014), as was the case in our current study (composite samples for the E, B, BC, C horizons separately in all 5 plots). Composite samples are normally used in weathering estimations due to the high cost of the total analysis. Horizon thicknesses were determined in the field at the time of sampling. Soil’s volumetric coarse fragment content (>2 mm) was estimated by Viro’s rod penetration method (Tamminen and Starr 1994). A steel rod was pushed into the soil at 40 points on the plot, and the mean penetration amount (cm) was recorded. Coarse fragment content (volume %) was calculated by the equation presented by Viro (1952) from the cm values. The method is based on the correlation between the rod penetration amount (cm) to the soil and independently measured volumetric coarse fragment content. The bulk density of the soil was determined by taking samples using steel cylinders (diameter 5.64 cm, length 6.14 cm). The cylinder -samples were taken from three soil pits in each plot and were combined to provide a single composite sample per plot. The samples were taken from the top mineral soil (E+B/BC horizons), because the bulk density is required only for the layer for which the elemental depletion is calculated (see equation below). The bulk density samples were dried in an oven at 105 °C for at least 48 hours, and the dry weight of the sample was then determined.

The soil samples were air-dried and sieved, and a <2 mm fraction was stored. Powder pellets were made for the XRF analysis. The total concentrations of SiO₂, CaO, MgO and Zr were determined by XRF (accredited method, FINAS Finnish Accreditation Service, TO25, EN ISO/IEC 17025) (Korhonen 2008; Lindroos et al. 2016a). Element concentrations were corrected for organic matter content of the soil samples (carbon analyzer). The detection limits were: SiO₂ 0.021%, CaO 0.0042%, MgO 0.020%, and Zr 0.001%. The long-term weathering rates of Ca and Mg (E+B/BC horizons, 10 000–11 500 years) were determined for all the sample plots (Birkeland 1999; Starr et al. 2014). The mass transfer coefficient forms basis for the calculation (Nesbitt 1979; Brimhall and Dietrich 1987; Anderson et al. 2002). The C horizon was used as a parent material.

The calculation is based on the total concentrations of Ca, Mg and Zr in the fine earth fraction, the bulk density of the soil, the volume of the coarse fragments in the soil, the thicknesses of the soil horizons in the weathering layer, and the time of the soil profile development (Starr et al. 2014).

\[
W_{j,w} = \left(100 \times d_w \rho_w \left(C_{j,p} \left(C_{Zr,w} / C_{Zr,p}\right) - C_{j,w}\right)\right) / t ,
\]

where:

- \(W_{j,w}\) = Weathering rate of element \(j\) (Ca or Mg) in weathered soil layer \(w\) (g m⁻² yr⁻¹)
- \(d_w\) = soil layer thickness (cm)
- \(\rho_w\) = bulk density of the weathered soil layer \(w\) (g cm⁻³)
- \(C_{j,p}\) = concentration of element \(j\) in parent material \(p\) (%) (C horizon)
- \(C_{Zr,w}\) = concentration of Zr in weathered soil layer \(w\) (%)
- \(C_{Zr,p}\) = concentration of Zr in parent material \(p\) (%) (C horizon)
- \(C_{j,w}\) = concentration of element \(j\) in weathered soil layer \(w\) (%)
- \(t\) = time

The weathering rate was corrected for coarse fragment content.

The weathering index (\(Wi, Zr\% × 100/(CaO\% + MgO\%)\)) was calculated for the undisturbed soil profiles according to Starr et al. (1998). This index combines the changes that have occurred in total concentrations in weathered layers in the top mineral soil compared to deeper soil. The calculation method assumes that the soil material was homogenous from the top mineral soil down to the parent material when soil development started. The ratio of SiO₂/Zr was used to evaluate this.
according to Starr et al. (2014). The SiO$_2$ concentration was assumed to partly reflect the quartz content, and Zr the zircon content in the soil, which are relatively resistant minerals to weathering. This ratio has earlier been used in Finnish studies (Starr et al. 2014), and for comparison it was also included in our current study. If the ratio remains constant with depth, this may partly indicate the uniformity of soil material according to Starr et al. (2014). The proportion of mafic minerals (e.g. pyroxenes and amphiboles) was determined by grain counting, using a microscope (Lindroos et al. 2016a). The relationships between the total concentrations, weathering rates, and proportion of mafic minerals were determined by Spearman’s correlation coefficient.

### 2.2 Effect of mechanical soil disturbance on total concentrations

The changes of Ca and Mg concentrations in 17 years in the exposed BC horizon after a clear-cut and mechanical soil disturbance (ploughing) was also determined for one of the plots, i.e. the Karkkila plot (Table 1).

After the clear-cut of a Norway spruce (*Picea abies* (L.) H. Karst.) stand in 1979, the soil was ploughed and planted with Norway spruce. Mineral soil samples were taken from different locations in the ploughed soil 17 years after ploughing. Samples were taken from the BC horizon of the undisturbed soil, and in disturbed parts of the soil, i.e. in the tilts and furrows, where the topmost mineral soil layer after ploughing was the BC horizon (Fig. 1). The BC horizon samples from the disturbed part of the soil represented the top 0–5 cm layer. For both undisturbed soil and disturbed parts of the soil, the BC horizon was collected from 8–11 randomly chosen points from the 30 m × 30 m sample plot. Subsamples were combined to provide one composite sample for disturbed part of the soil and one composite sample for the undisturbed soil.

The total concentrations of CaO, MgO, and Zr were determined by XRF as described in 2.1.

![Fig. 1. After ploughing, the topmost mineral soil layer in tilt and furrow is BC-horizon. BC horizon (depth 0–5 cm) sample was taken from disturbed parts of the soil and total concentrations were compared to those in undisturbed BC horizon. Sampling was performed 17 years after ploughing (Lindroos et al. 2016a).](image-url)
2.3 Weathering rates during a rotation period

The weathering input of Ca and Mg was calculated for 70-year period corresponding to a rotation period. This was calculated for the undisturbed soils from the annual mean values for all five sample plots according to the principles described in 2.1. The weathering rates were calculated for the E+B/BC horizons (Table 2). Values were multiplied by 70 years, and they are presented in kg ha\(^{-1}\) in 70 years. The values are expressed as kg ha\(^{-1}\) because this is largely used unit in forestry and elemental cycling studies of forest ecosystems.

3 Results

3.1 Elemental depletion and weathering rates

Weathering during the period of soil formation (10 000–11 500 years) was reflected in the topsoil as decreased concentrations of CaO and MgO, and the increased concentration of Zr compared to the deeper soil in all the studied soil profiles (Fig. 2). This change in depth in the concentrations took place in all the plots, although the starting concentration level in the C horizon for weathering effect varied among the plots (Fig. 2). The weathering index (Wi) also decreased from the topsoil to the deeper soil in all the plots (Fig. 3). The \(\text{SiO}_2 \times 10^{-3} / \text{Zr} \) ratio (Fig. 4) was stable with depth on all the plots reflecting the uniformity of the soil material, except for the Tammela plot, where a slight increase in ratio was detected with depth.

The long-term weathering rate of Ca and Mg (E+B/BC horizons) was higher in the Karkkila gabbro plot than the granitic plots (Fig. 5). The highest Ca and Mg weathering rates were found together with the highest CaO and MgO concentrations (C horizon) in the Karkkila gabbro plot, but the correlation in the whole dataset was not significant. The CaO concentrations were positively correlated with the proportion of mafic minerals (p < 0.01), and this was also found for MgO (Fig. 6).

3.2 Effect of mechanical soil disturbance in the Karkkila ploughing experiment

Seventeen years after the mechanical soil disturbance, the concentrations of CaO and MgO decreased in the Karkkila gabbro plot in the disturbed top mineral soil layer of 5 cm (BC horizon) compared to those in the same horizon in the undisturbed soil. The Zr concentration increased correspondingly (Fig. 2).
Fig. 2. The CaO, MgO and Zr concentrations with depth in undisturbed soils of the sample plots (Utti, Lapinjärvi, Evo, Tammela, Karkkila), and in the disturbed soil in the Karkkila experiment.
Fig. 3. Weathering index (Wi) with depth in undisturbed soil of the sample plots.

Fig. 4. SiO$_2$ $\times 10^{-3}$ / Zr ratio with depth in undisturbed soils of the sample plots.
3.3 Weathering input during a rotation period

The input of Ca and Mg from mineral weathering was calculated for the 70-year period, corresponding to a typical rotation period of the boreal forest stand in southern Finland. The weathering rates were higher in the gabbro than granitic plots for the undisturbed soil. The weathering inputs formed an important source for Ca and Mg during the 70-year period when comparing to the outputs of Ca and Mg in tree material in final cutting of the stands of about 70 years (Fig. 7).
Fig. 7. The input of Ca and Mg in the soil (E+B/BC horizons) due to weathering in the sample plots during a period of 70 years (rotation period) in comparison to Ca and Mg amount in tree material in about 70-year-old spruce stands in southern Finland (Ukonmaanaho et al. 2008). Tree-total = nutrient amount in all above ground tree compartments. Tree-stem = nutrient amount in stem + bark.

4 Discussion

4.1 Long-term weathering rates

The weathering release of Ca and Mg in the upper mineral soil with no mechanical soil disturbance was indicated by the changes in total concentrations of CaO and MgO. These changes in weathering rates during soil formation are in accordance with the observations reported previously (Olsson and Melkerud 1991; Starr et al. 1998, 2014; Starr and Lindroos 2006). The long-term Ca weathering rates varied in our plots from 3 to 20 mmol m\(^{-2}\) yr\(^{-1}\), and that of Mg from 2 to 18 mmol m\(^{-2}\) yr\(^{-1}\).
These values are very comparable to those reported by Olsson et al. (1993), who also used similar approach in Sweden. According to Akselsson et al. (2004), the short-term Ca weathering rate was about 40 mmol m$^{-2}$ yr$^{-1}$, and that of Mg 15 mmol m$^{-2}$ yr$^{-1}$ for forest soils in Sweden based on the PROFILE model. In a Canadian study using the PROFILE model, the short-term Ca weathering rate was 23 mmol m$^{-2}$ yr$^{-1}$, and that of Mg 16 mmol m$^{-2}$ yr$^{-1}$ (Koseva et al. 2010), i.e. close to long-term Ca and Mg weathering rates for the Karkkila gabbro plot in our study. Weathering rates have also been estimated in many other studies using various methods (Ouimet and Duchesne 2005; Bazilevskaya et al. 2013).

The proportion of mafic minerals was positively correlated with the total concentrations of CaO and MgO. The highest long-term weathering rate for Ca and Mg were found in the gabbro area.

4.2 The effect of mechanical soil disturbance on total concentrations and weathering

A strong influence of mechanical soil disturbance on the liberation of secondary Al compounds in weathering and dissolution processes in the exposed B horizon has previously been reported by Tanskanen and Ilvesniemi (2004). According to their results, as much as 13% of secondary Al accumulated during soil formation of 10000 years in the B horizon, was mobilised from the exposed soil layers in seventeen years after ploughing in the same experiment we used in our study in Karkkila, southern Finland. Tanskanen and Ilvesniemi (2004) reported that this rate greatly exceeded those rates observed in areas that received the highest acid deposition loads in the 1980s and 1990s. A strong release was observed in our study for Ca and Mg due to mechanical soil disturbance in the topmost layer of 0–5 cm. The CaO and MgO concentrations decreased in the exposed BC horizon already in 17 years after mechanical soil disturbance, and the Zr concentration increased correspondingly. These changes indicated strong weathering release in the topsoil after ploughing.

4.3 Rotation period weathering rates

The weathering input of base cations is important for the long-term productivity of forest soils (Starr et al. 2014). Ca and Mg are lost from the forest ecosystem in cuttings, and weathering input has been shown to replace the lost cations (Olsson et al. 1993). According to Ukonmaanaho et al. (2008), stemwood and bark contain about 200 kg Ca ha$^{-1}$ in spruce stands close to the age of final cutting (about 70 years) in southern Finland. If the final cutting covers this part of the tree material (output), the weathering input on three of our sites would be high enough to replace the lost Ca amount in harvesting. In addition, the atmospheric bulk deposition input is c. 70 kg ha$^{-1}$ 70 yrs$^{-1}$ in southern Finland (Lindroos et al. 2007). The weathering input of Ca in the undisturbed soil did not compensate the lost Ca through whole-tree harvesting. Mechanical site preparation seems to increase the weathering input.

The situation for Mg seems to differ from that for Ca. The weathering input of Mg in the case of no soil disturbance was sufficient to replace the lost Mg in stem-wood and bark (18 kg ha$^{-1}$ in 70-year-old spruce stands, Ukonmaanaho et al. 2008). In addition, the atmospheric bulk deposition of Mg in southern Finland is about 13 kg ha$^{-1}$ 70 yrs$^{-1}$ (Lindroos et al. 2007). Mechanical soil disturbance seems to increase the weathering input of Mg because the Mg concentration decreased clearly in the ploughed topsoil.

The calculation of long-term weathering rates has uncertainties, e.g. related to the time of soil development after deglaciation. Our plots were, however, located on flat areas without sloping landscapes, and the soil development was assumed to be relatively stable. The used XRF analysis had relatively low detection limits in relation to measured values, and the determined concentra-
tions were considered accurate. Our presented concentration values were, however, based on the composite samples of several subsamples. It would be beneficial in the future studies to have repetitions in the concentration values on a plot level to cover variation statistically.

Our results show that because weathering rate of Ca is insufficient to replace the lost Ca in final cutting (whole-tree harvesting), an additional Ca input is required to balance the loss. Weathering rate for Mg was sufficient to replace the lost Mg in stemwood harvesting during a rotation period.

The mechanical soil disturbance seems to increase the weathering release of Ca and Mg as indicated by the changes in total concentrations of CaO, MgO, and Zr. The reason for the rapid release of Ca and Mg after mechanical soil disturbance is undoubtedly that less weathered soil material is exposed to weathering processes on the soil surface as shown by Tanskanen and Ilvesniemi (2004) for secondary Al compounds in relation to ploughing. Starr and Lindroos (2006) reported strong weathering in the case of early stages in soil development in young soils, and laboratory dissolution experiments have indicated that Ca and Mg are liberated strongly in the early stages of experiments (Lindroos et al. 2003). The biotic weathering is undoubtedly very important process after mechanical soil disturbance in ploughed areas. New trees are planted on the soil surface of the mechanically disturbed soil as well as the ground vegetation is rapidly developed, and nutrient uptake and leaching of organic matter are subsequently the factors that can enhance weathering from the disturbed BC horizons. Litter is also accumulated rapidly on the soil surface and leaching of dissolved organic matter can increase weathering (Lundström 1991, 1993). We compared the weathering release between the disturbed and undisturbed BC horizons, and although the undisturbed BC horizons have been weathered as well at the same time as disturbed horizons, the biological weathering seems to have a very strong effect on the disturbed soil horizons.

The long-term weathering rates are normally estimated for undisturbed soils. Our concentration results demonstrated also, that there is a clear direction in the weathering processes in which mechanical soil disturbance increases weathering rates. In future studies, it will be important to study this phenomenon using various approaches (Chadwick et al. 1990).

We found that mechanical soil disturbance related to forest soil management practices considerably affected the total concentrations of CaO and MgO already in less than 20 years. Soil disturbance is also possible for natural reasons related to storms and subsequent windthrows. The roots of fallen trees cause mixing and disturbance to the topsoil, and an increase in weathering rates in these spots may be comparable to that found in our study and will be interesting to study in the future.

**Declaration on the availability of research materials**

Data and research materials are available upon request from authors/Luke.

**Authors’ contributions**

Both authors have substantial contribution to the conception of research question and design of the work, acquisition, analysis and interpretation of data and results, as well as scientific writing of the work.
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