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Weathering rates in the Hietajärvi Integrated Monitoring catchment

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Rates of Ca and Mg release by weathering were calculated for four soil profiles (Haplic Podzols) in a small forested catchment in eastern Finland (63°10´N, 30°43´E). Three of the profiles were developed on glacifluvial fine sand and one on till, and all derived from granodiorites. Soil weathering rates ($\text{mmol}_c\ \text{m}^{-2}\ \text{a}^{-1}$) were calculated using three methods: Zr depletion, Ca + Mg\temperature sum regression, and the PROFILE model. The first two methods give long-term average rates while the latter gives the current rate. According to the Zr depletion method, the weathering rate of Ca was 7–32 (mean = 19) and that of Mg, 3–16 (mean = 9). According to the regression method, the weathering rate of Ca was 14–19 (mean = 15) and that of Mg, 5–9 (mean = 7). The mean values using the PROFILE model were 10 (Ca) and 3 (Mg). Values were corrected for stone content. Catchment input-output budgets gave values of 18 (Ca) and 8 (Mg).

Introduction

The dominant weathering process in soils in the boreal zone is the acid hydrolysis of silicate minerals. As a result of this process, protons are consumed and metal cations released to the soil solution, and the primary minerals altered into clay minerals. Once in solution, the cations released during weathering are subject to biological uptake and recycling, cation exchange retention, re-precipitation (as clays and sesquioxides), and leaching. The uptake and leaching of "base" cations (primarily, calcium and magnesium) and accumulation of aluminium and iron released during weathering push the soil towards acidification while the recycling (involving the litterfall and decomposition) and cation exchange of base cations (high base saturation) counter soil acidification (van Breemen *et al*. 1984). Weathering is therefore a vital process in the functioning of forest ecosystems; providing nutrients for biological activity and a mechanism by which acidity is neutralised for as long as the weatherable pool of minerals in the soil lasts (Bache 1983, Schnoor and Stumm 1986, Wilson 1986).

In pre-industrial times, sources of protons were organic acids associated with the decomposition of organic matter and carbonic acid (from the atmosphere and soil respiration). Acidic deposition, primarily related to anthropogenic emissions of SO_2 and NO_x, during industrial times has superseded carbonic acid and can be expected to have resulted in intensified weathering and base cation release. The release of base cations by weathering is by far the most important parameter in the calculation of critical loads of acidic deposition to forest soils (Hettelingh and Janssen 1993).

There are difficulties in measuring weathering rates directly (Hatton *et al.* 1987). However, there are a number of ways weathering and base cation release rates can be estimated. These include stream chemistry methods, catchment mass balances, soil profile elemental and mineral depletion methods, bedrock geology, laboratory experiments, and modelling (Clayton 1979, Jacks 1990). Depending on the method, the weathering rates are either current or long-term (Holocene) average values and either for a particular soil or an integrated value for the entire catchment.

In this paper, we have estimated weathering rates (base cation release) in the soil at four locations in a small forested catchment in eastern Finland using three methods. The results are compared to input-output mass balance values for the catchment. The purpose was to compare methods for estimating soil weathering rates and to obtain a more complete picture of the biogeochemistry of the catchment. Similar comparative weathering method studies have been carried for Scottish (Bain *et al.* 1995, Bain and Langan 1995, Langan *et al.* 1995), Scottish and Norwegian (Bain *et al.* 1990), Norwegian (Frogner 1990), Swedish (Lång 1995), and US (April *et al.* 1986) sites. However, this is the first such study carried out in Finland. We have also corrected our weathering rate values for soil stone content. The paper is based on an earlier published abstract (Lindroos *et al.* 1995).

Study area, sampling and analysis

The Hietajärvi catchment

The study was carried out at Hietajärvi, a small (4.6 km^2) forested headwater catchment located in the Patvinsuo National Park, in eastern Finland (Fig. 1). The catchment is one of the UN-ECE Integrated Monitoring Programme areas (EDC 1993, Bergström *et al.* 1995).

The bedrock of the area is formed of Archean granitoids (ca. 2.7 Ga), mainly porphyritic granodiorites (Korsman *et al.* 1997). The area was deglaciated ca. 10 200 years BP (Rainio *et al.* 1995) and is supra-aquatic (i.e. has always been above the highest post-glacial shoreline). Elevation varies between 165 and 214 m a.s.l. and the thickness of the overlying drift deposit, which is mainly loose fine till, from 1 to 15 m (mean = 5.6 m). Glacial meltwaters have washed out the finer material from the upper layer. Some small eskers, esker-like formations, and glacifluvial deposits also occur in the area. The upland area (194 ha) is dominated by Haplic Podzols, some having leptic and rudic phases (FAO 1990). Gleyic properties are associated with the lower-lying soils. Fibric Histosols cover about 146 ha, accounting for ca. 43% of the land area. There is also a small area of Lithic Leptosols. Most of the land area (82%) is covered by fire-regenerated Scots pine (*Pinus sylvestris*) stands. The stands are unmanaged and vary in age from 100 to 200-years old. The non-forested areas are mainly open treeless peatland. The catchment contains a number of small lakes and ponds and a large lake, Iso Hietajärvi (82 ha, mean depth of 3.6 m), from which the catchment outlet stream drains. About 27% of the catchment area is water covered. The average annual temperature sum (> + 5 °C) for the area is 1 000–1 028 °C, the annual mean temperature is + 2.0 °C, and the annual precipitation is 592 mm.

Sampling and chemical analysis

Ten permanent plots were established in the catchment for various monitoring purposes, including soil and soil water chemistry (Starr *et al.* 1995). The plots were situated in the dominant site types and at sites that were considered homogeneous with regard to soil, ground vegetation and tree stand (Fig. 1). The soil and soil water chemistry monitoring subprogrammes were most easily carried out on flat sites and soils with a low stone content. Most of the permanent plots are therefore located on glacifluvial material rather than till.

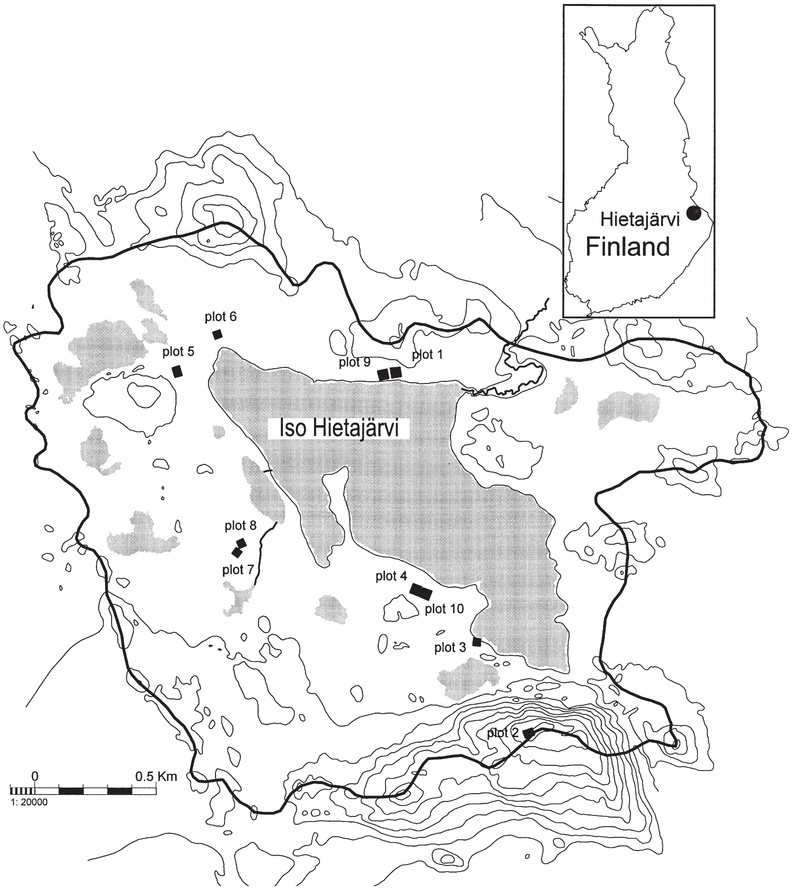

Fig. 1. Location of the Hietajärvi catchment and study plots (plots 1, 2, 4, 5, 9 and 10 were on upland soils while plots 3, 6, 7 and 8 were on peatland). (Legend: black squares = plots, shaded areas = lakes and ponds, thick line = catchment boundary, medium line = streams, thin line = contours.)

For the purposes of this weathering study, soil samples that had been collected (1989) from four of the six upland plots were analysed (plots 1, 2, 4 and 5; Fig. 1). The soil at plots 1, 4 and 5 has developed in glacifluvial material and that at plot 2, in till material. A soil profile description of a pit dug adjacent to each plot is given in Table 1.

Samples of the E, Bs and CB or C pedogenic horizons were taken from the soil pits (Starr 1995a). A composite sample of the entire thickness of the drift layer was also taken from nearby the plot using a percussion drill. It consists of 3–5 subsamples, the first from 1-m depth, the last from just above the bedrock, and the others (2–3) from intermediate depths. If the drift layer was homogeneous, only one intermediate subsample was taken; if the drift layer was heterogeneous, then 2–3 intermediate subsamples were taken. The glacifluvial material at plots 1, 4 and 5 changed to till at a depth of ca. 1 m. The percussion drill sample at these plots was therefore till material and is referred to as 2C (Table 2). The percussion drill sample at plot 2 was considered to be the same material as that in which the soil had developed and is therefore referred to as C2 material (Table 2).

The stone content of each horizon was visually estimated from the walls of the soil pits (Table 1). In addition, the stone content of 0–30 cm layer for the entire plot was determined using the rod penetration method (Viro 1952, 1959). By this method, the mean depth to which a 1 cm diameter steel rod can be pushed vertically into the soil is converted into a stone content ($m^3 m^{-3}$) using an empirically derived function.

Concentrations of elements in < 2-mm fraction were determined using both X-ray fluorescence (*XRF*) and hot *aqua regia* (*AR*) digestion/ICP methods after first grinding a subsample in a tungsten-carbide swing mill (Koljonen *et al.* 1992, Niskavaara 1995). Total C was determined using a LECO carbon analyser. Other soil chemical properties are reported elsewhere (Starr 1995b).

Mineralogy

Soil mineralogy of the < 2-mm fraction was required as input data for running the PROFILE model (*see* below). We used NORMA, a normative mineral distribution model (Räisänen *et al.* 1995, Tarvainen *et al*. 1996), to derive the mineralogy of our soil samples. NORMA uses the *XRF*, *AR* and carbon chemical data above to calculate the amount (% wt.) of some 20 minerals. It was developed to calculate the normative mineralogy of acid and intermediate plutonic rocks and till deposits. We have applied NORMA to the glacifluvial deposits at Hietajärvi because they are also derived from granitoid material.

Weathering rate methods

Zr depletion method

The principle of this traditional weathering method was described by Bain *et al.* (1990). Zirconium (Zr) occurs principally in the form of the mineral zircon ($ZrSiO_4$), which is extremely resistant to weathering (Tole 1985). Zirconium can therefore be used as an internal standard by which the depletion of other elements can be judged. At the time of deglaciation, the amount of Zr is assumed uniform throughout the profile. With time, the weathering products, including base cations, are progressively removed either by plant uptake or by leaching, leaving the upper layer relatively enriched in Zr. The depth to which this enrichment occurs defines the weathered layer. If there was no actual loss (weathering) of Zr, the ratio of base cations to Zr concen-

Table 1. Simple field based description of a soil pit at each plot.

Horizon	Depth (cm)	Description
		Plot 1 (fine sand)
O	4–0	Moist, slightly decomposed organic matter (mor); abrupt wavy boundary.
E	0–9	Light brownish grey (10YR 6/2), moist, fine sand; single grain; loose; stones none; roots v. few to few; abrupt wavy boundary.
Bs	9–26	Yellowish brown (10YR 5/6), moist, fine sand; single grain; loose; stones none; roots common to many; clear wavy boundary.
C	26–80+	Pale olive (5Y 6/3), moist, fine sand; single grain; loose; stones none; roots none.
		Plot 2 (fine till)
O	4–0	Moist, slightly decomposed organic matter (mor); abrupt smooth boundary.
E	0–8	Light grey (10YR 7/2), moist, silt; single grain; moderately firm; stones common; roots common to many; clear wavy boundary.
Bs	8–30	Yellowish brown (10YR 5/8), moist, silt; single grain; moderately firm; stones common; roots common to many; gradual wavy boundary.
C	30–70+	Light yellowish brown (2.5Y 6/4), moist, fine sand; single grain; very firm; stones many; roots none.
		Plot 4 (fine sand)
O	3–0	Moist, slightly decomposed organic matter (mor); abrupt smooth boundary.
E	0–9	Light brownish grey (10YR 6/2), moist, fine sand; single grain; moderately firm; stones none; roots common to many; clear wavy boundary.
Bs	9–32	Yellowish brown (10YR 5/8), moist; fine sand; single grain; moderately firm; stones none; roots common to many; gradual smooth boundary.
CB	32–80+	Light yellowish brown (2.5Y 6/4), moist, sand; faint mottles; single grain; moderately firm; stones none; roots v. few to few.
		Plot 5 (fine sand)
O	3–0	Moist, slightly decomposed organic matter (mor); abrupt smooth boundary.
E	0–9	Light brownish grey (10YR 6/2), moist, fine sand; single grain; moderately firm; stones none; roots common to many; clear wavy boundary.
Bs	9–24	Yellowish brown (10YR 5/8), moist, fine sand; single grain; moderately firm; stones none; roots common to many; clear wavy boundary.
CB	24–80+	Light yellowish brown (2.5Y 6/4), moist, fine sand; faint mottles; single grain; very firm; stones none; roots v. few to few.

trations in the unweathered zone should equal the ratio of base cations plus the weathering loss to Zr in the weathering zone. This constancy of the base cation to Zr ratios enables the amount of base cations lost from the weathered layer to be calculated. By dividing the amount of base cations lost from the weathering layer by the number of years since deglaciation, a mean annual base cation weathering rate for the Holocene is derived. Deposits in supra-aquatic areas are particularly suitable for such calculations because there was no subsequent reworking (fluvial) of the deposit.

To determine the depth of weathering at each plot, we calculated a weathering index, Wi (= Zr,% × 100/(CaO,% + MgO,%). Accordingly, the weathered layer is seen to consist of at least the E and Bs horizons (Fig. 2). We, therefore, used the depth of the lower boundary of the Bs horizon (Table 1) to define the weathering depth.

Ca + Mg\temperature sum regression

Simple linear regression models to estimate the mean annual rates of Ca and Mg loss (weathering) during the Holocene from Swedish till soils were developed by Olsson and Melkerud (1991) and Olsson *et al.* (1993). Using data from eleven soil profiles developed in till located throughout Sweden, they found that the total concentrations of Ca and Mg in the < 2-mm fraction of the C horizon (80–150 cm) multiplied by the present-day effective temperature sum (a surrogate for time since deglaciation) explained much of the variance in base cation losses determined using the Zr depletion method as described above. Conditions in Finland are relatively similar to those in Sweden and we therefore consider it appropriate to apply these regression equations to our site.

The PROFILE model

PROFILE is a steady-state soil chemistry model used to calculate weathering rates for a defined number of soil layers (Sverdrup and Warfvinge 1988, Warfvinge and Sverdrup 1992, Sverdrup and Warfvinge 1993, Alveteg *et al.* 1995). The version of PROFILE we used (PC version 3.01) is based on the weathering rates of 15 common minerals: quartz, K-feldspar, anorthite and albite plagioclases, calcite, hornblende, pyroxene, epidote, garnet, biotite, muscovite, chlorite, apatite, vermiculite and kaolinite. The mineral dissolution rates used in PROFILE are based on kinetic rates determined in laboratory dissolution experiments. The rates are subsequently modified for field conditions using H^+, CO_2, dissolved organic carbon (DOC), base cation and Al concentrations, and corrections for soil moisture content, temperature, soil surface area and bulk density. The weathering rate is increased by high surface areas, H^+ concentrations, soil moisture contents, and CO_2 pressures. Because a steady-state approach is used in PROFILE, only single values for each input parameter can be given, although the property may show considerable seasonal variability.

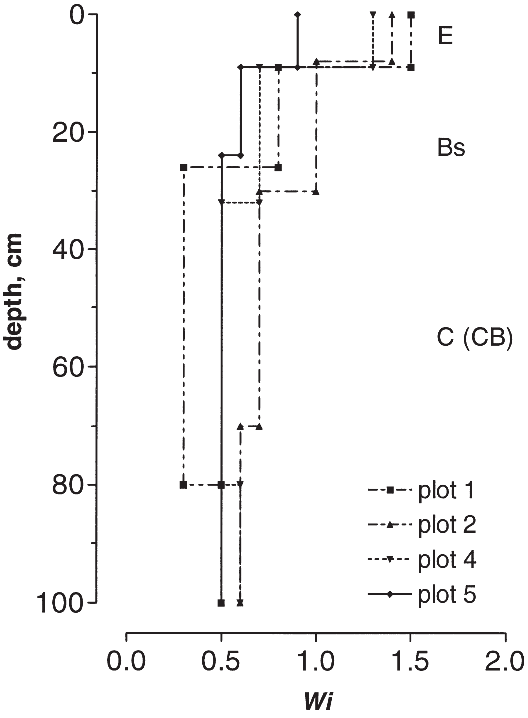

Fig. 2. Weathering index, Wi (Zr, % × 100/(CaO, % + MgO, %), by horizon for each plot.

We ran PROFILE using input values averaged from data collected at the permanent plots described above. The mineralogy (% wt) input data was that of the < 2-mm fraction as determined by NORMA. For precipitation, we used a value of 0.53 m (annual throughfall, mean of plots 1 and 4, 1990–96), 0.37 m for runoff (mean catchment runoff for 1990–91), and 2 °C for soil temperature (mean annual air temperature). Annual total depositions of cations and anions were calculated from bulk open deposition, and throughfall deposition (mean of plots 1 and 4) data for the period 1990–96, using a procedure described by Bredemeier (1988). We did not use non-marine (anthropogenic) deposition since we were not running PROFILE to investigate the effect of anthropogenic deposition on stream chemistry and critical loads. We used the kinetic aluminium model option (using the gibbsite model option made no difference), and a nitrification rate of zero (using the "low" option, made no difference). We defined the model for four soil layers: the humus layer, and E, Bs, and C (CB) horizons. For the thickness of each horizon we used the mean of the values for plots 1, 2, 4 and 5 presented in Table 1. In the absence of data at present, we used the default option of 0.2 $m^3 m^{-3}$ for soil moisture content for all four layers. For bulk density (< 2-mm fraction) and particle size fraction values, the mean of measured values from the plots were used. We chose to use values of 3, 5, 10 and 30 (multiples of atmospheric pressure), for CO_2 pressures respectively in the O, E, Bs and C horizons. Soil solution DOC concentrations of 55 (O), 17 (E), 13 (Bs) (suction lysimeter data for plots 1, 4, 9 and 10, 1991-96), and 5 (C) mg l^{-1} (judgement) were used. Although nutrient uptake is not used in the calculation of weathering rates, a value has to be given in order to run the model (nutrient uptake is used in the calculation of soil, soil solution and stream chemistry model outputs). We used mean annual net uptake values, calculated by dividing the estimated amounts of nutrients in the total stand biomass at plot 4 by the age of the stand (ca. 200 years).

Catchment input-output budgets

For catchments in which the biomass and soil exchangeable pools of Ca and Mg are both in steady-state, the difference between the total deposition and discharge of Ca and Mg is a measure of the present day weathering rate (Clayton 1979, White and Blum 1995). For Hietajärvi, which is remote, undisturbed and has old-growth forests, the above assumptions are realistic. In addition, stand net base cation uptake (so far, only estimated for plot 4) was shown to be almost zero (Starr *et al*. 1998), indicating steady-state nutrient cycling. A further assumption of the mass balance method is that the catchment is sealed, i.e. the only output of solutes from the catchment is by discharge. Chloride budgets calculated for 1988–91 (Forsius *et al*. 1995), and for 1990–96 indicated there is no significant ($p < 0.05$) leakage from the catchment. We calculated the mean annual input-output budgets for the Hietajärvi catchment for the period 1991–96. The estimated annual total deposition to the catchment was used as the input value. This was calculated using bulk deposition for the open (non-forested and surface water) area and the estimated total deposition for the forested area (described above).

Results

Mineralogy

The mineralogy of the < 2-mm fraction in each soil horizon calculated using the NORMA model are presented in Table 2. As expected from the bedrock geology, the mineralogy of the soil matrix in Hietajärvi was dominated by quartz (~ 40%) and plagioclase feldspars (~ 43%) (Table 2). Quartz, which is highly resistant to weathering, was strongly enriched in the E horizons, while the plagioclase feldspars, albite and anorthite, which are susceptible to weathering, were depleted in the E and Bs horizons.

Hornblende, which is a typical accessory amphibole mineral in granitic rocks, is rich in Ca and Mg and easily weathered. Normative hornblende was depleted in the E horizons. Apatite, which is a common accessory mineral in Archean basement gneisses and rich in Ca, is easily weathered.

Normative apatite was depleted in the E horizons and enriched in the Bs horizons. This apparent eluviation-illuviation of apatite maybe due to the accumulation of Fe- and Al-organic phosphate complexes in the Bs horizon however. Phosphorous in such complexes would be soluble in *AR* and included in the calculation of normative apatite (Räisänen *et al*. 1995).

Chlorite, which is a clay mineral either inherited as a primary metamorphic mineral or associated with the chloritization of biotite, is a source of Mg and easily weathered. Normative chlorite (calculated from the amount of Mg remaining after the formation of normative biotite and with the chemical formula of clinochlore) was depleted in the E horizons. However, chlorite's tendency to weather may be masked by a tendency to transfer to finer particle size fractions (Bain and Duthie 1984). Räisänen *et al.* (1995) found that much of test samples of vermiculite was allocated to chlorite using NORMA.

Normative hydrous aluminosilicates (HAS) are allophane-like materials, including allophane, imogolite, and analogous materials (Huang 1991). NORMA calculates HAS from the amount of *AR* soluble Al remaining after the calculation of normative biotite and chlorite and using the chemical formula of imogolite as described by Cradwick *et al.* (1972). Such materials are associated with podzolization (Farmer 1982), which explains the strong peak in HAS in the Bs horizons. Goethite, an iron oxide, is also typical of podzol Bs horizons. Normative goethite, calculated from the content of *AR* soluble Fe remaining after the calculation of normative biotite and chlorite, shows a clear eluviation-illuviation distribution.

Weathering rates

The soil weathering rates calculated for each plot using the Zr depletion and Ca + Mg\temperature sum regression methods are presented in Fig. 3. We used the C and CB horizons as the reference horizon (parent material) for plots 1, 4 and 5 (glacifluvial deposits) and the 2C horizon for plot 2 (till).

A comparison of soil weathering rates obtained by all methods, including the catchment input-output value, is presented in Fig. 4.

Discussion

Based on the normative mineralogy of the soil profiles (Table 2), the present weathering supply of Ca at Hietajärvi is derived primarily from anorthite plagioclases, hornblende and apatite, and that of Mg from hornblende, chlorite and biotite.

We recognise there are limitations in using normative methods to determine mineralogy, particularly if there is a difference between minerals actually present and those included in the normative. The mineralogy of our samples is currently

Table 2. Normative soil mineralogy (% wt) at the four study plots according to the NORMA model.

Plot	Horizon	Quartz†	Albite†	Anorthite†	K-feldspar†	Hornblende†	Biotite†	Apatite†	Chlorite†	Hydrous alumino-silcates‡	Goethite	Others
1	E	51.7	24.9	7.4	8.5	1.8	1.3	0.1	0.1	1.2	0.1	3.0
	Bs	38.4	27.2	8.9	8.2	3.0	1.3	0.5	0.6	8.2	1.8	2.1
	C	37.0	32.0	10.3	9.4	3.3	1.5	0.3	1.5	2.0	1.0	1.8
	2C	39.9	32.5	10.7	8.7	4.1	1.3	0.2	0.6	0.4	0.2	1.5
2	E	51.8	25.6	7.7	8.3	1.9	1.3	0.1	0.1	0.5	0.1	2.8
	Bs	39.8	28.4	9.5	8.3	3.3	1.3	0.5	0.7	5.1	1.3	1.9
	C	42.6	31.4	9.0	8.5	2.5	1.3	0.2	0.8	1.3	0.6	1.8
	C2	39.9	32.9	10.6	8.7	3.0	1.7	0.2	0.8	0.3	0.3	1.6
4	E	60.9	21.9	5.7	7.5	0.8	0.7	< 0.1	0.1	0.4	0.0	2.2
	Bs	43.0	27.9	8.4	8.4	2.4	1.3	0.4	0.4	5.2	0.7	1.9
	CB	40.3	33.5	8.8	9.7	1.5	1.8	0.2	0.9	1.1	0.3	2.0
	2C	37.3	33.6	10.2	10.7	3.3	1.7	0.2	0.8	0.6	0.3	1.3
5	E	56.6	23.7	6.4	8.5	1.1	0.8	< 0.1	0.1	0.3	0.0	2.5
	Bs	41.8	28.5	7.9	8.0	2.0	1.3	0.3	0.5	5.3	0.8	3.7
	CB	44.6	31.6	8.4	8.7	1.8	1.3	0.1	0.6	0.9	0.3	1.8
	2C	39.3	33.2	10.2	8.8	2.1	2.8	0.2	1.1	0.4	0.1	1.8

† included in PROFILE
‡ allophane-like material

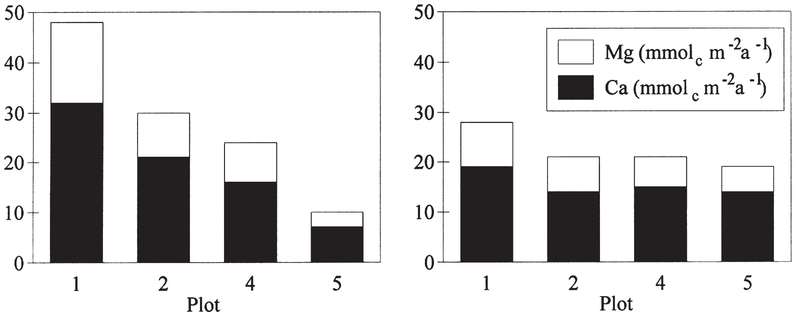

Fig. 3. Comparison of base cation weathering rates calculated by the Zr depletion (left) and Ca + Mg\temperature sum regression (right) methods for each plot.

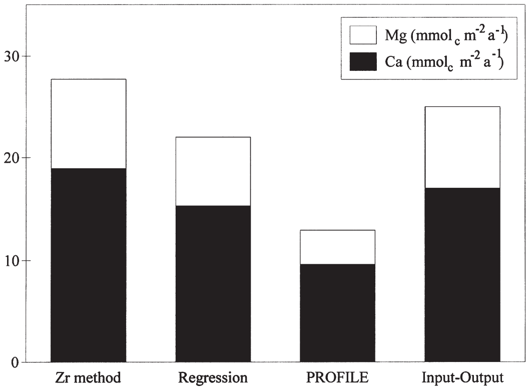

Fig. 4. Comparison of weathering rates calculated by the four methods. Zr depletion, Ca + Mg\temperature sum regression and PROFILE model values are means of plots 1, 2, 4 and 5. The input-output budget was determined for the whole catchment.

being checked using X-ray diffraction (*XRD*) of silt and clay fractions and by polarization microscopy of the fine sand fraction. Earlier testing of NORMA reported non-significant correlations between the results from *XRD* and optical microscopy and those from NORMA (Räisänen *et al.* 1995). The authors attributed this discrepancy to problems with the *XRD* and microscopy results, namely inhomogeniety in subsampling and unknown/misidentification of minerals. However, the amounts of standard mineral estimated by NORMA varied from 50 to 99 per cent (Räisänen *et al.* 1995). The presence of clay minerals and weathering products, in particular, are problematic because of their variable composition. Weathering products and organic matter are much more abundant in the soil compared to the non-pedogenic parent material for which NORMA was intended. The NORMA values for HAS and goethite (Table 2) should therefore be taken as only indicative of the abundance of final weathering products.

It is difficult, if not impossible, to quantify the uncertainty in the weathering rate values associated with each method. The chemical composition (stoicheiometry) of the minerals used in NORMA (Räisäsen *et al.* 1995) and PROFILE (Hodson *et al.* 1997) are different. NORMA is unable to distinguish muscovite and, if present, it is incorporated into orthoclase (Räisäsen *et al.* 1995). Similarily, NORMA allocates vermiculite mostly to chlorite. According to Tarvainen *et al.* (1996), NORMA hornblende refers to amphiboles and pyroxenes, which have many features in common. Enstatite is the only amphibole specifically distinguished by NORMA. PROFILE hornblende should presumably include also other amphiboles and it is unclear why garnet should be included in PROFILE since garnet is an accessory mineral and resistant to weathering. The Ca + Mg/temperature sum regression method does not explain all the variance in base cation loss ($R^2 = 74\%$ for Ca and 79% for Mg). A number of factors involved, including the distribution of elements and minerals in the soil profile, the particle size fraction on which the total analysis or mineralogy is determined, and the thickness of the weathering layer, are all subject to sampling and measurement error. Uncertainty in weathering rates associated with PROFILE input parameters has been investigated by Jönsson *et al.* (1995), and a critical evaluation of the structure and formulation of the model itself has been made by Hodson *et al.* (1997). The documentation for PROFILE input parameters are ambiguous, particularly concerning soil moisture saturation, movement, and the definition of particle size fractions. In running the PROFILE model, we used catchment runoff and not the soil water flux, since this data is not presently available. The soil water flux, however, is central to weathering and leaching processes.

Nevertheless, and in spite of all the uncertainties mentioned above, the weathering rates calculated by the various methods were rather similar to each other (Fig. 4). The Zr depletion method gave the highest values and PROFILE the lowest. The values were also rather similar to that presented by Johansson and Tarvainen (1996) for tills in the Hietajärvi region using the Ca + Mg\temperature sum regression method, 22–25 mmol$_c$ Ca + Mg m^{-2} a^{-1}.

Catchment weathering rates based on input-output budgets were found both higher and lower than soil weathering rates (e.g. April *et al.* 1986, Bain *et al.* 1990). Catchment budget values may be expected to give higher values because they include cations released from the weathering of the entire drift deposit and from the surface of the bedrock (Hornung *et al.* 1986). It was argued that catchment budget values include exchangeable cations, but this fraction is likely to be balanced by cations released by weathering and maintaining the exchangeable cation pool in steady-state (Cronan 1985). Conversely, catchment budget values may be less than soil weathering rates because the latter represent long-term averages. The presence of fresh and easily weatherable minerals and surfaces is now less compared to immediately after deglaciation.

It may also be argued that the estimates of base cation weathering loss should be reduced by the amount of atmospheric base cation deposition. The annual deposition of Ca and Mg collected in the open at Hietajärvi averaged ca. 5 mmol$_c$ m^{-2} during 1989–91 (Ruoho-Airola 1995). Presumably, the weathering rates given by PROFILE are corrected for deposition since base cation deposition values are given as input. This would explain, at least partly, the lower weathering rate obtained with PROFILE compared to the values obtained by the other methods (Fig. 4).

The weathering rate of the soil calculated using PROFILE is the current weathering rates in principle. Lång (1995) reported lower Zr depletion weathering rates than those obtained with PROFILE in a Swedish study. The author attributed the difference to possible differences in the elemental concentrations of different particle size fractions, the amounts of which vary among the till types studied. Tarvainen (1995) found concentrations of total Ca and Mg in the < 0.06-mm fraction of Finnish tills to be higher than in < 2-mm fraction, but to be strongly correlated.

Comparison of the plot weathering rates in Figure 3 show that they decreased in the order: 1 > 2 > 4 > 5. The difference is the strongest with the results of Zr depletion method. The proportion of fines (< 0.06 mm) in the < 2 mm soil was 44%, 26%, 13% and 20% respectively for plots 1, 2, 4 and 5. The fines values refer to the 20–40 cm layer at plots 1, 4 and 5 and to the 5-20 cm layer at plot 2. The above order in plot weathering rates therefore appears to be more related to the amount of fines in the soil than to the type of parent material (i.e. glacifluvial *vs.* till).

Most weathering studies apparently do not correct for soil stone content. Forest soils in Finland are typically very stony (~ 40% v/v) (Viro 1959), and failure to correct for this can be expected to result in a corresponding overestimation of weathering rates. The values we have presented have been corrected for stone content (0.005 m^3 m^{-3} for plots 1, 4 and 5, and 0.167 m^3 m^{-3} for plot 2). This correction had little effect in the case of plots 1, 4 and 5 but resulted in a 17 per cent reduction in the uncorrected weathering rate of Ca + Mg in the case of plot 2. The problem of stone content needs to be addressed if estimates of weathering rates are to be more realistic. We have now sampled and described several more profiles and hope in the near future to be able to obtain a better estimate of the average weathering rate for the catchment.

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