

The effect of site fertility and climate on current weathering in Finnish forest soils: Results of a 10–16 year study using buried crushed test-rock material

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ABSTRACT

Knowledge of the weathering rates in forest soils is needed when nutrient balances and the sustainability of silvicultural practices are estimated. The effects of site fertility and climate on weathering rates were studied in boreal coniferous forest soils in Finland by following transformations in crushed rock (Spectrolite, a dark, anorthosite feldspar dominated gabbro) confined in porous bags inserted into E-, B- and C-horizons along fertility and climate gradients, and left to weather for 10, 11 or 16 years. Organic carbon (OC) was accumulated in E-horizon incubated crushed test-rock material and it was more acidified and weathered than that deeper in the soil. There was a tendency for faster weathering of the C-horizon bags in the fertile sites than in the poor sites. Multivariate analyses indicated that more OC was accumulated in the bags in fertile sites than in poor sites, and that the crushed rock was more weathered in north than in south Finland although temperature sum and precipitation decreased northwards. The results suggest that humidity is an important climatic factor determining weathering rates and that fertile sites have greater potential to release base cations through weathering and sequester C to mineral surfaces than do poor sites.

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1. Introduction

Weathering determines soil formation, the supply of plant-available mineral nutrients, and the capacity of soils to buffer acidification (Birkeland, 1999). Weathering rates in soil are dependent on texture and mineralogy of parent material, soil age, vegetation, atmospheric deposition, and climate, principally temperature and moisture conditions (Augusto et al., 2000, 2001; Birkeland, 1999; Johnson-Maynard et al., 2005; Kump et al., 2000; Lundström and Öhman, 1990; Starr and Lindroos, 2006; van Breemen et al., 2000; White and Brantley, 1995). While it is uncertain how sensitive weathering rates will be to climate change weathering plays an important but often ignored role on the nutrient balance and productivity of forest ecosystems.

The supply of plant available mineral nutrients, primarily Ca^{2+} , Mg^{2+} and K^{+} cations, to the soil exchange system and plants is ultimately related to the weathering of soil minerals. Timber harvesting removes mineral nutrients from the soil, which may result in a decrease of soil fertility if the nutrient losses are not replenished through atmospheric deposition and mineral weathering. Sustainable forest management requires that the amount of nutrients exported in the harvested biomass does not exceed the replenishment rate. The use of logging residues

and stumps for biofuel has increased considerably during recent years in Finland (Peltola, 2009). Whole-tree harvesting results in a 3–5 times greater loss of nutrients than conventional stem-only harvesting (Röser et al., 2008); however little is known about the capacity of soils to replenish mineral nutrients through weathering and how weathering varies with site fertility and location (climate) in boreal forests. The rates of mineral nutrients released from minerals in the soil through weathering can be determined by means of laboratory experiments, catchment input–output budgets, soil profile elemental and mineral depletion methods and modelling (Jacks, 1990; Melkerud et al., 2003; Olsson and Melkerud, 2000; Starr and Lindroos, 2006; Starr et al., 1998; Sverdrup and Warfvinge, 1993). Laboratory experiments do not correspond to the conditions in the field and weathering rates derived in the laboratory experiments are often several orders of magnitude higher than those inferred from field studies (White and Brantley, 2003). The disadvantage of the catchment mass balance approach is that it requires a lot of accurate data on various elemental fluxes. Soil profile elemental and mineral depletion methods, in turn, represent long-term average weathering rates rather than the current rates (Melkerud et al., 2003; Olsson and Melkerud, 2000; Starr and Lindroos, 2006). The buried test-mineral (rock) method, however, provides means to study the current weathering rates in the soil in relation to prevailing conditions and without the need for detailed biogeochemical measurements (Augusto et al., 2001; Hatton et al., 1987; Jamet et al., 1996; Ranger and Nys, 1994; van Rompaey et al., 2007). The test-mineral (rock) method consists of burying porous bags containing homogenous test-mineral (rock) material in the soil and determining the changes in elemental composition after a defined time period.

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Table 1

General properties of the horizons at the Calluna type (CT), Vaccinium type (VT), Myrtillus type (MT) and Oxalis-Myrtillus type (OMT) sites.

Soil horizon	CT			VT			MT			OMT		
	E	B	C	E	B	C	E	B	C	E	B	C
pH ^a	4.07	4.67	4.94	3.59	4.64	4.88	3.58	4.55	4.76	3.49	4.39	4.64
CEC _e ^b	1.70	0.68	0.29	1.60	0.79	0.31	1.90	1.13	0.52	1.60	1.55	0.63
BS (%) ^c	10	13	29	7	14	30	8	15	29	11	11	18
Silt (%) ^d	4.1	3.2	1.4	6.1	4.5	2.7	8.9	7.6	11.2	10.6	9.0	14.1
Sorting ^e	2.08	2.01	1.82	2.11	2.06	1.87	2.67	2.49	2.61	2.67	2.72	3.22

^a 0.01 M CaCl₂ = 1: 2.5 (v/v).

^b Ca + Mg + H + Al extracted by 1 M KCl.

^c Σ (Ca, Mg) * 100 / CEC_e.

^d The proportion of silt-sized particles (2–60 µm); determined using the pipette method.

^e Sorting index = $\sqrt{D_{75}/D_{25}}$, where D₇₅ and D₂₅ are particle diameters corresponding to the upper and lower quartile cumulative particle size percentage, respectively.

In this study we have determined current weathering rates in Finnish forest soils using the test-rock method. Our objectives were to determine the chemical changes in the test-rock as a result of *in situ* weathering and how the changes vary in relation to incubation depth, incubation period, site fertility, soil properties, and climatic conditions. The results indicate the potential of different sites to replenish plant available Ca, Mg and K through weathering. To our knowledge, this is the first published study of the current weathering rates in boreal coniferous forests determined using the test-rock method.

2. Materials and methods

2.1. Study sites

2.1.1. Fertility gradient

The effect of site fertility on current weathering rates was studied by burying crushed test-rock in the soil of site of differing fertility

(stand productivity). The sites were located in a 400 km² area near the Helsinki University Forestry Station, Hyytiälä (61° 48' N, 24° 19' E), in southern Finland.

The soils are podzols and parent material consisted of either till or glacial deposits sorted by wind or glaciofluvial action (Table 1). The ice sheet from the last glaciation melted away from the area 9500–11,000 years ago and the highest post-glacial shore-line is some 160 m above the present sea level (Eronen and Haila, 1981). As the elevation of the study sites ranged from 120 m to 176 m above present sea level, both sub- and supra-aquatic sites are included in the study. The bedrock of the area is mainly acidic granite, granodiorite and mica-gneiss with some small intrusions of gabbro and peridotite. The sites were flat or slightly southward facing.

The sites ranged from xeric and nutrient poor *Calluna* (CT) through sub-xeric *Vaccinium* (VT) and mesic *Myrtillus* (MT) to moist fertile herb-rich *Oxalis-Myrtillus* (OMT) site types. The site types are according to the Finnish forest site type classification, which classifies the site productivity of a site on the basis of the composition of the ground vegetation (Cajander, 1925; Mikola, 1982; Nieppola and Carleton, 1991). The average annual volume growth of managed Scots pine stands in southern Finland for typical CT, VT, MT and OMT sites is 3.0, 4.0, 5.5 and 6.5 m³ ha⁻¹, respectively (Hotanen et al., 2008). The tree stands of the CT and VT site types in our study were dominated by Scots pine (*Pinus sylvestris* L.), while the OMT site types were dominated by Norway spruce (*Picea abies* Karsten). The MT sites had spruce or pine dominated stands. The mean annual air temperature in the study area was 3.8 °C, annual effective (>5 °C) temperature sum 1191 °C and amount of precipitation 645 mm during the 11-year study period (1988–1999). Respective values for the 16-year study period (1988–2004) were 3.9 °C, 1215 °C and 644 mm.

2.1.2. Climate gradient

The effect of climate on weathering was studied by incubating crushed test rock material buried in the soil in four areas (Tammela,

Table 2

Background information of the climate gradient study sites. Latitudes (Lat.) and longitudes (Long.) are expressed in decimal degrees. The pH, effective cation exchange capacity (CEC_e), base saturation (BS), the proportion of silt-sized particles and sorting index of parent material. Annual temperature, temperature sum (>5 °C, degree-days) and precipitation are annual mean values (± SE) for the years 1994–2004. Climate data for study sites was calculated by using the model by Ojansuu and Henttonen (1983).

Study area	Lat.	Long.	Elevation	Tree	Site	Site	pH ^c	CEC _e	BS ^e	Silt ^f	Sorting ^g	Annual temperature	Temperature sum	Precipitation
	°N	°E	(m a.s.l.)	sp.	type ^a	index ^b		cmol ₍₊₎ kg ⁻¹ d	(%)	(%)		(°C)	(d.d.)	(mm)
Tammela	60.73	24.08	123	Pine	CT	22.7	5.09	0.10	80.2	0.6	1.97	4.6 (0.18)	1346 (30)	636 (24)
Tammela	60.75	24.08	125	Pine	CT	22.4	5.02	0.15	87.5	0.8	1.78	4.6 (0.18)	1342 (31)	635 (24)
Tammela	60.65	23.88	113	Spruce	MT	20.9	4.86	0.61	64.8	19.6	3.25	4.8 (0.18)	1367 (31)	640 (25)
Ähtäri	62.75	23.88	185	Pine	CT	16.8	4.93	0.05	59.2	0.2	1.35	3.2 (0.19)	1143 (31)	613 (17)
Ähtäri	62.75	23.87	180	Pine	CT	17.1	4.91	0.05	65.4	0.4	1.46	3.2 (0.19)	1146 (31)	613 (17)
Ähtäri	62.77	23.87	185	Pine	CT	16.6	4.92	0.06	63.0	0.4	1.49	3.2 (0.19)	1142 (31)	610 (17)
Ähtäri	62.67	24.13	175	Spruce	MT	24.5	4.81	0.20	52.0	10.5	2.73	3.3 (0.19)	1161 (31)	633 (16)
Vaala	64.55	27.00	138	Pine	ECT	14.3	4.81	0.09	18.8	0.5	1.62	2.4 (0.19)	1123 (25)	583 (23)
Vaala	64.57	26.43	138	Pine	ECT	16.0	4.77	0.03	19.3	0.7	1.39	2.0 (0.19)	1081 (26)	556 (24)
Vaala	64.57	26.65	108	Spruce	MT	16.9	4.57	0.23	19.2	9.0	1.87	2.2 (0.19)	1107 (25)	566 (23)
Vaala	64.57	26.62	105	Spruce	MT	16.3	4.65	1.30	81.7	25.3	2.68	2.2 (0.19)	1107 (25)	564 (23)
Vaala	64.60	27.17	133	Spruce	MT	15.8	5.88	0.11	51.7	7.6	2.36	2.0 (0.19)	1080 (25)	594 (23)
Pelkosenniemi	67.08	27.38	163	Pine	MCCIT	13.1	4.67	0.27	16.6	3.1	1.84	0.0 (0.24)	872 (26)	557 (24)
Pelkosenniemi	66.63	27.70	155	Pine	MCCIT	14.0	4.96	1.10	91.1	5.0	2.25	0.6 (0.24)	941 (25)	556 (26)
Pelkosenniemi	67.07	27.43	160	Spruce	HMT	13.8	4.39	0.52	43.4	8.0	1.69	0.0 (0.24)	873 (26)	557 (24)
Pelkosenniemi	67.02	27.72	175	Spruce	HMT	9.5	4.52	0.67	54.9	6.9	2.15	0.0 (0.24)	863 (25)	558 (24)
Pelkosenniemi	66.95	27.72	195	Spruce	HMT	8.1	4.51	0.46	52.6	5.1	2.09	0.0 (0.24)	861 (25)	558 (24)
Pelkosenniemi	67.00	27.72	225	Spruce	HMT	9.5	4.71	0.48	59.1	7.9	2.12	0.2 (0.24)	838 (25)	559 (24)

^a Xeric nutrient poor heath forests: CT = *Calluna*, ECT = *Empetrum-Calluna*, MCCIT = *Myrtillus-Calluna-Cladonia* types, and mesic moderately fertile heath forests: MT = *Myrtillus* and HMT = *Hylocomium-Myrtillus* types.

^b Dominant height of trees (m) at an age of 100 years.

^c 0.01 M CaCl₂ = 1: 2.5 (v/v).

^d Sum of Ca, Mg and exchangeable acidity extracted by 1 M BaCl₂.

^e Σ (exchangeable Ca, Mg) * 100 / CEC_e.

^f Particle size fraction 2–60 µm; determined using the pipette method.

^g Sorting index = $\sqrt{D_{75}/D_{25}}$, where D₇₅ and D₂₅ are particle diameters corresponding to the upper and lower quartile cumulative particle size percentage, respectively.

Vaala, Ähtäri and Pelkosenniemi) forming a 800 km-long latitudinal transect from south to north Finland (61–67° N). In total there were 18 sites all having soils of similar age, parent material, vegetation and topography (Table 2). The sites were selected using information gained from geological and soil maps, soil uplift curves and forest inventory data. The sites became deglaciated and subject to weathering and soil formation 9300–10,900 years ago. All sites are subaquatic and have flat topography. Soils were podzols and the parent material is glacial till derived from acidic bedrock material. Half of the sites were Scots pine stands and the other half Norway spruce stands. The stands were mature (approximately 100-years-old) and the site types were CT or MT (and corresponding site types (Table 2).

2.2. The test-rock bags

Crushed spectrolite, the commercial name for a coarse grained, non foliated deep grey to black gabbro dominated (>80%) by labradorite from Ylämaa, southeastern Finland, was used as the standard rock (Table 3). Labradorite is a sodium–calcium plagioclase feldspar ($\text{Na}(\text{AlSi}_3\text{O}_8)\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$). There was a small difference in the composition of the crushed rock used in the fertility and climate gradient studies (Table 3, Figs. 1–3).

The rock material was crushed, sieved and <2.0 mm fraction used in the study. In each plot 100–150 cm³ sized test-mineral samples were placed in 10 cm × 15 cm bags made from polypropylene geotextile (DuPont, Typhar SF32) with a mean mesh size of 140 µm. After digging a soil pit in a representative point in each stand the bags containing the crushed rock material were inserted horizontally into the soil profile at various depths and the pit back filled to be as similar to the original soil profile as possible.

The fertility gradient bags were inserted in replicate in 30 study sites at the surface of the E-horizon (mean ± SD depth 4.6 ± 2.4 cm), into upper part of the B-horizon (mean ± SD depth 20.3 ± 6.6 cm), and into the C-horizon (mean ± SD depth 50.4 ± 13.5 cm) on August 1988. One set of bags was retrieved in June 1999 (11 year study) and the other set in June 2004 (16 year study). Some of the bags were destroyed or they were not found because clear-cuttings and soil preparation had been carried out at some sites during the study. As a result, the 11-year incubated bags were retrieved from 22 of the original 30 study sites (6 CT, 6 VT, 6 MT and 4 OMT site types) and the 16-year incubated bags retrieved from 20 of the study sites (5 CT, 5 VT, 6 MT and 4 OMT site types).

For the climate gradient experiment a single set of bags were inserted underneath the humus layer on top of the E-horizon (mean ± SD depth 4.4 ± 1.5 cm), into upper (mean ± SD depth 7.4 ± 4.3 cm) and lower (mean ± SD depth 22.3 ± 6.7 cm) B-horizon, and into the C-horizon (mean ± SD depth 56.6 ± 18.8 cm) at the 18 study sites in June 1994. The bags were retrieved after 10 years of incubation in June 2004.

Table 3
Major element composition (wt.%) of the test-rock before incubation determined by XRF.

Element	Fertility gradient	Climate gradient
SiO ₂	53.72	54.03
TiO ₂	0.76	1.15
Al ₂ O ₃	24.98	21.79
FeO	3.77	6.47
MnO	0.05	0.10
MgO	1.15	1.96
CaO	10.31	9.16
Na ₂ O	4.18	3.79
K ₂ O	0.91	1.31
P ₂ O ₅	0.18	0.23

2.3. Laboratory analyses and calculations

Each incubated sample and five samples of the non incubated crushed rock (representing the initial unweathered state) were analysed for the following properties. Organic carbon (C) concentrations were determined with a CN analyzer (Leco CNS-1000). Exchangeable cations were determined by extracting samples with 100 ml of 0.1 M BaCl₂ solution. After shaking the suspensions they were filtered through a 0.45-µm filter (Millipore HAWP 47 mm) with vacuum and subsample taken for immediate measurement of pH (pH BaCl₂) and determination of the exchangeable H⁺ and exchangeable acidity ($\text{Al}^{3+} + \text{H}^{+}$) by titration with 0.02 M NaOH to pH 7. Concentrations of Al^{3+} , Ca^{2+} and Mg^{2+} were determined using an atomic absorption spectrophotometer (AAS) (Perkin-Elmer 5100 PC) and K⁺ by flame photometer (Corning Flame Photometer 410). Effective cation exchange capacity (CEC_e) was calculated by summing exchangeable acidity and exchangeable base cation (Ca, Mg and K) concentrations and base saturation calculated by dividing the sum of base cations (Ca, Mg and K), by CEC_e, and expressed as a percentage. Total Al, Ca, Mg and K concentrations were determined from a HNO₃–H₂O₂ digestion using an ICP atomic emission spectrophotometer. Amorphous (non-crystalline) iron and aluminium oxides and organically complexed Fe and Al were extracted with 0.2 M acid (pH 3) ammonium oxalate. Samples were shaken with the oxalate buffer solution (sample/solution ratio 1:50) for 4 h, after which they were centrifuged, filtered through a 0.45-µm filter (Millipore HAWP 47 mm) and then analysed with AAS (Perkin-Elmer 5100 PC).

2.4. Statistical analyses

Differences in the measured properties of the incubated crushed rock samples between soil horizon, site type and, in the case of the fertility gradient experiment, incubation period compared to the properties of the unweathered material were tested with a linear mixed model (SPSS 16.0, SPSS Inc., Chicago, IL, USA) by using of which the possible correlation of observations can be taken into account (Littell et al., 1996). In the case of the fertility gradient experiment, the 11 and 16 year incubation data were considered as repeated measurements. As the data from different soil horizons in the same soil pit are spatially autocorrelated, the sites were treated as random effects. The models were fitted using an unstructured variance structure (UN) for repeated effects and identity variance structure (ID) for random effects.

The variables describing the degree of weathering (changes in pH and concentrations of carbon and calcium, exchangeable bases and exchangeable acids) and their relationships to environmental factors (latitude, cumulative temperature sum, cumulative precipitation, total C, N, and Ca pools in the soil to a depth of 1 m, and the pools of silt and sand in the soil to a depth of 1 m) were examined using principal component analysis (PCA) (Canoco for Windows 4.5 software). Data from both the climate and fertility (11 year data only) gradients were included in the analyses. Latitude, precipitation and temperature sum are taken to describe the effects of climate, soil C, N and Ca pools to 1 m depth to describe site fertility, and the amount of silt and sand fractions to describe soil hydraulic properties. Redundancy analysis (RDA) was used to analyse whether the relationships between the chemical changes of the crushed rock and environmental factors were significant and to estimate the relative influence of the individual factors. The significance of environmental factors was evaluated using Monte Carlo permutation tests with 499 random permutations. Differences were considered significant if $P \leq 0.05$.

3. Results

3.1. Changes in crushed test-rock

After incubation of the crushed test rock material, total concentrations of Ca and K, exchangeable concentrations of Ca, Mg, and K,

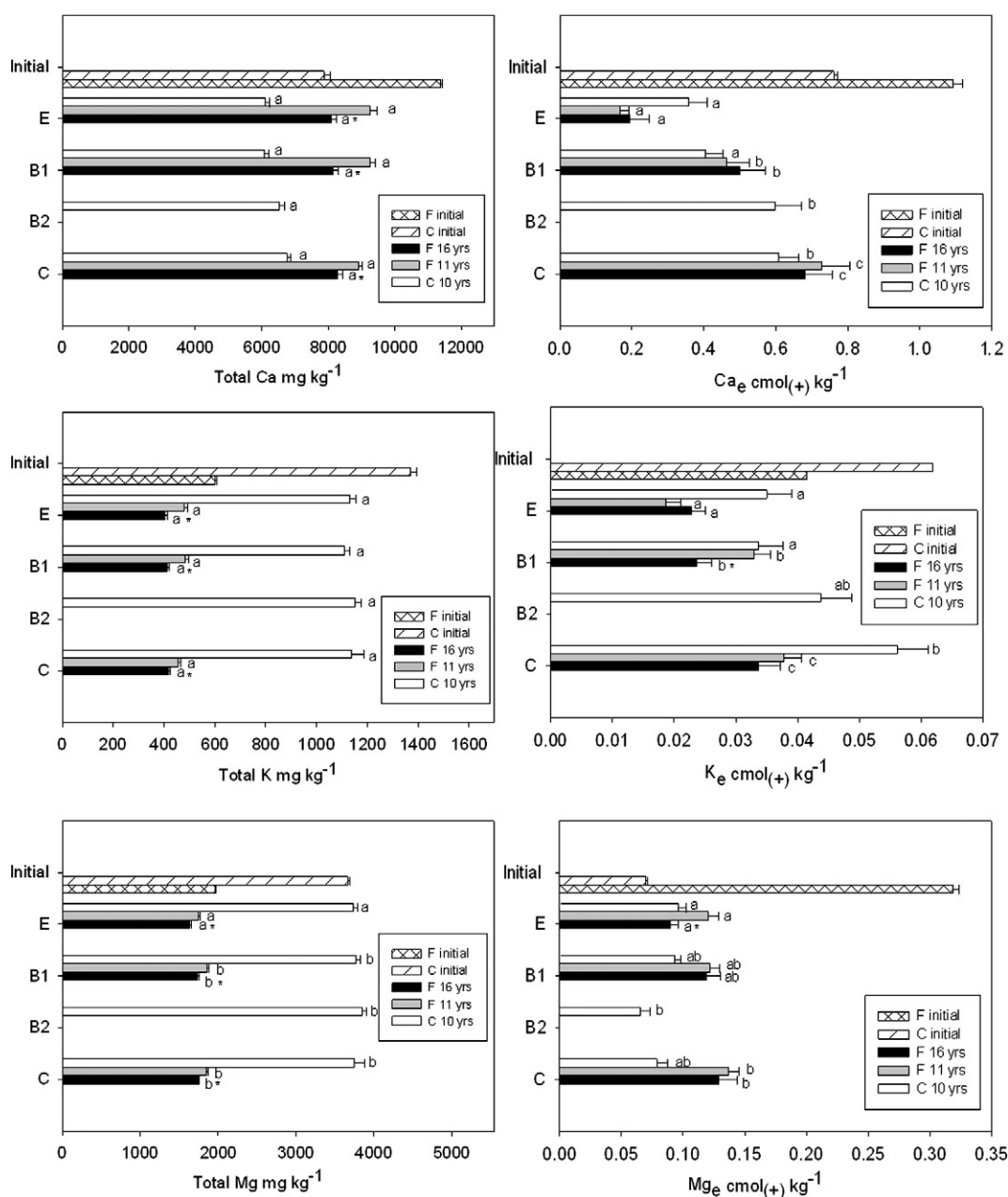


Fig. 1. Total and exchangeable calcium, magnesium and potassium concentrations (mean \pm SE) in the spectrolite test-rock before the experiment (Initial) and after 10, 11 and 16 years field incubations in the E-, upper part of B- (B1), lower part of B- (B2) and C- horizons collected samples in climate (C) and fertility (F) gradients (Initial $n=5$, climate gradient $n=18$, except 33 for the C-horizon, fertility gradient $n=22$ for 11 year data and $n=20$ for the 16 year data). The initial chemical composition of spectrolite that was used in the fertility and climate gradients differed slightly because spectrolite originated from a different batch. Statistically significant differences ($p<0.05$) among soil horizons are labelled with different letters. Bars labelled with * indicate statistically significant differences ($p<0.05$) between 11 years and 16 years incubated samples.

effective cation exchange capacity, base saturation and pH decreased and exchangeable acidity increased (Figs. 1 and 2). Total Mg concentrations remained nearly unchanged in the samples from the climate gradient and decreased slightly in the samples from the fertility gradient. The greatest changes in the test-rock occurred in the upper part of the soil profile. Total Ca, Mg and K concentrations in the E-horizon samples decreased on average by 29%, 17% and 33%, respectively, over the 16 year incubation period in the fertility gradient. Calcium and Mg were dominant cations on the exchange sites before incubation, accounting for 74% and 15% (mean for fertility and climate gradient) of CEC_e, respectively. After 10 (11) years, the proportion of exchangeable Ca was only 21% of CEC_e, that of Mg 9% and that of exchangeable acidity had increased from 7% to 68% in the E-horizon samples. Compared to the CEC_e of 1.26 cmol(+) kg⁻¹ (mean for fertility and climate gradient) of

the initial material, incubation decreased the cation exchange capacity of the crushed test rock material by 2, 26, 32 and 24% respectively for the E, upper part of B, lower part of B and C-horizons. The initial base saturation was >90% but it decreased markedly during 10 and 11 years being only 23% and 49% in the E-horizon samples in fertility and climate gradient, respectively. Organic C accumulated in the E-horizon incubated test-rock material with concentrations increasing about threefold during the incubation in both fertility and climate gradients. The pH of the crushed test rock material declined from initial levels of 6 by about two pH units in the E- and the upper part of B-horizon incubated samples. Over the incubation period the concentrations of exchangeable and oxalate extractable Al increased, whereas total Al concentrations decreased (Fig. 3). Oxalate extractable Fe concentrations also increased but total Fe concentrations decreased slightly.

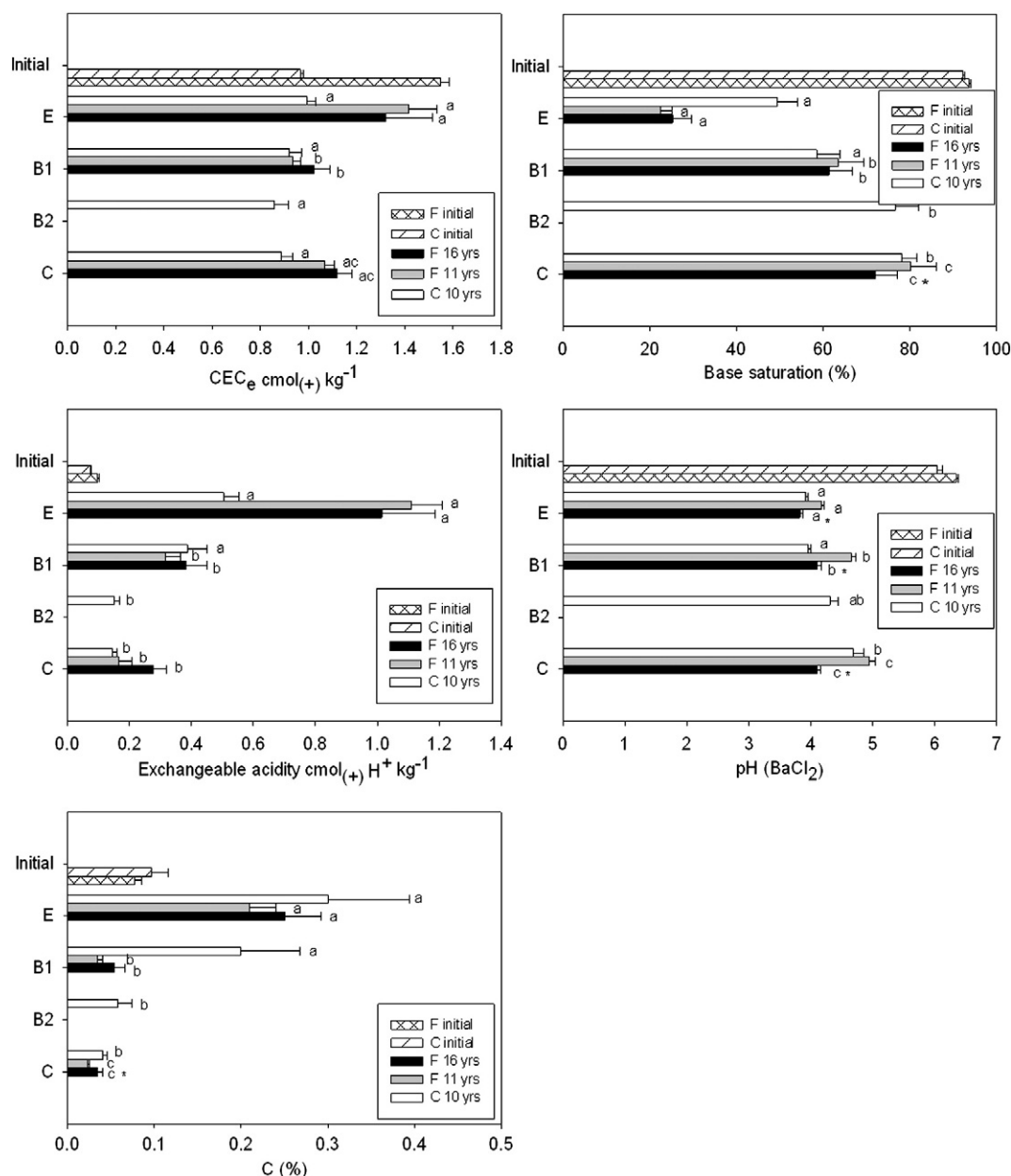


Fig. 2. Effective cation exchange capacity (CEC_e), base saturation, exchangeable acidity, pH and carbon concentration (mean ± SE) in the spectrolite test-rock before the experiment (Initial) and after 10, 11 and 16 years field incubations in the E-, upper part of B- (B1) and C-horizons collected samples in climate (C) and fertility (F) gradients (Initial $n=5$, climate gradient $n=18$, except 33 for the C-horizon, fertility gradient $n=22$ for 11 year data and $n=20$ for the 16 year data). The initial chemical composition of spectrolite that was used in fertility and climate gradients differed slightly because spectrolite originated from a different batch. Statistically significant differences ($p<0.05$) among soil horizons are labelled with different letters. Bars labelled with * indicate statistically significant differences ($p<0.05$) between 11 years and 16 years incubated samples.

3.2. Effect of incubation depth

The greatest changes in the test-rock occurred in the upper part of the soil profile (Figs. 1–3). In the E-horizon and the upper B-horizon incubated samples had significantly higher exchangeable acidity and C and exchangeable Al concentrations, and significantly lower pH, base saturation and the concentrations of exchangeable Ca and K than in the C-horizon incubated samples. The E-horizon incubated samples also had significantly higher oxalate extractable Fe and Al concentrations. Total Mg concentrations were significantly lower in E- than in B- and C-horizon incubated samples. Total Al concentrations were significantly higher in E-horizon than in C-horizon samples but total Fe, Ca and K concentrations did not differ between horizons.

3.3. Effect of site fertility

The test-rock samples that were incubated in the E-horizon did not differ statistically significantly between site types in any of the variables that were studied (Tables 4 and 5). In the B-horizon incubated test-rock samples, base saturation and the concentrations of exchangeable Ca were significantly lower in the CT than VT sites. Also CEC_e was significantly lower in the CT sites compared with both VT and MT sites. In the C-horizon, OMT site differed significantly from all other site types with respect to exchangeable acidity, base saturation and the concentrations of exchangeable Ca. The C-horizon samples had also significantly higher exchangeable Al concentrations and lower CEC_e in the OMT than CT and VT sites. Furthermore, exchangeable K concentrations of C-horizon samples were significantly lower in the OMT than CT

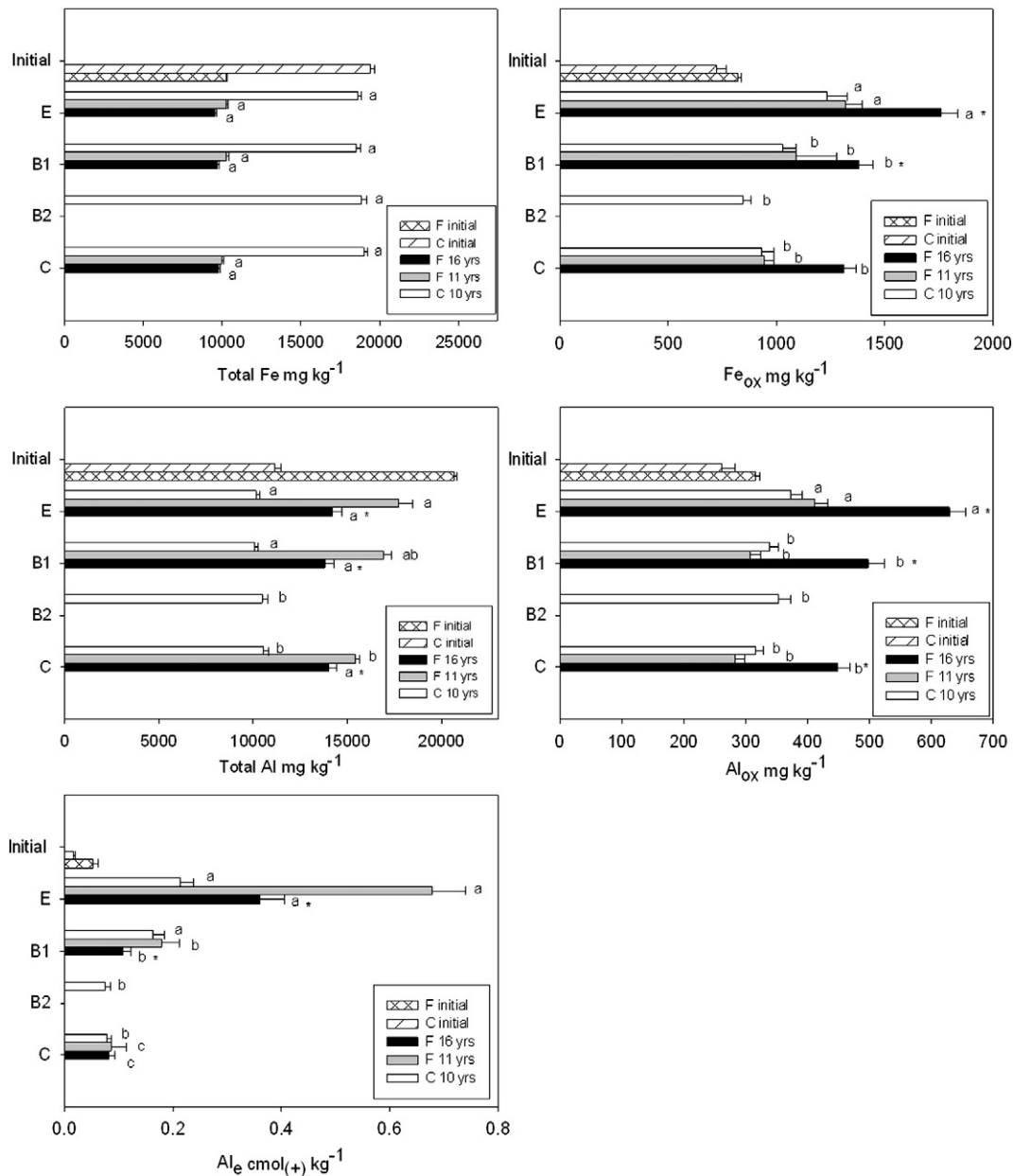


Fig. 3. Total and oxalate extractable iron concentrations, and total, exchangeable and oxalate extractable aluminium concentrations (mean \pm SE) in the spectrolite test-rock before the experiment (Initial) and after 10, 11 and 16 years field incubations in the E-, upper part of B- (B1), lower part of B- (B2) and C-horizons collected samples in climate (C) and fertility (F) gradients (Initial $n = 5$, climate gradient $n = 18$, except 33 for the C-horizon, fertility gradient $n = 22$ for 11 year data and $n = 20$ for the 16 year data). The initial chemical composition of spectrolite that was used in the fertility and climate gradients differed slightly because spectrolite originated from a different batch. Statistically significant differences ($p < 0.05$) among soil horizons are labelled with different letters. Bars labelled with * indicate statistically significant differences ($p < 0.05$) between 11 years and 16 years incubated samples.

sites. Carbon concentrations, pH, exchangeable Mg concentrations and total Ca, Mg, K, Al and Fe concentrations did not differ statistically significantly between site types in any soil horizon.

3.4. Effect of incubation period

The effect of incubation period on weathering was studied in the fertility gradient by comparing the changes in properties of the two incubation periods (11 and 16 years). Total Ca concentrations were significantly lower in 16 than 11 years incubated samples in all soil horizons, but the exchangeable Ca concentrations did not differ between incubation periods (Fig. 1). Also total Mg concentrations were significantly lower in 16 than 11 years incubated samples in all soil horizons but exchangeable Mg concentrations were significantly lower

only in the E-horizon samples after 16 than 11 years incubation. Total K concentrations were significantly lower in 16 than 11 years incubated samples in all soil horizons but exchangeable K concentrations were significantly lower only in the B-horizon samples after 16 than 11 years incubation. Samples incubated in the soil for 16 years had significantly lower pH than those left for 11 years in all soil horizons (Fig. 2). Carbon concentrations and base saturation differed statistically significantly between 16 and 11 years incubated samples only in the C-horizon. Exchangeable acidity and CEC_e did not differ significantly between 11 and 16 year incubated samples. Samples left in the soil for 16 years had significantly lower total Al concentrations and significantly higher oxalate extractable Al concentrations in all soil horizons compared with those left for 11 years (Fig. 3). The concentrations of exchangeable Al, in turn, were significantly lower in both E- and

Table 4
Mean (\pm SE) total (Tot mg kg⁻¹) and exchangeable (e, cmol kg⁻¹) concentrations of calcium, magnesium and potassium, effective cation exchange capacity (CEC_e cmol kg⁻¹) and base saturation (%) in the test-rock after 11 and 16 years incubation in E-, B-, and C-horizon samples at the *Calluna* type (CT), *Vaccinium* type (VT), *Myrtillus* type (MT) and *Oxalis-Myrtillus* type (OMT) sites.

		CT		VT		MT		OMT	
		11 years	16 years	11 years	16 years	11 years	16 years	11 years	16 years
Ca _{Tot}	E	9350.7 (327)	8007.7 (264)	9747.6 (407)	8188.4 (268)	8481.9 (293)	8036.2 (225)	9581.5 (602)	8216.8 (653)
	B	9569.3 (367)	7634.3 (256)	9153.3 (199)	8088.8 (237)	9039.5 (340)	8404.2 (306)	9248.0 (364)	8407.5 (549)
	C	8916.3 (150)	8097.5 (300)	9017.9 (281)	7956.4 (243)	8811.6 (159)	8561.8 (322)	8684.5 (208)	8465.4 (359)
Ca _e	E	0.16 (0.08)	0.12 (0.05)	0.12 (0.01)	0.18 (0.12)	0.21 (0.05)	0.28 (0.12)	0.18 (0.04)	0.19 (0.13)
	B	0.30 (0.06)	0.29 (0.04)	0.69 (0.07)	0.73 (0.09)	0.40 (0.15)	0.57 (0.14)	0.45 (0.24)	0.39 (0.22)
	C	0.89 (0.06)	0.83 (0.04)	0.88 (0.08)	0.89 (0.08)	0.70 (0.19)	0.29 (0.02)	0.30 (0.18)	0.26 (0.18)
Mg _{Tot}	E	1788.3 (10)	1662.8 (38)	1757.8 (22)	1629.8 (31)	1723.8 (51)	1619.3 (46)	1727.0 (24)	1618.0 (37)
	B	1825.8 (24)	1705.8 (42)	1906.5 (45)	1781.6 (13)	1877.7 (50)	1751.3 (31)	1832.0 (36)	1702.5 (40)
	C	1863.0 (24)	1750.0 (37)	1888.7 (30)	1741.0 (16)	1823.3 (28)	1777.7 (39)	1781.0 (46)	1700.0 (31)
Mg _e	E	0.10 (0.01)	0.06 (0.01)	0.10 (0.01)	0.09 (0.01)	0.14 (0.02)	0.10 (0.01)	0.15 (0.01)	0.10 (0.02)
	B	0.12 (0.01)	0.09 (0.01)	0.14 (0.01)	0.13 (0.02)	0.11 (0.02)	0.14 (0.02)	0.12 (0.01)	0.11 (0.03)
	C	0.14 (0.07)	0.11 (0.01)	0.15 (0.02)	0.13 (0.02)	0.12 (0.02)	0.15 (0.02)	0.13 (0.03)	0.12 (0.07)
K _{Tot}	E	484.9 (24)	380.8 (22)	510.2 (33)	414.6 (13)	429.5 (18)	414.4 (11)	497.1 (40)	400.0 (42)
	B	506.1 (30)	388.4 (18)	472.1 (13)	405.9 (9)	480.2 (26)	433.9 (15)	480.6 (29)	420.9 (30)
	C	464.6 (15)	402.2 (18)	454.1 (22)	405.8 (11)	455.0 (12)	425.0 (21)	434.1 (13)	431.8 (22)
K _e	E	0.02 (0.004)	0.02 (0.002)	0.02 (0.002)	0.02 (0.002)	0.03 (0.006)	0.03 (0.006)	0.01 (0.002)	0.02 (0.005)
	B	0.03 (0.003)	0.02 (0.006)	0.04 (0.004)	0.02 (0.004)	0.03 (0.007)	0.03 (0.003)	0.03 (0.005)	0.03 (0.005)
	C	0.04 (0.004)	0.04 (0.009)	0.05 (0.003)	0.04 (0.006)	0.04 (0.005)	0.04 (0.006)	0.03 (0.008)	0.02 (0.003)
CEC _e	E	1.15 (0.09)	1.09 (0.18)	1.13 (0.12)	1.32 (0.36)	1.81 (0.32)	1.50 (0.53)	1.67 (0.16)	1.35 (0.37)
	B	0.87 (0.03)	0.78 (0.05)	1.02 (0.04)	1.12 (0.06)	0.92 (0.09)	1.19 (0.13)	0.93 (0.09)	0.97 (0.19)
	C	1.16 (0.03)	1.14 (0.04)	1.15 (0.03)	1.27 (0.06)	0.99 (0.11)	1.14 (0.11)	0.91 (0.11)	0.87 (0.21)
BS	E	26 (9.7)	18 (1.6)	22 (2.0)	26 (11.8)	21 (2.0)	33 (9.8)	20 (0.8)	22 (8.5)
	B	51 (7.8)	52 (5.6)	85 (4.5)	78 (2.0)	54 (13.4)	64 (11.0)	62 (20.8)	49 (19.1)
	C	92 (3.6)	86 (1.5)	94 (3.5)	83 (3.6)	79 (13.5)	73 (3.4)	44 (15.2)	39 (17.2)

B-horizon samples after 16 years of incubation than after 11 years of incubation. Total Fe concentrations did not differ between incubation periods but oxalate extractable Fe concentrations were significantly higher in E- and B-horizon samples after 16 years of incubation than after 11 years of incubation.

3.5. Effect of climate and other environmental factors

Temperature and precipitation progressively decreased from south to north along the climate gradient. The effective temperature sum

decreased from about 1300 dd to 800 dd, the mean annual temperature from about 4.7 °C to about 0 °C, and the mean annual precipitation from about 640 mm to about 550 mm (Table 2). The PCA ordination indicated that Ca loss from test-rock material and the proportion of the exchangeable acidity was greater in northern sites where temperature sum and precipitation are lower (Fig. 4). The proportion of exchangeable bases associated with the incubated crushed test-rock material was, in turn, greater in southern than in northern sites. Carbon accumulation on the crushed test-rock material was related to site fertility as shown by the parallel trend in soil N, Ca and C pools and increase in

Table 5
Mean (\pm SE) pH (BaCl₂), organic carbon (C) concentrations (%), exchangeable acidity (EA, cmol H₍₊₎ kg⁻¹) and total (Tot, mg kg⁻¹), exchangeable (e, cmol kg⁻¹) and ammonium oxalate extractable (ox, mg kg⁻¹) concentrations of aluminium and iron in the test-rock after 11 and 16 years incubation in E-, B-, and C-horizon samples at the *Calluna* type (CT), *Vaccinium* type (VT), *Myrtillus* type (MT) and *Oxalis-Myrtillus* type (OMT) sites.

		CT		VT		MT		OMT	
		11 years	16 years	11 years	16 years	11 years	16 years	11 years	16 years
pH	E	4.4 (0.09)	3.9 (0.10)	4.2 (0.05)	3.9 (0.11)	4.1 (0.10)	3.8 (0.03)	4.0 (0.05)	3.7 (0.09)
	B	4.5 (0.07)	4.0 (0.11)	4.8 (0.07)	4.4 (0.21)	4.7 (0.17)	4.0 (0.05)	4.7 (0.26)	3.9 (0.09)
	C	5.0 (0.17)	4.2 (0.17)	5.0 (0.11)	4.2 (0.06)	5.1 (0.19)	4.0 (0.01)	4.5 (0.16)	3.9 (0.12)
C	E	0.14 (0.029)	0.19 (0.043)	0.14 (0.026)	0.22 (0.041)	0.31 (0.089)	0.30 (0.114)	0.27 (0.049)	0.31 (0.110)
	B	0.03 (0.004)	0.04 (0.011)	0.04 (0.019)	0.06 (0.014)	0.04 (0.012)	0.04 (0.010)	0.02 (0.004)	0.08 (0.054)
	C	0.02 (0.003)	0.04 (0.019)	0.03 (0.006)	0.04 (0.009)	0.02 (0.002)	0.03 (0.003)	0.03 (0.003)	0.04 (0.009)
EA	E	0.87 (0.15)	0.88 (0.13)	0.88 (0.12)	1.03 (0.40)	1.43 (0.25)	1.10 (0.45)	1.33 (0.12)	1.0 (0.35)
	B	0.42 (0.07)	0.38 (0.06)	0.15 (0.05)	0.25 (0.02)	0.38 (0.11)	0.45 (0.19)	0.32 (0.18)	0.45 (0.20)
	C	0.09 (0.04)	0.16 (0.02)	0.06 (0.04)	0.21 (0.04)	0.14 (0.08)	0.29 (0.02)	0.46 (0.11)	0.48 (0.19)
Al _{Tot}	E	18015 (1227)	13838 (953)	19402 (1543)	14352 (706)	15150 (683)	14012 (813)	18688 (2173)	14858 (1997)
	B	18355 (1325)	12552 (773)	16230 (443)	13136 (701)	16347 (734)	14623 (919)	17028 (972)	14985 (1409)
	C	15410 (414)	13400 (646)	15403 (694)	12900 (773)	15497 (220)	14737 (940)	15453 (741)	15003 (1033)
Al _e	E	0.55 (0.09)	0.27 (0.02)	0.52 (0.08)	0.40 (0.11)	0.90 (0.13)	0.38 (0.11)	0.78 (0.11)	0.39 (0.09)
	B	0.22 (0.03)	0.10 (0.01)	0.07 (0.04)	0.08 (0.01)	0.24 (0.08)	0.12 (0.04)	0.19 (0.12)	0.12 (0.04)
	C	0.01 (0.01)	0.05 (0.01)	0.02 (0.01)	0.06 (0.02)	0.10 (0.05)	0.09 (0.02)	0.27 (0.09)	0.13 (0.04)
Al _{ox}	E	430.8 (44)	643.0 (40)	341.6 (43)	595.6 (52)	447.1 (21)	659.4 (68)	435.4 (50)	609.8 (27)
	B	278.0 (10)	506.9 (60)	263.1 (12)	441.6 (17)	374.5 (48)	495.4 (63)	320.1 (24)	560.3 (59)
	C	261.2 (20)	423.3 (26)	237.1 (15)	406 (40)	321.5 (42)	435.8 (39)	328.3 (32)	550.5 (40)
Fe _{Tot}	E	10220 (137)	9458 (324)	10425 (182)	9743 (230)	10072 (266)	9532 (207)	10495 (127)	9313 (219)
	B	10277 (167)	9195 (176)	10558 (281)	9953 (181)	10165 (316)	10050 (124)	10128 (295)	9628 (364)
	C	9971 (236)	9344 (303)	10352 (197)	9678 (165)	9725 (199)	10248 (147)	9613 (231)	9731 (133)
Fe _{ox}	E	1134.8 (108)	1602.7 (175)	1107.7 (44)	1920.3 (141)	1498.4 (201)	1820.5 (157)	1646.3 (60)	1661.6 (127)
	B	876.1 (84)	1418.0 (179)	832.9 (58)	1316.3 (111)	1629.8 (631)	1359.4 (114)	7884.4 (1103)	1439.9 (191)
	C	849.7 (32)	1267.1 (82)	835.2 (60)	1228.3 (75)	1000.7 (77)	1279.2 (98)	1166.3 (126)	1513.4 (195)

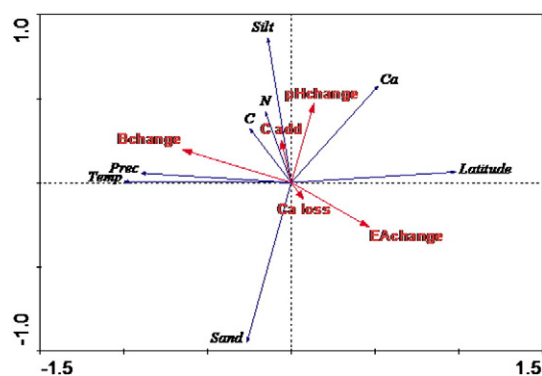


Fig. 4. Principal component analysis (PCA) ordination. The diagram shows the main patterns of variation in total calcium concentrations (Ca loss), exchangeable bases (Bchange, the sum of exchangeable Ca, Mg, K), exchangeable acidity (Echange), pH (pHchange) and carbon concentration (C add) of the E-horizon incubated test-rocks in relation to latitude, cumulative temperature sum (Temp), cumulative precipitation (Prec), soil carbon (C), nitrogen (N) and calcium (Ca) pools, and the proportion of silt- (Silt) and sand-sized (Sand) fractions in the soil. The values of test-rocks are the differences between initial and final concentrations.

the proportion of silt. Carbon concentrations are correlated with pH. The first axis accounted for 91% of the total variance.

RDA analysis indicated that latitude, cumulative precipitation, cumulative temperature sum, soil Ca, C and N pools and the proportion of silt and sand fractions explained 43% of the observed variation in the crushed test-rock material pH, C content, exchangeable acidity and concentrations of exchangeable bases and total Ca. The first axis explained 26% of the variation ($F = 10.871$, $P = 0.002$). Precipitation ($F = 10.72$, $P = 0.002$) and proportion of silt fraction in the soil ($F = 6.30$, $P = 0.004$) best explained the variation in crushed test-rock. Together these two variables accounted for 33% of the variation.

4. Discussion

The crushed test-rock material was significantly transformed during the incubation in the field. Base cations were lost resulting in a decrease in base saturation. However, CEC_e did not correspondingly decrease which can be attributed to the effect of the accumulation of organic C on the surfaces of the crushed test-rock material and increase in associated exchangeable acidity and lowered pH. The exchangeable base cations were largely replaced by Al^{3+} ions. Aluminium is the dominant exchangeable cation on soil exchange sites in podzolized forest soils (Tamminen and Starr, 1990). At least part of the increase in exchangeable Al came from the weathering of the crushed rock as concentrations of total Al (and Fe) decreased, indicating weathering losses from the primary minerals. Some of the Al and Fe released through weathering also appeared to have complexed with organic matter and precipitated on to the surfaces of crushed test-rock particles as oxalate extractable Al and Fe concentrations increased. All these observed changes reflect processes of podzolization (Lundström et al., 2000).

As previous studies (Augusto et al., 2000, 2001; Jamet et al., 1996), the closer the test-rock bags were to the top of the soil profile, the more the samples were weathered and acidified. This is related to the decrease in acidity and ionic strength of soil solution in contact with minerals that occurs with depth. Organic acids, produced by organic matter decomposition and root exudation, accelerate the dissolution of minerals (Lundström and Öhman, 1990; Raulund-Rasmussen et al., 1998), and their concentrations in soil solution are generally highest in the topsoil (Lundström et al., 2000).

The effect of site fertility was most pronounced for the test-rock samples incubated in the C-horizon. In the most fertile sites (OMT sites), the C-horizon test-rock samples had statistically significantly

lower exchangeable Ca and K concentrations, CEC_e and base saturation, and significantly higher exchangeable acidity and exchangeable Al concentrations than the least fertile sites (CT sites). The soil parent material at fertile sites is generally more fine-textured than at less fertile sites (Table 1) and the resulting slower percolation of water and longer contact times with the crushed test-rock material with organic acids explains the more intense weathering in the OMT sites. The differences in weathering between the site types may also partly be due to differences in tree species. The poorer sites are dominated by Scots pine and the more fertile sites dominated by Norway spruce (Table 1). Weathering has been found to be faster in Norway spruce stands than in Scots pine stands (Augusto et al., 2001) and due to the production of more acidic soil solutions (Ranger and Nys, 1994) and higher concentrations of dissolved organic carbon (Smolander and Kitunen, 2002) in spruce than in pine stands.

Organic C was sequestered onto the incubated test-rock material in the E-horizon. Organic matter can be bound to mineral surfaces via ligand change, anion-cation exchange and cation bridges (Mikutta et al., 2007). Sorption of organic matter to mineral surfaces accelerates the retention and stabilization of C making the organic matter less easily decomposed (Kaiser and Guggenberger, 2003; Kalbitz et al., 2005). Carbon concentrations in the E-horizon crushed test-rock samples were, on average, about two times higher in the MT and OMT sites than in the poorer sites (Table 5), reflecting the greater litterfall production (Starr et al., 2005) and soil carbon densities (Liski and Westman, 1995) of more fertile sites. The multivariate analysis indeed indicated that C concentrations in test-rock samples were positively related to soil C, N, and Ca pools and the proportion of silt fraction and negatively related to the proportion of sand fraction.

The incubated test-rock material in the north contained less total Ca and exchangeable bases and had higher concentrations of exchangeable acidity than the samples incubated in southern sites. As temperature, precipitation and acidifying atmospheric deposition decrease northwards (Joki-Heiskala et al., 2003), the greater weathering in the north is contrary to what one might have been expected. However, because evaporation is lower in higher latitudes, humidity and runoff are greater in north than in south Finland (Korhonen, 2007). The observed greater weathering in northern Finland may thus be due to greater percolation flows through the soil profile resulting in greater fluxes of weathering reactants arriving to and weathering products from the mineral surfaces.

The test-mineral (rock) method has been criticized on the grounds that it might not fully correspond to the real *in situ* weathering rate because the soil structure is disturbed when the bags are inserted, water flow and water contact can be lower for material in mesh bags than the surrounding soil, and the small size of the bag may not be representative of the bulk soil horizon (Augusto et al., 2000; Hatton et al., 1987). Such incubation experiments also require a long time and so cannot be used routinely to estimate the degree and rate of weathering. However, we found the method provided valuable information and insight about current pedological processes and the capacity of forest soils to replenish mineral nutrients through weathering in different site types and climatic conditions.

5. Conclusions

The study showed that site fertility and climatic conditions are important factors determining weathering rates and that weathering rates should be considered in evaluating the sustainability of mineral nutrient pools in the soil. The results show that the more fertile sites have greater potential to replenish the soil pool of exchangeable base cations and to sequester C to mineral surfaces than less fertile sites, and that greater humidity and percolation fluxes in north Finland may offset the effect of lower temperatures and result in faster weathering rates than in south Finland.

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