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GEODERMA

Geoderma 73 (1996) 1–21

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Received 6 July 1995; accepted 11 April 1996

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AN INTERNATIONAL JOURNAL OF SOIL SCIENCE

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Publication information
Geoderma (ISSN 0016-7061). For 1996 volumes 69–74 are scheduled for publication. Subscription prices are available upon request from the publisher. Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by surface mail except to the following countries where air delivery via SAL is ensured: Argentina, Australia, Brazil, Canada, Hong Kong, India, Israel, Japan, Malaysia, Mexico, New Zealand, Pakistan, PR China, Singapore, South Africa, South Korea, Taiwan, Thailand, USA. For all other countries airmail rates are available upon request. Claims for missing issues must be made within six months of our publication (mailing) date. Please address all your requests regarding orders and subscription queries to: Elsevier Science B.V., Customer Support Department, P.O. Box 211, 1000 AE Amsterdam, The Netherlands. Fax: +31-20-4853432.

US mailing notice – *Geoderma* (ISSN 0016-7061) is published montly by Elsevier Science B.V. (Molenwerf 1, Postbus 211, 1000 AE Amsterdam). Annual subscription price in the USA US$ 1482 (US$ valid in North, Central and South America), including air speed delivery. Application to mail at periodicals postage rate is pending at Jamaica, NY 11431.
USA POSTMASTERS: Send address changes to *Geoderma*, Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.
Airfreight and mailing in the USA by Publications Expediting.

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Abstract

Knowledge of rates of release of base cations from mineral dissolution (weathering) is essential to understand ecosystem elemental cycling. Although much studied, rates remain enigmatic. We compared the results of four methods to determine cation (Ca + Mg + K) release rates at five forested soils/sites in the northcentral U.S.A. Our premise was that multiple approaches, each with their own specific strengths and weaknesses, would yield a "best" overall estimate. We used (1) a cation input–output budget on a pedon scale; (2) trends in elemental and mineral depletion in silt-size particles; (3) a laboratory batch dissolution technique, with the results adjusted for field conditions; and (4) a steady-state soil chemistry model, PROFILE. The soils included a loamy sand Typic Udipsamment, a sandy loam Spodic Udipsamment, a fine sandy loam Typic Dystrochrept, a very fine sandy loam Glossic Eutroboralf, and a clayey Glossic Eutroboralf. Weathering rates varied among both soils and methods, and neither methods nor soils could easily be grouped; the data spanned a continuum with overlapping ranges of least significant differences. Although the assumptions necessary for some methods were better suited to specific soils, we rejected only one method–soil combination as being inappropriate (input–output budget for the clay). Mean release rates for the sum of cations ranged from 470 eq ha^{-1} yr^{-1} for the clayey soil, to 460 for the fine sandy loam soil, to 430 for the very fine sandy loam soil, to 375 for the sandy oam soil, to 195 for the loamy sand soil. These rates are lower than those reported for similar soils in the literature because most reported rates are based on watershed studies. Our low rates of cation release within soil pedons, the ultimate source of nutrient ions for plant growth, has mplications for estimated nutrient budgets and long-term soil sustainability.

1. Introduction

Knowledge of rates of cation release from the dissolution of primary and secondary minerals (weathering) is intrinsic to the understanding of forest nutrient relationships,

PII S0016-7061(96)00037-7

secondary mineral formation, buffering capacity of soils to acidification, soil water chemistry, and processes involved in surface water acidification. Intensive forest harvesting in the northern Lake States has generated concern with respect to the role of aspen (*Populus tremuloides* Michx. and *Populus grandidentata* Michx.), two commercially important species, in depleting some soils of calcium (Ca) and magnesium (Mg), and the consequent effects on long-term productivity (Alban, 1982; Federer et al., 1989; Ruark and Bockheim, 1987). The long-term ability of a soil to meet plant requirements for Ca and Mg is controlled by their rate of release by weathering. In spite of the importance of weathering rates within the solum, they are difficult to determine because they are extremely slow, weathering products are sequestered by secondary mineral formation, weathering occurs in open systems where inputs and outputs are uncertain, and initial states of the system are often indeterminate. The many studies that have attempted to quantify weathering rates can be categorized as (1) laboratory studies, (2) field studies, and (3) mathematical models.

Laboratory studies include (1) mineral dissolution experiments, (2) soil batch studies, and (3) soil column studies. Laboratory conditions allow variation in parameters such as pH, ionic strength, concentration and types of organic materials, surface area, and temperature. Mineral dissolution experiments emphasize individual mineral species and enhance understanding of weathering mechanisms. Differences in mineral composition (even within a single mineral species) and methodology inhibit direct comparisons among studies, but measured cation release rates are commonly up to three orders of magnitude higher than rates determined from field studies (Velbel, 1990). Batch studies are similar to mineral dissolution experiments, but use native soils with mixed mineral suites. Use of stagnant soil suspensions with periodic replacement yields lower rates of cation release than does either stirring or shaking suspensions. Even in the former technique, however, release rates were one to two orders of magnitude higher than estimated field rates for Mg, K and Si (Van Grinsven and Van Riemsdijk, 1992). In column studies, soil columns are leached at rates typical of saturated to unsaturated conditions (the latter using tension). Their primary utility lies in determining comparative rates of cation release among specific soils or soil horizons. As with other studies, varying methodology inhibits inter-study comparisons, and release rates from column studies also overestimate presumed field rates.

Field studies of cation release generally fall into two categories (1) watershed mass balance studies, and (2) mineral or elemental depletion studies. Weathering rates on a watershed basis are commonly estimated with input–output budgets and mass balances based on surface water chemistry (White et al., 1990). The derived rates are affected by weathering in both the solum and in the deeper unconsolidated regolith. Because of its greater mass, the long residency of solutions therein, and presence of more readily soluble minerals such as calcite, rates from the regolith are usually several orders of magnitude greater than those from the solum. Regolith weathering, however, has little effect on ecosystem nutrient relationships unless soils are shallow. Profiles of mineral or elemental depletion within soil pedons have also been used to estimated long-term cation release rates (April et al., 1986). Assumptions include minimal surface erosion, initial homogeneity of materials, insignificant and short-term storage of base cations in biomass, and loss of all weathered base cations from the system.

Mathematical models attempt to synthesize the results of the many studies of weathering. The steady-state soil chemistry model PROFILE (Warfvinge and Sverdrup, 1992) is an example of such an approach. It was developed as part of Sweden's assessment of acid-sensitive areas, and has been applied in northern and central Europe as well as in the northeastern U.S. (Sverdrup et al., 1992, 1994). It uses soil physical and chemical properties and climatic and plant properties to estimate field weathering rates.

2. Objective

Our overall objective was to estimate rates of weathering in the northcentral U.S.A., to help assess impacts of forest harvesting. Because of the assumptions and uncertainties implicit in individual methods of determining weathering, we used four different methods and compared the results. Our premise was that because each method has specific strengths and weaknesses, an estimate from a variety of methods should be better than that from any single method. We used an input–output budget on a pedon scale, based on soil solution sampled below the rooting zone; trends in elemental and mineral depletion of silt-size particles; a laboratory batch dissolution technique, with the results adjusted for field conditions; and a mathematical model, PROFILE, to predict cation (Ca + Mg + K) release rates from five soils spanning a range in properties from the northcentral U.S.

3. Materials and methods

3.1. *Site description*

Study sites were located on the Cloquet Experimental Forest in northeastern Minnesota (lat. = 46.7°N, long. = 92.4°W), the Pike Bay Experimental Forest in northcentral Minnesota (lat. = 47.4°N, long. = 94.6°W), and on the Brule River State Forest in northwestern Wisconsin (lat. = 46.6°N, long. = 91.6°W) (Fig. 1). All soils are derived from Late Wisconsinan-age glacial and glacio-fluvial sediments. The two Cloquet sites have sandy outwash parent material from the Superior Lobe (Omega and Cloquet series, sandy loam Spodic Udipsamment and fine sandy loam Typic Dystrochrept, respectively). At Pike Bay the site is a relatively dense glacial till from the Des Moines Lobe (Warba series, very fine sandy loam Glossic Eutroboralf). One site at Brule River is a glacio-lacustrine till (Ontonagon series, clayey Glossic Eutroboralf) while the other is a sandy to gravelly outwash deposit from the Superior Lobe (Omega taxadjunct, loamy sand Typic Udipsamment). Although two of the outwash sites fell on similarly named mapping units, they differed taxonomically and the taxadjunct at Brule River will hereafter be referred to as the Solon Springs soil in reference to the proximity of that municipality. All sites are dominated by mature aspen. Time since glaciation is approximately 11,600 BP (Teller, 1987) for all soils except the Ontonagon. That soil, located approximately 2.5 km from Lake Superior, was presumably in the basin of proglacial Lake Duluth until about 9500 BP (Teller, 1987). The climate of the study area

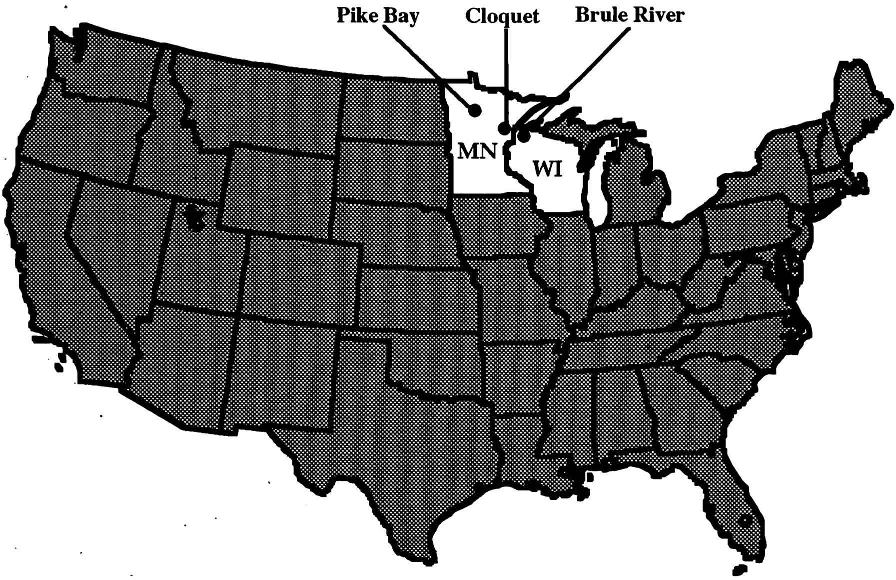

Fig. 1. Site locations of the five soils studied (MN = Minnesota, WI = Wisconsin).

is humid temperate, with mean annual temperature ranging from 3°C at the Warba site to 4°C at the Ontonagon site, and mean annual precipitation ranging from 66 cm at the Warba site to 79 cm at the Solon Springs site (U.S. Department of Commerce, 1992).

3.2. Field sampling

Soil pits were excavated to 150 cm, profiles were described and soil samples were collected by horizon. Samples were collected during three seasons (spring, summer, and fall) for extraction of soil solution. For those seasons, samples were collected from the pit and with a bucket auger from sites two metres on either side of the pit. The three samples were composited for subsequent analysis. All samples were cooled in an ice chest and kept at 3°C until shipment back to the laboratory. Samples were promptly frozen until processing.

3.3. Physical and chemical properties of the soils

Particle-size analysis was by the pipette method (Gee and Bauder, 1986). Field bulk density was measured by the excavation method (Blake and Hartge, 1986), and field soil pH with a portable flat electrode. Loss on ignition (LOI) was determined by ashing overnight at 450°C. Cation exchange capacity (CEC) for surface and subsurface soils was based on pH, clay, and LOI, and estimated from multiple regression equations developed from a large database ($n = 167$, $r^2 = 0.88$ for surface horizons, $n = 332$, $r^2 = 0.87$ for subsurface horizons) from the northcentral U.S. (Ohmann and Grigal, 1991). The soils differed in most measured properties (Table 1), ranging, for example, from 9% to 28% clay at the surface and 9% to 72% clay in the subsurface.

Table 1
Physical and chemical properties of the soils studied

Horizon	Depth (cm)	pH (H_2O)	Bulk density ($g cm^{-3}$)	LOI (% dry wt)	CEC ($cmolc kg^{-1}$)	Clay (% dry wt)	Sand (% dry wt)
Cloquet fsl							
A	0–6	5.01	1.18	7.92	9.4	9	56
E	6–15	5.09	1.21	2.27	7.2	14	52
Bw1	15–25	5.31	1.42	2.20	5.8	9	53
Bw2	25–50	5.65	1.54	1.18	5.7	11	53
2Bw3	50–65	6.03	1.46	0.93	3.3	7	81
2Bw4	65–135	6.17	1.85	0.58	2.3	5	88
2C	135–150	5.45	1.85	0.63	1.5	8	89
Omega sl							
A	0–10	5.40	1.36	7.50	10.0	11	62
E	10–20	5.01	1.71	3.61	5.8	8	65
Bw1	20–35	5.11	1.76	1.81	3.6	8	72
Bw2	35–65	5.65	1.48	1.02	2.8	7	82
C	65–150	6.40	1.65	0.64	2.4	4	94
Ontonagon c							
A	0–5	5.17	0.85	13.67	19.6	28	49
E of E/B	5–25	4.82	1.75	0.74	6.4	15	59
B of E/B	5–25	4.83	1.55	3.25	24.5	62	18
Bt	25–60	6.22	1.33	3.24	27.7	66	18
Btk	60–85	7.06	1.50	2.07	27.2	60	20
Ck	85–150	7.74	1.90	1.78	35.9	72	15
Solon Springs ls							
A	0–20	5.16	0.97	3.25	3.9	9	83
Bw1	20–65	5.93	1.70	0.52	0.8	6	90
2Bw2	65–100	6.00	1.93	0.82	0.1	5	92
2C	100–150	6.14	1.93	0.36	2.0	9	90
Warba vfsl							
A	0–10	6.72	1.30	2.43	11.4	11	61
E	10–20	6.70	1.93	0.88	6.0	8	68
E of E/B	20–55	5.59	1.87	0.78	7.2	11	64
B of E/B	20–55	5.59	1.56	1.10	10.7	27	52
Bt	55–90	5.14	1.56	1.16	10.5	27	53
Btk	90–125	7.74	1.70	1.33	19.1	24	55
Ck	125–150	7.79	1.84	1.28	19.0	22	55

3.4. Methods for weathering estimates

Each method used to estimate weathering rates will be briefly described (Fig. 2). They are described in more detail in Kolka (1993).

3.4.1. Input–output balance

Soil solutions were extracted from composited samples taken below the rooting depth of aspen. A dense (1.9 g cm^{-3}), inert fluorocarbon solvent (FC70) was used for solution

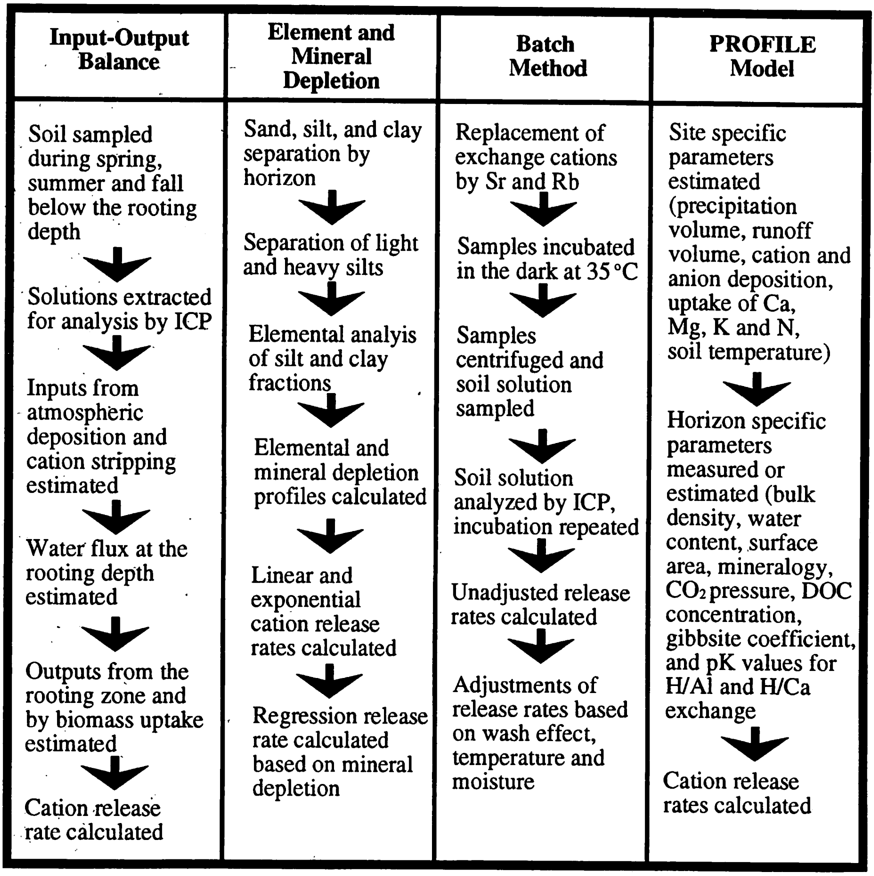

Fig. 2. Comparative diagram summarizing the major steps in the four methods used to determine cation release rates from weathering.

extraction (Kittrick, 1983). After a subsample was removed to determine water content, 30 g samples of field-moist soil were placed in 50 mL polycarbonate centrifuge tubes, ca. 22 mL of FC70 was added to each tube, and it was centrifuged at 15,000 rpm for 120 minutes. The displaced soil solution was filtered through 0.4 μm polycarbonate filters, pH was measured on one subsample, and another 5 mL subsample was acidified and analyzed for major cations by inductively coupled plasma atomic-emission spectroscopy (ICP-AES). The recovery of total soil water ranged from 7% in the Ontonagon-summer sample to 70% in the Omega-spring sample, and was related to the initial soil water content, sand and clay content, and bulk density ($r^2 = 0.91$, $p = 0.0001$, $n = 18$). We tested the solubility of cations in FC70 by analyzing deionized water shaken overnight with FC70 that had been previously used and recycled; all cations were below detection limits for ICP-AES. Samples from one soil and season (Omega-summer) were carried in triplicate through the extraction procedure to assess variability. Concentrations ranged from 0.11 mM ± 4.3% for Ca (mean ± coefficient of variation), 0.06 mM ± 5.5% for

Mg, and 0.025 mM ± 8.2% for K. Because of this reproducibility duplicate analyses were not performed on other samples.

Cation deposition was estimated by multiple regression based on knowledge of depositional gradients across the Lakes States (Grigal and Bates, 1992). For site specific data, regressions based on latitude and longitude were developed to interpolate wet and dry cation and hydrogen deposition from stations maintained by the Minnesota Pollution Control Agency (1991). To determine the annual flux of cations from the rooting zone, concentrations in extracted soil solution were multiplied by the flux of water leaving the rooting zone during a particular season, and were summed for the year. A modified version of the Thornthwaite equation was used to estimate water flux (Kolka, 1993). Soil water storage was estimated with three prediction equations (Gupta and Larson, 1979; McBride and Mackintosh, 1984; Saxton et al., 1986) and with tabulated data for each soil in published soil surveys. Maximum and minimum estimates of storage were used in the water balance model.

The accuracy of the rate of release estimated by the input–output method depends on two fundamental assumptions. The first, commonly used in mass-balance studies on watersheds, is that the biomass and forest floor are at a steady state with no net accretion of cations. Although all stands in this study had closed canopies so that the annual mass and nutrient content of leaves was relatively constant; trees continue to accumulate woody tissue. Based on cation concentrations and rates of production of mature aspen wood from these sites (Peter Bates, pers. commun., 1993), uptake of cations (Ca + Mg + K) ranged from 216 eq ha^{-1} yr^{-1} for the Ontonagon site to 417 eq ha^{-1} yr^{-1} for the Warba site (Table 2).

The second common assumption is that the soil cation exchange pool is essentially constant (Clayton, 1988; Mast et al., 1990); cation stripping due to acidic precipitation or long-term soil acidification is insignificant. Although cation stripping from the unconsolidated regolith may be relatively insignificant in watershed studies, it must be considered at the scale of the pedon. Total proton deposition in the study area ranges from 106 eq ha^{-1} yr^{-1} at the Warba site to 196 eq ha^{-1} yr^{-1} at the Solon Springs site (Minnesota Pollution Control Agency, 1991). The cation release rate by weathering can be calculated by considering inputs to equal outputs (Eq. (1)),

$$\mathrm{W} + \mathrm{CS} + \mathrm{AD} = \mathrm{BU} + \mathrm{CRRD} \tag{1}$$

where inputs include cations release by weathering (W), cation stripping (CS) and atmospheric deposition of cations (AD). Outputs include the uptake of cations by biomass (BU) and cations released at the rooting depth (CRRD).

3.4.2. Elemental and mineral depletion

The silt fraction (2–50 μm) of each soil horizon was isolated by wet sieving to remove sand and by multiple centrifugations to remove clay. Concentrations of light and heavy silts were determined by centrifugation with sodium polytungstate solution adjusted to density ≈ 2.95 g cm^{-3}. Elemental analysis of the silts was by an energy-dispersive X-ray microprobe (EDAX model 711F) coupled to a scanning electron microscope (Phillips SEM 500). Each analysis was performed at low magnification (40 ×) and encompassed thousands of silt grains. Duplicate analysis showed little variation

Table 2
Basic measurements of the input–output budget of the five soils used to determine weathering rates

	Units	Cloquet fsl	Omega sl	Ontonagon c	Solon Springs ls	Warba vfsl
Rooting depth	cm	150	150	60	150	90
Annual precipitation	cm	78	78	75	79	66
Atmospheric deposition	eq ha^{-1} yr^{-1}					
Ca		173	173	157	176	150
Mg		16	16	13	17	11
K		19	19	18	19	17
H		179	179	192	196	106
Vegetation uptake	eq ha^{-1} yr^{-1}					
Ca		147	163	116	119	253
Mg		194	195	84	103	154
K		13	13	16	13	10
Solution concentration [a]	mg L^{-1}					
Ca		1.97	2.72	32.6	4.08	25.0
Mg		0.37	0.75	35.7	1.06	8.00
K		0.49	0.59	0.41	0.38	2.14
Weathering rate	eq ha^{-1} yr^{-1}					
Ca		163 (14) [b]	252 (95)	1238 (170)	390 (110)	705 (200)
Mg		210 (5)	274 (50)	2206 (255)	262 (54)	431 (98)
K		16 (2)	22 (10)	50 (12)	18 (6)	338 (47)

[a] Mean annual volume-weighted concentration at base of rooting zone.
[b] Standard deviation based on maximum and minimum values for hydrologic flux.

among results and was subsequently discontinued. The elemental composition of light and heavy silts was obtained as weight fractions relative to silicon. Mineral species in the light and heavy silts were identified by X-ray diffraction using a Philips APD 3720 X-ray diffractometer. The results of elemental analyses and X-ray diffraction were used to assign elements into their respective minerals to obtain an empirical mineralogy (Table 3). Estimates of clay mineral composition were obtained by elemental analysis of the < 2 μm fraction by ICP-AES (Kolka et al., 1994).

The elemental analyses from EDAX/SEM were converted to elemental percent, and these were corrected with Si for absolute changes in mineralogy and chemistry with depth. Parent material was assumed to be similar in composition to the material at 150 cm in outwash soils and to the uppermost calcareous horizon in the tills (90 and 60 cm for the Warba and Ontonagon soils, respectively). These depths were also the approxi-

Table 3
Silt mineralogy of the soils studied (% by weight). Quartz comprises the remaining mineral mass

Soil/horizon	K-spar	Albite	Anorthite	Micas	Apatite	Hornblende	Epidote	Pyroxenes	Other [a]
Cloquet fsl									
A	14.3	4.9	0.0	3.8	1.2	0.1	0.5	0.8	2.5
E	10.1	5.9	1.0	9.4	0.8	0.2	1.0	1.0	3.6
B	14.2	6.4	2.8	4.8	0.6	0.3	1.3	1.4	4.3
2B	14.0	7.6	1.4	8.1	1.0	0.6	1.8	1.9	5.5
2C	12.3	7.2	7.7	14.0	0.6	1.0	2.4	2.2	6.2
Omega sl									
A	15.3	4.8	1.4	2.8	0.9	0.1	0.3	0.5	1.5
E	13.6	4.2	0.5	3.1	0.9	0.1	0.5	0.6	1.9
B	13.6	6.3	1.1	5.1	0.9	0.5	1.3	1.4	4.1
C	7.9	7.2	9.5	13.0	0.8	1.5	2.5	4.5	9.9
Ontonagon c									
A	19.0	3.2	0.0	3.8	1.1	0.0	0.2	0.3	2.3
E	17.2	4.1	0.0	2.9	1.1	0.0	0.3	0.5	3.5
B	20.9	4.9	1.1	5.9	0.9	0.2	0.8	1.0	3.6
C	15.7	3.7	17.0	11.8	0.8	0.3	0.8	1.3	3.6
Solon Springs ls									
A	14.1	3.8	0.0	4.4	1.0	0.4	1.1	1.0	4.0
B	14.9	6.1	0.0	7.5	0.9	0.8	1.9	1.6	5.6
2B	1.2	8.4	8.7	22.3	0.7	1.9	1.7	4.6	8.5
2C	8.2	7.7	7.6	15.2	0.6	1.6	0.8	5.8	9.3
Warba vfsl									
A	14.6	5.6	1.1	1.7	0.8	0.2	0.8	0.9	2.5
E	14.8	5.7	0.5	3.7	1.1	0.3	1.1	1.3	3.6
B	13.7	6.1	1.7	4.6	1.0	0.3	1.1	1.6	3.9
C	7.8	4.4	15.0	7.5	0.9	0.3	0.9	1.5	3.4

[a] Other includes olivines, garnets, and oxides of Fe, Mn, and Ti.

mate rooting depth of aspen at the sites. Elemental loss in silts by horizon, based on the difference between silts in that horizon and in parent material, was multiplied by the silt mass in that horizon (from bulk density, particle size analysis and horizon thickness), corrected for oxides.

We defined two *mean annual* release rates, using either a linear or an exponential function of cation depletion in silt with time since deglaciation. Although actual depletion may not follow either function, we assumed that they provided reasonable boundary conditions for rates. We also estimated *regression* release rates. Multiple regression was used to describe elemental depletion (keq ha^{-1} cm^{-1}) as a function of the depletion of minerals bearing that element in each horizon (in Mg ha^{-1} cm^{-1}) and the logarithm of horizon depth. Mineral content was corrected with a conservative mineral (quartz) for absolute changes with depth. Because the outwash soils had different relationships than the till soils, soils were grouped into two sets. Independent variables (minerals) that were highly correlated were summed for use in the regressions.

The resulting regressions were used to predict present cation release rates based on the current soil mineralogy. The regression approach assumes that cation release is proportional to mineral loss, but does not assume any specific mathematical function for depletion of elements and minerals. It further assumes that the average weathering environment since deglaciation is similar to that of the present.

When rates of cation release are based on elemental or mineral depletion within pedons, the depth chosen to represent unweathered or minimally weathered material is important. April et al. (1986) chose 1 m as the baseline depth, based on lack of variation in the percent hornblende and opaque heavy minerals below this depth, and they used linear interpolation between horizon midpoints to ascertain depletion. In contrast, we used either 150 cm or immediately above a calcareous horizon as our baseline, and used discrete steps corresponding to pedogenic horizons to describe changes. This is consistent with soil genesis, leading to horizons in which chemical and physical properties are relatively homogeneous within and heterogeneous between. The release rate as defined here is the depletion of Ca, Mg, and K from the silt fraction (2–50 μm). Cation depletion with depth in the < 2 μm fraction showed inconsistent results and was not included in release rates. Clay formation and lessivage, the dominant processes in the < 2 μm fraction in these soils, consume cations so that concentrations are generally highest in the middle horizons. Since separation of primary minerals from secondary clays in the < 2 μm fraction is not possible, elemental analysis reflects both. Primary mineral composition becomes diluted and trends become indistinguishable because of varying clay composition. Weathering rates in the > 50 μm fraction were assumed to be negligible because of the relatively low surface area and lack of easily weatherable minerals in that fraction.

3.4.3. Batch method

Thawed, field-moist samples (ca. 10 g oven-dry) were placed in 50 mL centrifuge tubes and pretreated with washes of formaldehyde, solutions of 0.02 M $SrCl_2$–0.01 M RbCl–chloroform, and finally solutions of 1.0 mM $SrCl_2$–0.5 mM RbCl–chloroform. These washes replaced all exchangeable cations while maintaining ionic strength in an unbuffered solution; formaldehyde and chloroform inhibited microbial activity. The supernatant from the last wash was filtered (0.4 μm), acidified, and analyzed by ICP-AES to confirm cation replacement. After pretreatment, samples were washed with the final dilute Sr–Rb–chloroform mixture and incubated in the dark at 35°C. After incubation periods ranging from 13 to 42 days, samples were centrifuged and solutions were filtered, acidified, and analyzed by ICP-AES. Incubations were repeated 7 times for surface horizons and 6 times for lower horizons.

Changes in rates of release are commonly observed in mineral dissolution and batch studies. Washing by vortexing and centrifugation abrades particles, destroys coatings, and breaks down organic matter, creating new reaction sites that lead to preferential weathering and high rates (White et al., 1990). Conversely, ligand-promoted dissolution (Bloom and Nater, 1991) tends to decrease with number of washes due to losses of dissolved organic acids. Rates of cation release therefore tend to change with number of washings, but usually trend logarithmically toward an asymptote. To correct for such disturbances, we adjusted measured rates by a logarithmic function of the number of washes, statistically separating the wash effect from the background weathering rate that we assumed remained constant. By assuming biologically-mediated weathering by organic acids is minor when compared to that from acidity, we will tend to underestimate field rates (Boyle and Voigt, 1973). The wash effect was statistically most obvious for Ca and Mg and was more tenuous for K. The K-bearing minerals weather much more slowly than Ca- and Mg-bearing minerals, yielding low solution concentrations of K that were often near or below detection limits of the ICP-AES. Our primary objective was determination of rates of Ca and Mg release, and to maintain consistency the wash correction was applied to all ions. The regressions were significant in most cases for Ca and Mg, and in about one-third of the cases for K (Kolka, 1993).

We adjusted the laboratory-derived rates for differences in temperature and water content between laboratory and field. We assumed that the temperature dependence of rates of reaction followed first-order kinetics (Wood and Walther, 1983). We adjusted rates based on weekly soil temperature data for 1986–1993 from six depths to 200 cm collected under an aspen forest at the Marcell Experiment Forest (centrally located among the sites, lat. = 47.6°N, long. = 93.7°W) (Dale Nichols, pers. commun., 1993). Rates for soil temperatures $\leq 0°C$ were assumed to be zero. This yielded adjusted cation release rates approximately one order of magnitude lower than laboratory rates.

Temperature-adjusted rates were normalized for differences in water status between laboratory (continuously saturated) and field, assuming that water content influenced either reaction rates or diffusion of products with respect to their accumulation (Burch et al., 1993, Nagy et al., 1991). Rates were decreased as a linear function of the water status of the soil as it dropped below field capacity (Rowell et al., 1967). Soil water status was based on the Thornthwaite equation and on partitioning of evapotranspiration with depth. Depending on assumed water storage and root distribution, this yielded four alternate assumptions of water content with depth. Weathering rates for the soil solum are the sum of rates for individual horizons to the rooting depth of aspen.

3.4.4. PROFILE model

The steady state soil chemistry PROFILE model required numerous input variables that describe the site, including climate, soil properties, and vegetation. Most of these data had been collected for use in the other estimates of weathering. Other variables, such as soil surface area, were estimated with relationships with texture from Sverdrup et al. (1990). Partial pressure of CO_2 was estimated from Sverdrup et al. (1990), as were gibbsite equilibrium coefficients and selectivity coefficients for H/Al and H/Ca exchange. Dissolved organic carbon (DOC) in soil solution was estimated from a literature search where soils with similar vegetative cover and particle-size were assumed to yield similar DOC concentrations as the study soils.

One of the important issues with use of any mathematical model is identification of the parameters that have a significant effect on model outputs. An analysis of the PROFILE model found that results were most sensitive to particle surface area, bulk density, and soil water content, followed by mineralogy (Jonsson et al., 1995). Other parameters had little to no effect on the calculated release rate, but were more important in predicting acid loading. We therefore emphasized the accuracy of those four parameters as inputs to the model. Soil water content was difficult to estimate because the model requires an annual average, and seasonal fluctuations affect computation of that average. We therefore used both maximum and minimum water contents for each soil.

3.4.5. Multiple approach

The results of all methods were compared via analysis of variance (ANOVA). The data did not conform to a normal distribution, and were subjected to $\log_e$ transformation before analysis. A two-way ANOVA was used to test for significant differences among soils, methods, and the interaction between soils and methods for individual cations and the sum of cations. Bayes least significant difference (BLSD) was used to determine significance of differences between individual soils and methods (Smith, 1978). When converted to arithmetic values, $\log_e$ means were corrected for bias (Koch and Link, 1970).

4. Results and discussion

4.1. Input–output balance

Strong linear relationships existed between rates of Ca and Mg release and the mass of the clay fraction ($r^2 = 0.99$ and 0.97, $p < 0.001$). Resulting estimates of weathering fell within the range reported in many other studies (Kimmins et al., 1985; White et al., 1990) (Table 2). Few estimates of weathering rates are available for the northcentral U.S. A watershed mass balance on the Warba soil in Minnesota (Verry and Timmons, 1982) yielded apparent release rates of Ca = 170 eq ha^{-1} yr^{-1}, Mg = 140 eq ha^{-1} yr^{-1}, and K = 40 eq ha^{-1} yr^{-1}. A study in Wisconsin used the pedon input–output approach but with ceramic samplers for soil solution (Bockheim et al., 1983). They reported release rates in outwash sand from the Wisconsinan age underlaying a red pine (*Pinus resinosa* Ait.) plantation of Ca = 1100 eq ha^{-1} yr^{-1}, Mg = 410 eq ha^{-1} yr^{-1}, and K = 180 eq ha^{-1} yr^{-1}. Although they considered biomass accumulation, they apparently did not consider cation stripping due to precipitation. If that is the case, their estimated rates should be higher than those using our approach.

One of the problems with the input–output approach is the possible effect of high solution concentrations in the lower rooting zones of soil due to either the presence of groundwater or capillary movement from calcareous lower horizons. Results from the Ontonagon clay appear to be affected by one or both of those processes, and rates of Ca and Mg release from that soil based on the input–output balance were about one order of magnitude higher than those from the other soils (Table 2).

4.2. Elemental and mineral depletion

Consistent differences were found in mean annual cation release rates for all ions under the two different assumptions of depletion, linear versus exponential (Table 4). The exponential loss assumes more rapid early rates of release and inevitably yields lower current rates. However, that assumption is arguably more realistic than the

Table 4
Cation release rates based on the depletion techniques for five northern Lake States soils (eq ha^{-1} yr^{-1})

Soil	Method	Ca	Mg	K
Cloquet fsl	linear	420	190	60
	exponential	250	100	30
	regression	360	120	180
Omega sl	linear	390	140	10
	exponential	180	60	5
	regression	180	60	100
Ontonagon c	linear	500	150	20
	exponential	140	50	20
	regression	110	30	100
Solon Springs ls	linear	80	30	5
	exponential	30	20	5
	regression	90	50	40
Warba vfsl	linear	670	160	10
	exponential	310	70	5
	regression	260	40	130

assumption of constant weathering rates through time. The multiple regression equations describing the mass of element depleted as a function of mass of mineral depleted and horizon depth had good statistical fits (R^2 near 1) because the same method (elemental analysis with EDAX/SEM) was used to determine both dependent and independent variables. Rates of Ca depletion were related to the depletion profiles for anorthite, apatite, hornblende, epidote and pyroxenes; of Mg to the depletion profiles for micas and hornblende, and for K to the depletion profile for micas and potassium feldspars (Table 3). Horizon depth added little additional explanation, with depletion of Ca and Mg decreasing with depth and a nondescript relationship for K.

Although the slopes of the relationships were approximately proportional to the weatherability of the minerals, they were affected by correlations among independent variables. Simple linear regression using each mineral separately was used to assess mineral weatherability. The results yield weathering indices that were normalized by considering potassium feldspar equal to unity: potassium feldspar = 1.0, biotite = 2.1, anorthite = 3.0, pyroxenes = 5.4, hornblende = 17.0, epidote = 17.0, and apatite = 18.8. These indices correlate fairly well with Bowen's reaction series; minerals formed at high temperatures are least stable at the earth's surface.

Regression-based rates of cation release for Ca and Mg were generally lower than mean annual linear rates and similar to mean annual exponential rates (Table 4). The exception is the Solon Springs soil, with slightly higher regression-based Ca and Mg release rates. All soils have an aeolian silt-rich surface, with an apparent silt enrichment more pronounced in the outwash soils because of absence of silt in the original deposit. The majority of weathering occurs in this surficial material, and the Solon Springs loamy sand has less of this material than the other soils (Table 1). The regression

Table 5
Cation release rates based on the batch method for five northern Lake States soils (eq ha^{-1} yr^{-1})

	Cloquet fsl	Omega sl	Ontonagon c	Solon Springs ls	Warba vfsl
Initial rate [a]					
Ca	8800	8800	8300	5800	5700
Mg	9300	8700	8000	13000	1600
K	1500	13000	390	8100	880
Temperature correction [b]					
Ca	970	980	920	630	620
Mg	1100	860	900	1400	150
K	160	2000	40	860	90
Water correction [c]					
Ca	97 (30) [d]	135 (70)	100 (40)	65 (35)	75 (45)
Mg	115 (30)	140 (70)	115 (45)	140 (75)	30 (20)
K	105 (40)	285 (145)	15 (6)	80 (40)	15 (10)

[a] Based on release under laboratory conditions.
[b] Rates adjusted for differences in temperature between laboratory and field.
[c] Rates adjusted for differences in water content between laboratory and field.
[d] Standard deviation based on four different assumptions of water storage and root distribution.

approach, based on the historical depletion of minerals over all (outwash) soil horizons, therefore yields higher rates of weathering in the Solon Springs soil.

In contrast to Ca and Mg, the regression approach predicts much higher rates of K release than either the linear or exponential mean annual rates. Depletion of the more easily weatherable Ca- and Mg-bearing minerals in the surface horizons leads to the relative enrichment of the more recalcitrant K-bearing minerals. Although biotite generally increases in concentration with depth, potassium feldspar decreases or remains constant with depth, with trends similar to those for quartz (Table 3). This suggests that rates of K release were initially higher than present and the easily weatherable K-bearing materials (either because of small particle-size or fresh surfaces) are now gone, leaving the more recalcitrant K-bearing materials. The rate coefficients for potassium feldspar in the regressions therefore overestimate true rates. The mean annual exponential rates of cation release appear to be more realistic than either of the other two approaches.

4.3. Batch method

Weathering rates determined with the batch method (Table 5) fall within the range of other estimates in the literature. Calcium release rates from mass balance studies in watersheds comprised of soils from glacial drift range from 60 to 1300 eq ha^{-1} yr^{-1} and for Mg from 100 to 1300 eq ha^{-1} yr^{-1} (White et al., 1990). Our rates are at the low end of those ranges because of the lesser depth of weatherable materials that we considered compared to the entire unconsolidated and mostly saturated regolith usually considered in watershed studies.

The estimated release rates from the batch method also relate well to the physical properties of the five soils. Calcium release from the three outwash soils is related to the mass of the silty aeolian cap that contains an abundance of weatherable silt and clay-size primary minerals. The rates of Mg release in the Solon Springs soil are relatively high because of the presence of a more Mg-rich second parent material at 65 cm. We only considered the upper 60 cm of the Ontonagon soil and the upper 90 cm of the Warba soils because of the presence of underlying calcareous horizons. These horizons had approximately seven-fold higher rates of Ca and Mg release than the overlying horizons. If the rate determined from the lowest-lying noncalcareous horizon were extrapolated to 150 cm, the Ontonagon soil would continue to have the highest rate of Ca release. This is expected based on its heavier texture and consequently greater soil surface area for solution contact. However, even if extrapolated to 150 cm, the Warba soil would have lower Ca and Mg release rates than expected based on its intermediate texture between the outwash sands and the Ontonagon clay. Differing parent material mineralogy is the most likely cause for these differences.

Reliable estimates of field rates are based in part on laboratory protocols. Use of field-moist samples prevented irreversible changes upon drying (Bartlett and James, 1980). Exchangeable divalent and monovalent cations were replaced with ions of similar charge, Sr^{2+} and Rb^{+}. Replacement solutions were at an ionic strength that approximated that of the soil solution and were unbuffered so that they quickly reached pH equilibrium with the soil. The pH of the wash after the final incubation was similar (±0.5 units) to that of the soils when sampled. Microbial activity was inhibited with formaldehyde and chloroform. These protocols, and the mathematical adjustments described herein, led to reasonable estimates of field weathering rates.

4.4. PROFILE model

The version of the model used does not calculate release rates of individual ions, but rather the sum of cations weathered (Ca + Mg + K). Mean release rates ranged from 70 ± 70 eq ha^{-1} yr^{-1} (mean ± standard deviation) for the Solon Springs soil, to 140 ± 100 for the Omega soil, 310 ± 240 for the Warba soil, 410 ± 160 for the Cloquet soil, and 1100 ± 750 eq ha^{-1} yr^{-1} for the Ontonagon soil. The high standard deviations reflect the dependence of the model on average soil water. The rates are in the same range calculated with the model for other sites in Maryland and Europe (150–2800 eq ha^{-1} yr^{-1}, Sverdrup and Warfvinge, 1992).

The calculated rates of cation release generally follow expectations when considering the morphology of these soils. For the outwash sands, the weathering rates correlate well with the mass of the aeolian surface, which is least expressed in the Solon Springs loamy sand and most strongly expressed in the Cloquet fine sandy loam. The effects of the aeolian surface are much harder to discern in the two till soils (Warba and Ontonagon) because of their inherently heavier texture. Although a lesser rooting depth was considered in these soils, the weathering rate for the Warba very-fine sandy loam was similar and the Ontonagon clay was considerably higher than those for the other soils. The rates seem reasonable when considering the particle size and subsequent surface area of these soils as compared to the outwash soils. The PROFILE model appeared to adequately quantify current weathering rates for the five soils.

Table 6
Results of two-way ANOVA, testing significance of differences in weathering rates among soils and methods of determination

Cation	Treatment	MSE [a]	F [b]	df [c]	prob [d]
Ca	Soil	0.2592	2.98	4,29	0.0354
	Soil × Method	0.2592	3.70	7,29	0.0056
Mg	Soil	0.2512	1.29	4,29	0.2966
	Soil × Method	0.2512	5.07	7,29	0.0008
K	Soil	0.7537	1.49	4,29	0.2313
	Soil × Method	0.7537	7.38	7,29	0.0001
Sum	Soil	0.3001	5.65	4,34	0.0013
	Soil × Method	0.3001	5.50	11,34	0.0001

[a] Mean square error from ANOVA, analysis used $\log_e$ transformation.
[b] F-statistic.
[c] Degrees of freedom.
[d] Probability of larger F-statistic.

4.5. Multiple approach

Our working premise was that the "best" estimate of cation release rates is that based on multiple approaches. In an ideal world, all methods would converge on the same rate. Because of differences among the methods and their inherent assumptions, however, estimates varied for individual soils. Individual methods have both strengths and weaknesses related to their ease of application and their suitability for a specific soil. In general, the greater the ease of use, the greater the number of assumptions necessary to justify the results. As the number of assumptions increases, the degree of uncertainty increases. We have previously discussed some problems with assumptions. For example, the input–output budget can be affected by contact with groundwater via capillarity, especially if that water is in equilibrium with $CaCO_3$-rich materials. Regression estimates of weathering based on mineralogy are influenced by the concentration of K-bearing minerals, especially potassium feldspars, at the surface related to their resistance to weathering. Finally, slow rates of dissolution of K-bearing minerals and the assumption of minimal organic-promoted dissolution affect estimates of release rates using the batch technique.

The statistical tests quantitatively verified our assessment of the data. A two-way ANOVA, with treatments of method and soil, indicated that interactions were significant for all cations. In other words, rates varied among both soils and methods, and no method or soil had consistently higher or lower rates (Table 6, Fig. 3). Based on the results of the ANOVA, the rate of release of the sum of Ca + Mg + K from individual method-soil combinations ranged from 3480 eq ha^{-1} yr^{-1} for the Ontonagon clay soil using the input–output method to 48 eq ha^{-1} yr^{-1} for the Solon Springs loamy sand using the PROFILE model. Neither methods nor soils could easily be grouped; the data spanned a continuum with overlapping ranges of least significant differences (Fig. 3).

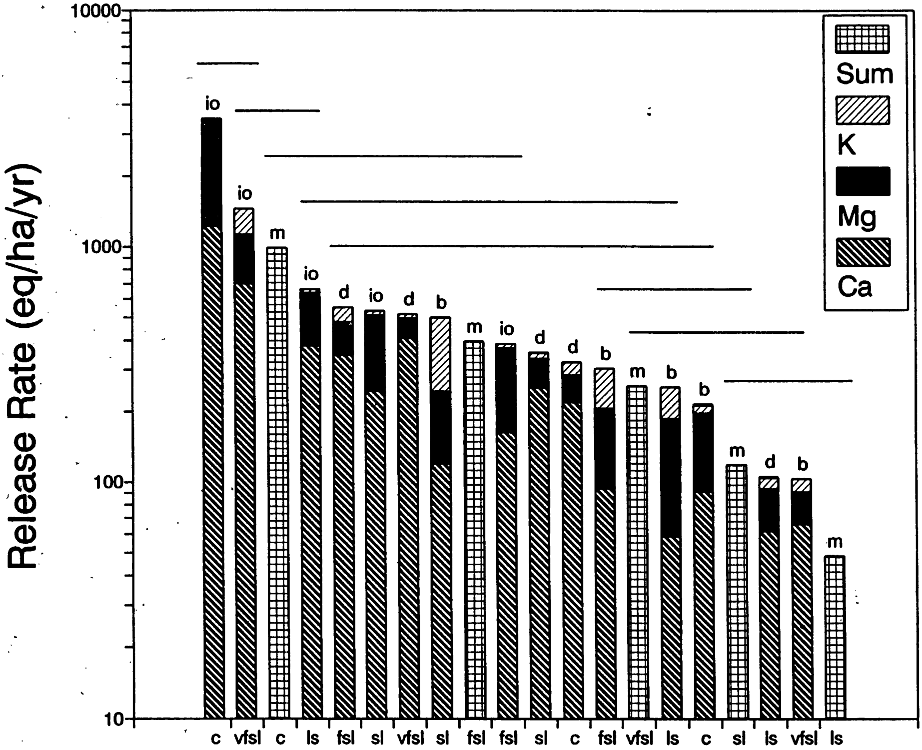

Fig. 3. Rates of release of Ca, Mg, K, and their sum for five soils based on four methods of determination, input–output budgets (**io**), pedon depletion profiles (**d**), a laboratory batch method (**b**), and a mathematical model (**m**). Soils are Cloquet fine sandy loam (**fsl**), Omega sandy loam (**sl**), Ontonagon clay (**c**), Solon Springs loamy sand (**ls**), and Warba very fine sandy loam (**vfsl**). Results are least-square means based on two-way analysis of variance, with treatments of soils and methods. Solid lines above bars indicate soil-method combinations that do not differ based on Bayes least significant difference (Smith, 1978).

Using overall means, the input–output method tended to yield the highest release rates, followed by the depletion method, the batch method, and finally by the PROFILE model. The mean for the input–output method was strongly influenced by the high rates in the Ontonagon clay. Although easy to apply, we believe the input–output method to be the least accurate of the methods because of the number and kinds of necessary assumptions. We consider the rates from the batch method to be more realistic because the assumptions are less tenuous. Conversely, the effort required to apply the batch method is also greater than that needed for the input–output method. Although the PROFILE model may appear to be relatively easy to use, it requires an existing database that is consistent with the desired degree of accuracy. Without that database, application of the model is difficult. In addition, many assumptions are inherent in the model, although field calibration during model development increases our confidence in its accuracy. Data acquisition for the depletion method was less laborious than for the batch and modeling methods, and we have more confidence in the validity of the assumptions underlying its use than the assumptions necessary for the other methods.

For further comparison, we propagated uncertainties from each step and measurement for each method (Harris, 1987, Fig. 2). For those cases where quantitative estimates of uncertainty were not available, we used reasonable estimates. As a function of the many variables and extrapolations necessary, the uncertainty in the input–output estimate was the highest among the four methods (±32%). The batch method, because of the mathematical manipulations associated with adjusting from laboratory to field conditions, also had a relatively high uncertainty (±27%). The field and laboratory measurements for the mineral depletion method were relatively straightforward, so the computed relative uncertainty is lower (±24%). Jonsson et al. (1995), performed an uncertainty analysis on weathering rates calculated with the PROFILE model. For the mean of three sites, the error propagated for all parameters was approximately ±35%. Variations in soil physical properties (bulk density, water content and specific surface area) led to the greatest uncertainty. Since we measured soil bulk density and particle size (specific surface area) and optimized water content as a boundary condition, our error should be somewhat less. We estimate the uncertainty associated with the PROFILE model as ±25%. The ranking of the methods by relative uncertainty conforms to our qualitative evaluation, with the input–output method being most uncertain and the depletion method having the least uncertainty.

Our ultimate interest was in ascertaining rates of cation release for each soil, and we viewed the individual methods as being means to that end. Although we were uncomfortable with some data because of the limitations discussed earlier, we were hesitant to accept or reject cation release rates from specific methods or soils. Based on our initial results (Fig. 3), we only excluded the rates determined by the input–output method for the Ontonagon clay from further consideration. That rate was much higher than that for any other combination of soil and method (Fig. 3), and the data appeared to violate an important assumption of the method. Because of relatively shallow groundwater and a calcareous subsurface horizon, soil solution that we collected was enriched in Ca and Mg; it did not only reflect inputs from overlying horizons.

The resulting analysis indicated statistically significant differences among soils in release rates for Ca and for the sum of cations (Table 6, Fig. 4). Release of Ca was lowest in the Solon Springs loamy sand; all other soils had similar rates (Fig. 4). Magnesium and K release rates were not significantly different among soils; release rates for K were the lowest among studied cations. Bias-corrected mean release rates for the sum of cations ranged from 470 eq ha^{-1} yr^{-1} for the Ontonagon clay soil to 200 eq ha^{-1} yr^{-1} for the Solon Springs loamy sand soil. Weathering rates declined with increases in sand content, and least significant differences overlapped over the range of soils (Fig. 4).

Although the results based on all methods are our best estimates of weathering rates, an important question is their comparability with other work. In a comprehensive review of rates for application to questions regarding forest harvesting in Minnesota, Grigal and Bates (1992) identified three classes of rates. The mean rate over all classes for the sum of cations (Ca + Mg + K) was 1200 eq ha^{-1} yr^{-1}, and for their lowest class was 448 eq ha^{-1} yr^{-1} (Ca = 207 eq ha^{-1} yr^{-1}, Mg = 187 eq ha^{-1} yr^{-1}, and K = 54 eq ha^{-1} yr^{-1}) (Grigal and Bates, 1992). The rates that we report here, with an overall mean for sum of cations of 386 eq ha^{-1} yr^{-1} (Ca = 209 eq ha^{-1} yr^{-1}, Mg = 134 eq ha^{-1} yr^{-1},

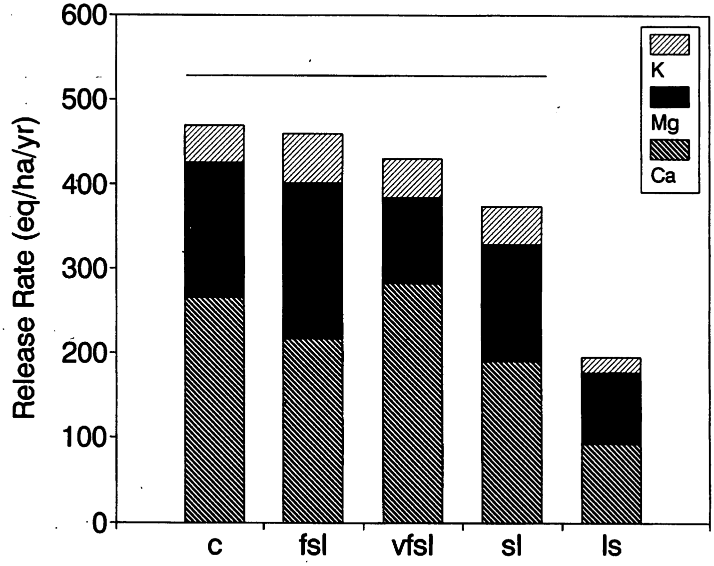

Fig. 4. Rates of release of Ca, Mg, K, and their sum for five soils based on four methods of determination, input–output budgets, pedon depletion profiles, a laboratory batch dissolution method, and a soil chemistry steady state model. Soils are Cloquet fine sandy loam (**fsl**), Omega sandy loam (**sl**), Ontonagon clay (**c**), Solon Springs loamy sand (**ls**), and Warba very fine sandy loam (**vfsl**). Results are least-square means based on two-way analysis of variance, with treatments of soils and methods. Solid lines above bars indicate soils that do not differ based on Bayes least significant difference (Smith, 1978). This analysis did not include rates from the Ontonagon clay via the input–output method.

and K = 43 eq ha^{-1} yr^{-1}) are lower than that class mean, but fall within a range of reasonable uncertainty. Our lower rates are not surprising because most studies are based on the watershed-level.

5. Conclusion

Four approaches were used to estimate cation release rates from weathering for five aspen forested sites in the northcentral U.S.A. Our "best" estimates, as the mean of the estimates from the four approaches, were lower than those reported for similar soils in the literature. In part, this is because our work was on a pedon-scale, not a watershed-scale. These low rates within soil pedons, the source of nutrient ions for plant growth, have implications for estimates of nutrient budgets that are based on the literature. Lower than expected cation release rates shorten the time a site can sustain reasonable production without amendment. Forest harvesting practices that recycle nutrients on site should be considered where current practices are determined to be mining soil nutrients. Site nutrient budgets should be reevaluated to determine if current and long-term projections for site sustainability are compatible with this new information.

Acknowledgements

Thanks to Dr. James Bockheim of the University of Wisconsin and Dr. Robert Dowdy of the USDA-ARS at the University of Minnesota for their insightful review comments. Also, thanks to Ashley Kolka, Judy Liddell, Linda Kernik and Jay Gallagher for their help in sampling and analyses. This project was partially funded by a grant from the Legislative Commission on Minnesota Resources and the Minnesota Agricultural Experiment Station on research conducted under project 25-054. This paper is published as No. 21,953 of the scientific journal series of that station.

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PRINTED IN THE NETHERLANDS

Volcanic Ash Soils

Genesis, Properties and Utilization

by **S. Shoji, M. Nanzyo** *and* **R.A. Dahlgren**

Developments in Soil Science Volume 21

Volcanic eruptions are generally viewed as agents of destruction, yet they provide the parent materials from which some of the most productive soils in the world are formed. The high productivity results from a combination of unique physical, chemical and mineralogical properties. The importance and uniqueness of volcanic ash soils are exemplified by the recent establishment of the Andisol soil order in Soil Taxonomy. This book provides the first comprehensive synthesis of all aspects of volcanic ash soils in a single volume. It contains in-depth coverage of important topics including terminology, morphology, genesis, classification, mineralogy, chemistry, physical properties, productivity and utilization. A wealth of data (37 tables, 81 figures, and Appendix) mainly from the Tohoku University Andisol Data Base is used to illustrate major concepts. Twelve color plates provide a valuable visual-aid and complement the text description of the world-wide distribution for volcanic ash soils. This volume will serve as a valuable reference for soil scientists, plant scientists, ecologists and geochemists interested in biogeochemical processes occurring in soils derived form volcanic ejecta.

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1993 312 pages
Dfl. 290.00
(US $ 165.75)
ISBN 0-444-89799-2

Elsevier Science B.V.
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The Netherlands

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NY 10160-0757

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