

Chemical weathering and chemical denudation dynamics through ecosystem development and disturbance

Zsuzsanna Balogh-Brunstad,¹ C. Kent Keller,¹ Bernard T. Bormann,² Rachel O'Brien,³ Deane Wang,⁴ and Gary Hawley⁴

Received 8 February 2007; revised 27 August 2007; accepted 2 November 2007; published 5 February 2008.

[1] Mineral weathering and chemical denudation of terrestrial environments are understood by both geochemists and ecologists to be affected by rooted plant growth. We used unique 20-year “sandbox” experiments to test the predictions of both disciplines regarding the influence of tree growth and harvest on chemical weathering and denudation of Ca^{2+} , Mg^{2+} and K^+ . Results showed 3 temporal phases: 1) *weathering-dominated* rapid uptake of mineral nutrients with retention in trees and soil, and low denudation; 2) *biocycling-dominated* nutrient uptake with slower tree growth, and chemical fluxes reduced to near zero; and 3) *denudation-dominated* loss of nutrient reserves after harvest by disruption of biotic regulation. Overall, a red pine sandbox used and retained its resources more effectively than a reference non-vascular system. The results suggest that disturbance may be an important factor controlling chemical denudation rates. Temporal variations of the fluxes highlight difficulties of extrapolating weathering and denudation rates over long timescales.

Citation: Balogh-Brunstad, Z., C. K. Keller, B. T. Bormann, R. O'Brien, D. Wang, and G. Hawley (2008), Chemical weathering and chemical denudation dynamics through ecosystem development and disturbance, *Global Biogeochem. Cycles*, 22, GB1007, doi:10.1029/2007GB002957.

1. Introduction

[2] Chemical weathering and chemical denudation play major roles in many Earth system processes. *Chemical weathering* is the process by which chemical reactions decompose primary minerals and rocks and transfer the products to other phases such as soil water, clays, and biomass [Drever, 1997]. *Chemical denudation* (or *chemical erosion*) is defined here as net dissolved mineral mass loss in solution from watersheds and continents, with associated transport via groundwater and rivers to the oceans. There are several important reasons for studying chemical weathering and chemical denudation processes. These processes drive soil development [Stallard and Edmond, 1987; Vitousek et al., 1997], soil nutrient availability to vegetation [Bormann and Likens, 1979; Likens and Bormann, 1995] and regulate erosion of landscapes and continents [Schlesinger, 1997]. Silicate mineral weathering in particular influences the chemistry of the oceans and atmosphere [Holland et al., 1986; Berner, 2004], by moving Ca^{2+} , Mg^{2+} and bicarbonate ions in continental runoff to the oceans where they

eventually precipitate as carbonates, thereby sequestering CO_2 and buffering atmospheric CO_2 levels on geologic timescales.

[3] Chemical weathering and chemical denudation have been studied from two relatively distinct perspectives in the Earth and environmental sciences. From the *geochemistry* perspective chemical weathering and chemical denudation occur essentially together and at the same rate, functioning to “tear down” continents in the planetary-scale rock cycle. In this view, biota and soils function as mediating agents for water-rock interactions; mineral mass passes briefly through soil on its path to the oceans. It is generally understood that rooted plants should increase weathering rates via organic acid production and by physically altering soils [Drever, 1994, 1997] and it is widely believed that the inception of vascular-plant ecosystems should have substantially affected atmospheric CO_2 levels during the Phanerozoic (see Berner, 2004 for a summary). Many studies have been conducted on chemical weathering rates of different environmental settings in watersheds [e.g., April et al., 1986; Hyman et al., 1998; Aghamiri and Schwartzman, 2002], and plant influence on chemical weathering [Basu, 1981; Knoll and James, 1987; Drever, 1994; Berner and Cochran, 1998; Kelly et al., 1998], but less attention has been paid to chemical denudation as such, or to weathering and denudation as distinct processes [however see Berner, 1992, 2004; Moulton et al., 2000; van Breemen et al., 2000].

[4] From an *ecosystem ecology* perspective, chemical weathering generates mineral-based nutrients for growth. Thus weathering is a key to sustainability in most ecosys-

¹School of Earth and Environmental Sciences, Washington State University, Pullman, Washington, USA.

²Forest Service, PNW, Corvallis, Oregon, USA.

³Department of Geology, Allegheny College, Meadville, Pennsylvania, USA.

⁴Rubenstein School of Environment and Natural Resources, University of Vermont, Burlington, Vermont, USA.

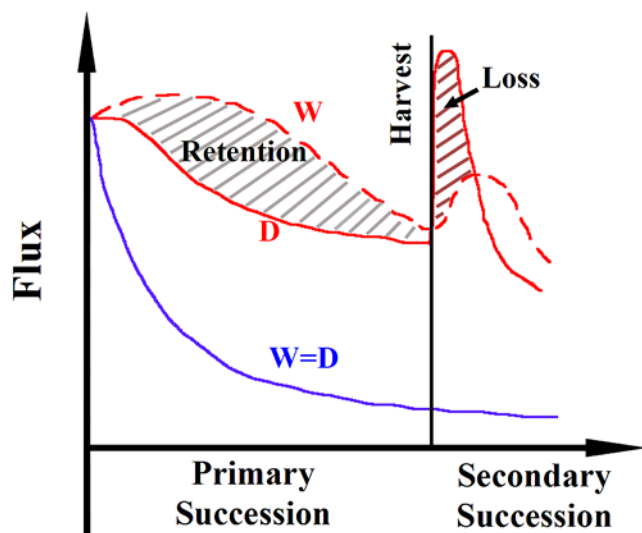


Figure 1. Theoretical model of chemical weathering (W) and denudation (D) fluxes over the course of ecosystem development and disturbance. Rapid tree growth drives weathering, and nutrient demand regulates denudation causing retention of cations during primary succession. Harvest disturbance, i.e., loss of biotic regulation, causes uncontrolled denudation early in secondary succession and moderate increase in weathering, which result in a net loss of cations from the system. Nonvascular system (lower line) lacks biology to drive weathering or retain nutrients, and the fluxes are equal.

tems [e.g., Bormann and Likens, 1979; Likens and Bormann, 1995] and is a “building” process in biocycles operating at the ecosystem scale rather than the planetary scale. In this view, biota and soils function as both mediating agents of weathering, and as pools where nutrients are stored. Chemical denudation is, on the other hand, a distinct process, which transports nutrients out of ecosystems in runoff, i.e., causes nutrient loss. Thus denudation proceeds at the expense of nutrient retention and accumulation. Many studies have been focused on limiting nutrients such as nitrogen and phosphorous [e.g., Bormann and Likens, 1979; Bormann et al., 1993], but considerable work has also been done on base cations (Ca^{2+} , K^+ , Mg^{2+} and Na^+) [Johnson et al., 1985; Likens et al., 1994; 1998; Watmough and Dillon, 2003]. The acid rain problem drew attention to Ca^{2+} depletion in the Northern temperate forest of Europe and America [Federer et al., 1989; Johnson et al., 1994, 2000; Sverdrup and Rosen, 1998] and Ca^{2+} dynamics continues to be an interest in forested ecosystems [Bailey et al., 1996, 2003; Likens et al., 1998; Blum et al., 2002].

[5] The purpose of this study was to employ ideas and tools from ecosystem ecology to better understand the effects of plant growth on chemical weathering and chemical denudation processes. By the 1970s, pioneering watershed-based biogeochemical cycling studies had generated enough data to show clearly that during periods of forest growth, the chemical denudation (usually termed “nutrient loss”) measured in streamflow leaving forested catchments was

accompanied by nutrient retention in biomass and perhaps in soils [Vitousek and Reiners, 1975; Bormann and Likens, 1979]. The studies also had clearly shown that forest disturbances (implemented by catchment-scale harvest experiments) could cause rapid failure of the retention mechanisms, as evidenced by the increased streamflows and stream water nutrient concentrations driving dramatic chemical denudation increases [Bormann and Likens, 1979]. The idea that retention and denudation depend on ecosystem development phase, and in particular on biomass increment or loss, is now a venerable and durable tenet of biogeochemical theory [e.g., Hedin et al., 1995; Romanowicz et al., 1996; Johnson et al., 1997; Valett et al., 2002; Bailey et al., 2003; Wang et al., 2006]. In these studies, weathering rates were hard to define because of landscape, soil and vegetation heterogeneity. However, they are expected to be driven to relatively high levels by vegetation growth during aggradation periods, particularly during “primary succession” as ecosystems featuring rapid-weathering pioneer species develop on fresh landscapes, but also during secondary succession, i.e., ecosystem redevelopment following disturbance [Gorham et al., 1979]. In general, models relating weathering to denudation and other ecosystem processes have been hard to support; review of the existing literature yields strikingly variable results independent of the age of the vegetation and landscape [Bain et al., 1994; Hornbeck et al., 1997; Land et al., 1999; Moulton et al., 2000; Aghamiri and Schwartzman, 2002].

[6] Our objective was to test the geochemistry-perspective idea that vascular plant growth increases chemical weathering and denudation, by investigating the temporal dynamics of the effect of red pine and associated microbial community on mineral weathering and denudation fluxes using unique experimental ecosystems [Bormann et al., 1987, 1993, 1998; Berner et al., 1998; O’Brien et al., 2004; Keller et al., 2006a] located at the Hubbard Brook Experimental Forest (HBEF). These simple systems allowed us to measure chemical denudation and estimate weathering with relatively great accuracy, and facilitated comparison of the weathering and denudation effects of a red pine monoculture with a reference system with no vascular vegetation. Our specific questions were: 1.) How does tree growth affect weathering and denudation fluxes compared to a system with non-vascular vegetation? 2.) How does the weathering-denudation relationship change over the course of ecosystem development and disturbance? Our starting point was a succession-based conceptual model featuring ideas taken from the forest-biogeochemical literature discussed above, and re-presented to emphasize the temporal dynamics of weathering and denudation. We hypothesized (Figure 1) that chemical weathering and denudation would be high initially due to abundance of fresh mineral surfaces in the sand, and weathering would outpace denudation yielding gain of available nutrients in the ecosystem during periods of most rapid tree growth or aggradation. We expected chemical weathering to be re-accelerated following harvest disturbance due to increased acid production by growth of microbial decomposers. We also predicted post-harvest denudation rates to dramatically rise due to absence of nutrient and water uptake by the trees,

Table 1. Light and Heavy (in bold) Mineral Composition of the Initial Sandbox Material and Total Ca, Mg, and K Content^a

Mineral	Wt. %	Ca	Mg, mol m ⁻²	K
Quartz	41	0	0	0
Plagioclase ⁹ (Ca-Na feldspar)	17	3195	0	0
Albite (Na feldspar)	11	0	0	0
K feldspar ^c	16	0	0	12750
Muscovite ^d	4	0	0	3180
Hornblende^{3,a}	2	870	123	160
Biotite^c	2	0	62	1590
Fe oxide	1	0	0	0
Clinopyroxene¹	1	495	71	0
Ilmenite	1	0	0	0
Epidote⁶	1	600	0	0
Garnet⁸	1	24	5	0
Chlorite	trace	0	17	0
Actinolite^{4,b}	trace	150	29	24
Apatite⁷	trace	645	0	0
Staurolite	trace	0	0	0
Sphene⁵	trace	195	0	0
Zircon	trace	0	0	0
Orthopyroxene²	trace	trace	12	0
Rutile	trace	0	0	0
Kyanite	trace	0	0	0
Andalusite	trace	0	0	0
Sillimanite	trace	0	0	0
Clay minerals	<2	trace	trace	75
Total	100	6174	319	17779

^aExpected order of weathering [Nahon, 1991] is indicated by the numbers for Ca-bearing minerals and by the letters for K-bearing minerals. Ca and Mg results modified from Bormann et al. [1998].

yielding depletion of available nutrients in the ecosystem for a period after the disturbance. We also hypothesized that the reference nonvascular system would exhibit a rapidly and irreversibly falling weathering rate due to the decrease of easily weatherable, fresh mineral surfaces in the absence of the acid-production, physical-perturbation, and nutrient-uptake capacities by growing rooted plants (Figure 1). Without a biomass pool for sequestration, we expected weathered nutrients to be denuded right away and at the same rate.

2. Methods and Materials

2.1. Site Description

[7] The HBEF is located in the White Mountains of North-Central New Hampshire, USA. Outdoor “sandbox” lysimeters were constructed in 1982–83 [Bormann et al., 1987] to study nitrogen cycling and fixation [Bormann et al., 1993]. The sandboxes (7.5 × 7.5 m wide × 1.5 m deep) were fully lined with industrial grade Hypalon membrane in order to collect and monitor drainage water, and filled with local homogenized glacial outwash sand. A 5 cm thick layer of the site’s original topsoil was rototilled into the upper 20 cm of the sand to promote seedling growth [Ingersoll et al., 1987]. At the inception of the sandbox experiment, initial physical substrate conditions among ecosystems were highly similar, and heterogeneities within ecosystems were minimized. The initial mineral composition and base cation contents are shown in Table 1. For the present study two sandboxes were monitored. One was planted with three-

year-old *Pinus resinosa* Ait. (red pine) seedlings during May 1983 [Ingersoll et al., 1987] and the other was kept free of vascular plants while it developed a non-vascular plant cover of *Cladonia cristatella* (a lichen) and *Polytricum spp.* (a moss) [O’Brien et al., 2004]. In 1998 the above-ground parts of the pine trees were carefully harvested and removed, and regrowth of vascular plants since then has been prevented by weeding [Keller et al., 2006a].

[8] Drainage pipes were installed in the bottom of each sandbox and were connected to an all-weather subsurface chamber, which allowed monitoring drainage water flow rates and cation concentrations all year around [Ingersoll et al., 1987; O’Brien et al., 2004]. Pore water samplers were also installed at depths of 15, 35, and 95 cm in 1995 to monitor soil water chemistry. These samplers consist of a glass porous plate affixed to a glass collection chamber, kept under 0.25 bar suction overnight before sample collection. Three replicated samplers were installed at each depth in boreholes, which were laterally hand-augered from the side of the sandboxes to minimize disturbance [O’Brien et al., 2004].

2.2. Sample Collection

[9] Samples were collected over a period of twenty water years, from June 1983 to May 2004. The water year at HBEF starts on 1 June and ends on 31 May of the next calendar year, because yearly precipitation and streamflow correlate best using this interval [Likens and Bormann, 1995]. Data collection lapsed between 1988 and 1992 due to lack of financial support.

[10] Drainage water samples were collected from both sandboxes; volume weighted and analyzed for base cation concentrations [Bormann et al., 1998; Keller et al., 2006a] at University of Vermont. Samples for chemical analysis were collected daily, weekly, biweekly, and triweekly over the course of the study (dependent on the objectives of the researchers). Drainage flow rates were measured instantaneously with proportional sampling until August 11, 1998 and with tipping buckets connected to a data logger after that [O’Brien et al., 2004]. Soil water was collected periodically between 1996 and 2004 [O’Brien et al., 2004; Keller et al., 2006a].

[11] Precipitation values were determined by taking weekly readings from a standard rain gage [Federer et al., 1990]. Bulk precipitation, which includes particles deposited between rain events, was collected at HBEF weather station 22 about 200 m northwest of the study area [Likens et al., 1994, 1998]. Bulk precipitation samples were analyzed for major elements and values are available at the HBEF website [Likens, 2004]. Fine dust and aerosols in canopy interception were not measured, which somewhat underestimates the total value of Ca and K in atmospheric input [Lovett, 1994; Lovett et al., 1997]. The White Mountain area is heavily forested, local dust generation is low and the red pine sandbox was surrounded with 3 to 6 tree-wide buffer zone, which also decreased dry deposition to the canopy [Bormann et al., 1998]. Furthermore studies by Likens et al. [1994, 1998] indicated that for both Ca and K, bulk precipitation at HBEF gives good estimate of total wet and dry deposition.

[12] Aboveground (foliage, stem, live branches, dead branches, and litter) and belowground (stumps, fine and coarse roots) biomass was sampled in 1983, 1988 [Bormann *et al.*, 1998], and 1998 [Keller *et al.*, 2006a], and was analyzed for total carbon, nitrogen and cation compositions. After oven drying at 65°C the biomass materials were ground, digested then analyzed using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) [Bormann *et al.*, 1998].

[13] Soil cores were collected at multiple locations in 1984–85, 1988, 1998, and 2002 in each sandbox and oven dried to a constant weight at 65°C and stored for further chemical analyses. Conventional ammonium acetate extraction procedure (adapted from McIntosh [1969]) was used on all archived subsamples to determine the soil-exchangeable cation pool. The solutions were analyzed for cation composition on an Inductively Coupled Argon Plasma Spectrometer in the Crop and Soils Department, at Washington State University. All soil core subsamples were extracted and analyzed at once to minimize analytical uncertainties.

2.3. Calculations

[14] The rate of chemical denudation (D) was quantified by taking the difference of leaching losses in drainage water (Dr) and bulk precipitation (P) input:

$$D = Dr - P \quad (1)$$

where the terms of the equation were defined as the sum of Ca^{2+} , Mg^{2+} and K^{+} fluxes in and out from the sandboxes ($\text{mol m}^{-2} \text{a}^{-1}$) on ground surface area basis. These elements are the most important essential base-cation nutrients for plant growth [Gorham *et al.*, 1979]. Sodium was not included because data collection was uneven over the entire period and Na^{+} is a conservative element, which is not taken up by vegetation in large amounts [Bailey *et al.*, 2003].

[15] The rate of chemical weathering was estimated using a modified form of the mass balance approach of Bormann *et al.* [1998]:

$$W = D + \Delta B + \Delta S \quad (2)$$

where W is the chemical weathering, D is the chemical denudation defined in equation (1), ΔB is change of cation content in pine biomass and ΔS is change in the products of weathering left in the soil, which is here defined as exchangeable cations [Markewitz and Richter, 2000]. The biomass and soil sampling times determined three intervals of chemical weathering estimations (1983–1988, 1988–1998, 1998–2002).

2.4. Statistical Analyses

[16] The variance of each term in equations (1) and (2) was determined and combined using standard methods to estimate denudation- and weathering-rate error for each sandbox [Balogh, 2006]. ANOVA with time series analysis was run using SAS on the denudation results for detection of differences over time and between the two boxes [Dean and Voss, 1999]. The analysis was divided for two periods: before and after harvest. Thus it was possible to make

limited statistical comparisons within and between the RP and NV sandbox “treatments”, even though there was no replication within the treatments.

3. Results

3.1. Hydrochemistry

[17] Cation concentrations in drainage water (gray symbols, Figure 2) in both boxes generally decreased over time. The concentration of both cations developed a seasonal pattern in the non-vascular (NV) sandbox (Figures 2a and 2b). A seasonal pattern was not detected in red pine (RP) sandbox (Figures 2c and 2d) as the trees evapotranspired nearly all incoming rainfall during the growing season. After the RP tree harvest (1998), K^{+} and Ca^{2+} “spiked” immediately and after 1 year, respectively, and then gradually declined [Keller *et al.*, 2006a]. However, the concentrations remained 2 to 4 times higher than NV even after 6 years (Figure 2). The Mg^{2+} concentrations of drainage were about one-fourth of Ca^{2+} concentrations in both boxes and tracked Ca^{2+} patterns very closely, so they are not shown.

[18] Soil water Ca^{2+} concentrations (open colored symbols, Figure 2) in RP were lower at 15 and 35 cm than in NV soil water ($p = 0.013$) and also lower than drainage waters from both boxes (Figures 2a, 2c), but only before tree-harvest. In contrast, K^{+} in soil water was always higher in RP compared to NV ($p = 0.005$) (Figures 2b and 2d). Concentrations of soil water, like drainage, “spiked” after tree-harvest – immediately with K^{+} and after delay with Ca^{2+} (Figures 2c and 2d).

3.2. Changes in Soil Exchangeable Cation Pool

[19] Depletion of exchangeable Ca^{2+} near the RP soil surface was evident after 5 years, but then reversed itself by year 15, perhaps as litter decomposed and replenished exchange sites. The harvest did not change this trend. Although it happened more slowly, Ca^{2+} depletion in NV was greater than RP by 2002, even at the deepest layers measured (Figures 3a and 3b). In contrast, soil-exchangeable K^{+} was enriched in the first 5 years near the surface in NV, then became more depleted with time at all depths (Figure 3c). In RP the surface layer enrichment continued until tree-harvest in 1998; then the topsoil layer lost a large amount of exchangeable K^{+} , which might have contributed to a slight enrichment at depth (Figure 3d). By 2002, the soil-exchangeable K^{+} depth profile in RP tracked the profile in NV, but the concentrations were higher.

[20] The concentration changes were used to calculate mass changes in exchangeable cations (ΔS , equation (2)). These changes were substantial after 15 and even larger after 20 years in both RP and NV (Table 2). Soil acidity was buffered by these depletions of base cations from exchange sites as the drainage water pH did not change significantly during the study [Keller *et al.*, 2006a].

3.3. Changes in Biological Uptake and Storage

[21] Red pine trees grew rapidly accumulating about $16 \text{ Mg ha}^{-1} \text{a}^{-1}$ of biomass in the first 5 years of the study [Bormann *et al.*, 1993]. Base cation uptake and storage in biomass (ΔB , equation (2)) contributed more than half of

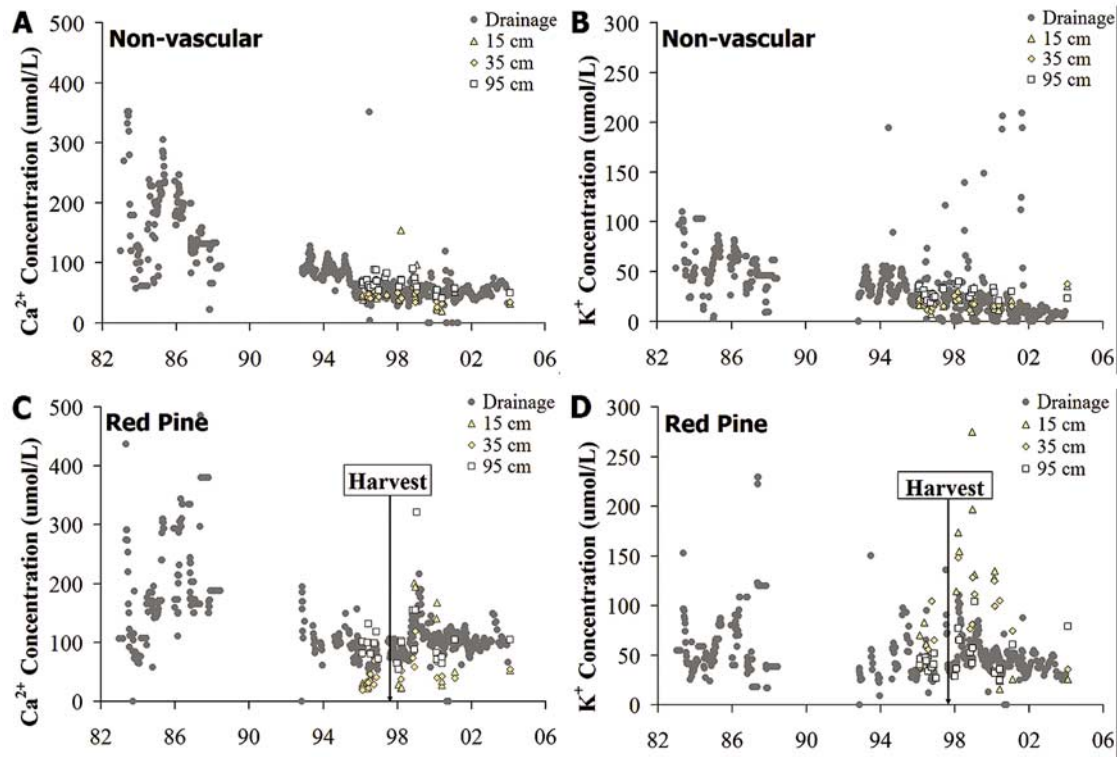


Figure 2. Time series of Ca^{2+} and K^{+} concentrations in drainage and soil waters (depth of samplers shown) of the nonvascular (NV) and the red pine (RP) sandboxes; years shown on x-axes. In RP, soil-water K^{+} concentrations generally exceeded drainage concentrations while the reverse was generally true for Ca^{2+} . The K^{+} increases were immediate after harvest but Ca^{2+} increases lagged by a year. Standard error is about 5% for drainage water values and about 7% for soil water values.

the total weathering flux during this period (Table 2). Between 1988 and 1998 growth decreased to about $6 \text{ Mg ha}^{-1} \text{ a}^{-1}$ of biomass. During this time ΔB , which included both living and dead biomass, dropped to only 3% of the previous period (Table 2). After tree harvest, the changes of the decaying belowground biomass were only indirectly monitored by measuring soil respiration [Keller *et al.*, 2006b]. The estimated respired carbon mass was used to estimate cation releases from biomass with the assumption of stoichiometric decomposition (Table 2). However, this might be an upper-limit estimate of change in biomass pool of cations, because soil respiration counts for the CO_2 release by both the belowground biomass decay and soil organic matter decomposition [Keller *et al.*, 2006b].

3.4. Chemical Denudation

[22] The denudation flux (D , equation (2)) declined for several years for both RP and NV (Figure 4) and dropped to $0.06 \text{ mol m}^{-2} \text{ a}^{-1}$ by 1993–94 water-year in NV; it followed precipitation variations, aside from the first year (Figure 4a, top). Before tree-harvest the pattern of denudation in RP was similar to NV, but the magnitudes were smaller and the proportional declines were larger, from $0.15 \text{ mol m}^{-2} \text{ a}^{-1}$ to about $0.03 \text{ mol m}^{-2} \text{ a}^{-1}$. Significant differences were detected in denudation among the years ($p = 0.004$) and also between the two boxes ($p = 0.014$)

excluding water year 1996 before the harvest [Balogh, 2006].

[23] After the harvest, the RP chemical denudation fluxes exhibited the predicted pattern after a major disturbance [e.g., Vitousek and Reiners, 1975; Bormann and Likens, 1979] peaking at $0.22 \text{ mol m}^{-2} \text{ a}^{-1}$ two years after tree-harvest, then declining rapidly. The RP denudation flux followed precipitation fluctuations (Figure 4a), but at substantially higher rates than before tree-harvest and than the NV flux. Significant differences were found between the denudation fluxes of the two boxes ($p = 0.02$) in the post-harvest period [Balogh, 2006].

[24] Prior to the disturbance chemical denudation was always larger in NV than in RP (Figure 4a). In addition, the cumulative denudation values were larger in NV than in RP, and the difference between the boxes increased until the harvest, after which it decreased by the large RP denudation fluxes (Figure 4b). For each of the 1988–1992 water-years we estimated denudation as the product of average concentration and flow for 1988 and 1992. This method might over-estimate chemical denudation for both boxes.

3.5. Chemical Weathering

[25] Weathering rates (W) were initially high in both ecosystems and then decreased significantly (Table 2, Figure 5). Results for the first 5 years of rapid growth in

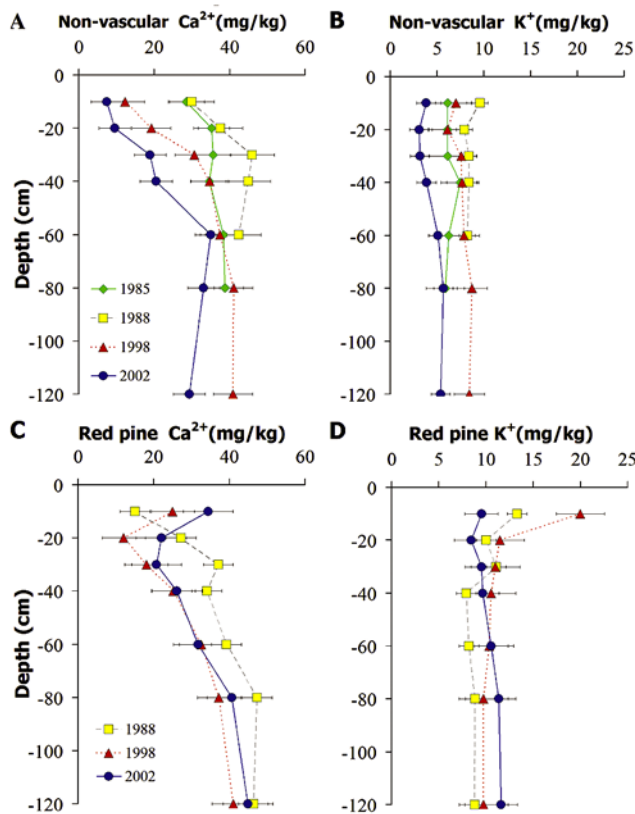


Figure 3. Exchangeable Ca^{2+} and K^{+} depth profiles in NV and RP sandboxes over time. The two sandboxes were assumed to be initially similar. NV: the top 40 cm was depleted in Ca^{2+} (a), but K^{+} did not change significantly (b) by the end of the study. RP: less overall Ca^{2+} depletion occurred and slight Ca^{2+} enrichment was observed in the top 10 cm by harvest in 1998 (c). Shallow K^{+} enrichment at this time was greater, but it had leached out by 2002 (d). Every point represents an average of 5–6 (1985–1988) and 10–12 (1998–2002) replicated core samples; error bars represent replicate plus analytical uncertainty.

RP are consistent with those reported for this system by Bormann *et al.* [1998], allowing for our more conservative weathering-rate estimates. Between 1988 and 1998 biomass accumulation of RP slowed (Table 2), and in the same time the weathering rate decreased about 50 times to 0.01 mol

$\text{m}^{-2} \text{a}^{-1}$ in RP. During this period weathering also declined in NV, but only about 7.5 times, from 0.3 to 0.04 mol $\text{m}^{-2} \text{a}^{-1}$ (Table 2).

[26] After harvest, chemical weathering became indistinguishable from zero in RP as the source of cations in drainage was attributed to rapidly decaying belowground biomass (equation (2)). The reported weathering value (Table 2) might be a minimum due to the selected methods of estimating changes in biomass pools. It also appears that weathering was close to zero in NV, which was attributable to the decreased denudation component and loss from the exchangeable cation pool (Figure 3, Table 2).

[27] The cumulative weathering flux was about 2.5 times greater than the cumulative denudation flux in RP after 15 years growth, while NV showed the opposite relationship (Figure 4b). In addition, the cumulative denudation was still less than cumulative weathering in RP after 6 years of prevented revegetation (Figure 4b).

4. Discussion

[28] As predicted by decades of ecosystem-ecology theory, vascular vegetation interacted strongly with weathering and denudation processes, and weathering and denudation rates were generally unequal and changed dramatically through time in response to biological nutrient demands and disturbances. These interactions can be understood as they play out across three phases (Figure 5) loosely tied to our theoretical ecosystem-development model (Figure 1).

4.1. Weathering-Dominated Nutrient Dynamics With Rapid Tree Growth (Phase 1)

[29] The first phase (1983 to 1988) was characterized by weathering at several times the rate of denudation (Figure 5) and at a higher rate than observed in other studies [e.g., April *et al.*, 1986; Bain *et al.*, 1994; Clow and Drever, 1996; Kolka *et al.*, 1996; Hornbeck *et al.*, 1997; Hyman *et al.*, 1998; Land *et al.*, 1999; Moulton *et al.*, 2000; Aghamiri and Schwartzman, 2002]. These weathering-dominated nutrient dynamics featured plant exploitation of available organic and mineral soil resources. Rapid weathering in RP was associated with the rapid growth of nutrient-rich biomass, averaging about 0.57 mol N $\text{m}^{-2} \text{a}^{-1}$ in the first 5 years [Bormann *et al.*, 1998, 2002]. Rapid biomass and N accumulation in pines required rapid uptake of base cations (about 0.5 mol $\text{m}^{-2} \text{a}^{-1}$; Table 2) derived mostly from weathering. Primary productivity is the likely source of organic acids needed to speed weathering (through roots

Table 2. Components of Chemical Weathering and Denudation Mass-Balance for Three Time Intervals in the NV and RP Sandboxes^a

	1984–1988		1988–1998		1998–2002	
	RP	NV	RP	NV	RP	NV
Precipitation (P)	0.005 (0.0005)	0.005 (0.0005)	0.005 (0.0005)	0.005 (0.0005)	0.005 (0.0005)	0.005 (0.0005)
Drainage (Dr)	0.114 (0.015)	0.206 (0.020)	0.054 (0.003)	0.090 (0.007)	0.143 (0.012)	0.064 (0.004)
Change in soil (ΔS)	0.092 (0.014)	0.100 (0.020)	–0.051 (0.021)	–0.049 (0.012)	–0.082 (0.011)	–0.099 (0.031)
Change in biomass (ΔB)	0.290 (0.058)	N/A	0.010 (0.002)	N/A	–0.120 (0.022)	N/A
Denudation (D) (Equation 1)	0.11 (0.015)	0.20 (0.020)	0.05 (0.003)	0.09 (0.007)	0.14 (0.012)	0.06 (0.004)
Weathering (W) (Equation 2)	0.50 (0.088)	0.30 (0.041)	0.01 (0.027)	0.04 (0.020)	–0.07 (0.045)	–0.04 (0.035)

^aAll values are the sum of Ca, Mg and K fluxes (mol $\text{m}^{-2} \text{a}^{-1}$). Standard error values are listed beneath each flux in parentheses. Change in biomass from 1998 to 2002 for RP was estimated from cumulative soil respiration flux following tree harvest (see text).

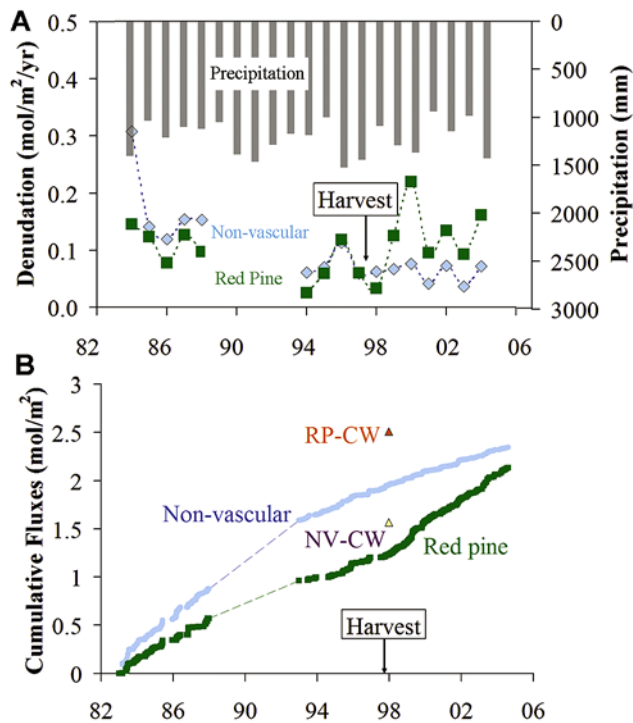


Figure 4. Precipitation amounts and Ca + Mg + K denudation fluxes (a), and cumulative denudation fluxes (b) plotted for both sandboxes. The yearly denudation fluxes were lower in RP than in NV before the harvest, but this relationship reversed afterward. The larger cumulative flux in NV persisted even after harvest, becoming statistically insignificant by 2004. In contrast to denudation, the cumulative weathering flux at harvest was 1.5 times larger in RP than in NV (triangle symbols). Dashed intervals represent estimated rates during period of no data collection.

and via mycorrhizal fungi), and vascular extension of roots throughout the rooting zone [Bormann *et al.*, 1993] increased access to mineral surfaces.

[30] The RP system exhibited a weathering rate about 1.5 times greater than NV, a denudation rate half as large as in NV (Table 2, Figure 5). Parallel outcomes are seen in studies of primary succession with early successional species that appear to exploit nutrient-poor soils with fresh, “active” mineral surfaces with the aid of symbiotic N₂-fixation [Bormann *et al.*, 1987, 1993]. In these cases, rapid nutrient transfers from primary mineral phases to biomass and to soil exchangeable pools [Vitousek *et al.*, 1997], with relatively small losses, are presumably associated with large differences between weathering and denudation rates. The large difference between weathering and denudation during rapid growth in our RP system was predicted by our model (Figure 1). However, the geochemistry perspective emphasized the power of vascular plants to denude (Figure 1); thus we had not expected the substantial depression of RP denudation relative to NV denudation during that time (Figure 3a). The explanation is that RP drainage flows were much smaller than NV drainage flows, while nutrient

concentrations in the drainage waters of the two boxes were similar (Figure 2). Also the incorporation of organic matter into the surface of the NV sandbox supported respiration [Keller *et al.*, 2006b] by microbes and non-vascular vegetation, which may have increased NV weathering relative to what would be observed in a purely mineral medium. In nature the soils of fresh and reset landscapes often contain organic matter or quickly develop some organic matter near the surface, such that respiration-driven weathering could become important. This could also have occurred on the continents before the advent of vascular plants [Keller and Wood, 1993].

[31] We had also expected that weathering and denudation fluxes would be equal in the NV system (Figure 1), which was not the case (Figure 5). Our model did not consider soil changes and in the NV system weathering exceeded denudation because cations were sequestered by accumulation on the soil cation exchange sites (Table 2).

4.2. Biocycling-Dominated Nutrient Dynamics With Slow Tree Growth (Phase 2)

[32] The second phase (1988 to 1998) was characterized by a dramatic decline of weathering fluxes to less than or equal to the denudation fluxes (Figure 5) with continued, but slower, tree growth in RP. Denudation also decreased about 50% in both sandboxes, but the NV flux remained 2 times larger than the RP flux. The denudation flux in RP was nearly equal to ΔS and it could be attributed to loss of exchangeable Ca²⁺ and Mg²⁺ (while exchangeable K⁺ increased, Figure 3d). The drop of weathering to such a low rate implies that a large portion (about 60%) of the cations that continued to accumulate in pines came from bioavailable forms returned to the soil through decomposition (biocycling; 0.006 mol m⁻² a⁻¹). The enrichment of exchangeable Ca²⁺ and K⁺ in the upper 10 cm during this period supports this conclusion (Figures 3b, 3d). Nitrogen supply is likely intertwined with weathering and growth rates. Wang and Hawley (unpublished data) found signs of decreasing N content in soil during the second period, which also could be related to slower growth and biocycling of nutrients. Increased evapotranspiration (73% of precipitation in RP, compared to 28% in NV) and low Ca²⁺ and Mg²⁺ soil water concentrations in the rooting zone (Figure 2c) were signals of strong biotic regulation during this phase. The weathering decrease in NV probably occurred as labile carbon was depleted by microbial activity, and when easily weatherable mineral surfaces decreased. Less biotic regulation and lack of biocycling by non-vascular vegetation, as compared to the vascular pine system, leads to greater nutrient loss (denudation) and soil depletion over time in NV.

[33] This phase differs from our prediction (Figure 1), most notably in timescale of developmental change as the RP denudation and weathering rates dropped dramatically to levels even lower than NV. Bormann and Likens [1979] estimated about 150–180 years to reach the maximum of forest aggradation when the output of limiting (N, P) and essential (base cation) nutrients is at the minimum in a hypothetical model of ecosystem succession [Vitousek and Reiners, 1975; Gorham *et al.*, 1979]. In contrast we

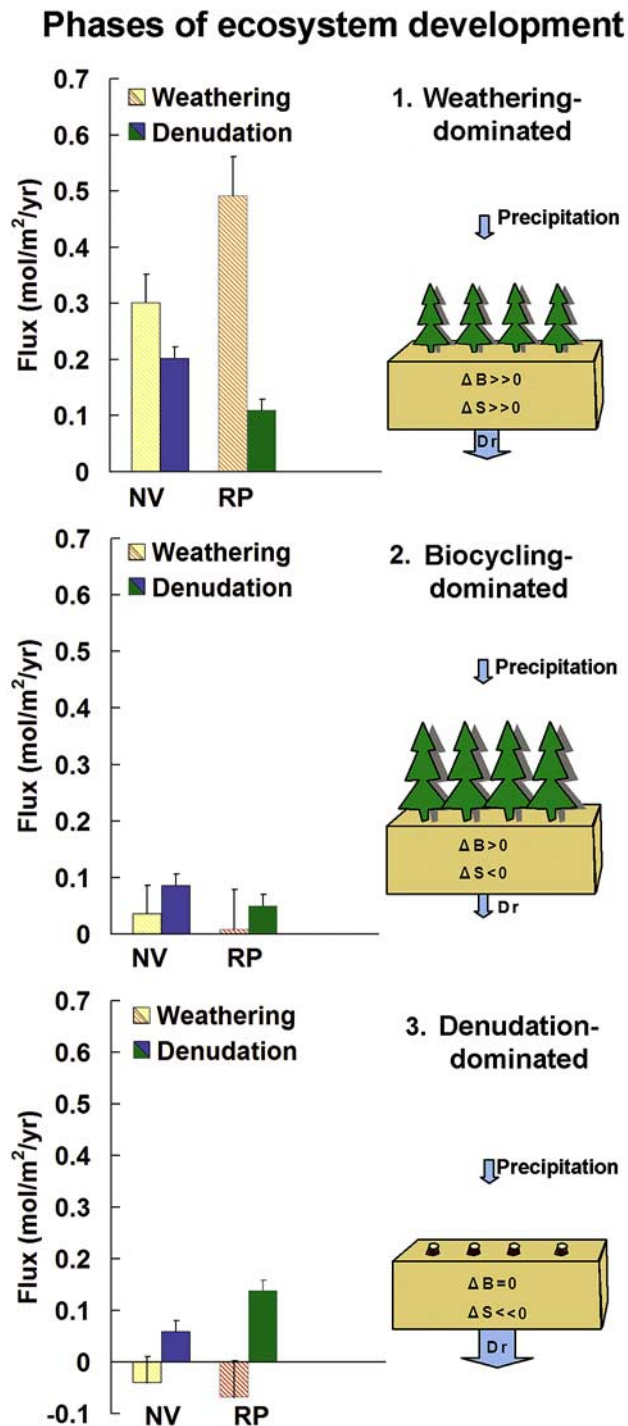


Figure 5. Influence of ecosystem development and disturbance on chemical weathering and denudation dynamics in the RP sandbox at Hubbard Brook. During first (rapid tree growth) and second (slow growth) phases, denudation was less than, and weathering changes were much greater than, in the reference NV system. In phase 3, after harvest, the weathering-denudation relationship reversed relative to phase 1.

observed low denudation rates develop much more rapidly, and we observed these low rates after tree growth rates had declined to much less than their maximum.

[34] The rapidity of phase 2 development may have resulted from the crowding of trees and associated biocycling. On the other hand, natural soil development is supposed to slow chemical weathering, because the parent material is sealed from weathering processes by thickening soil, and fresh surfaces become covered by organic and secondary coatings [Stallard and Edmond, 1987]. Scanning electron microscopy investigation of the sandbox soil minerals indeed showed biological and oxidative coatings on grain surfaces [Balogh *et al.*, 2004]. Either way, the phase-2 flux declines cannot be attributed to depletion of mineral in the substrate. Initially, the sand (Table 1) contained at least 100 mol m^{-2} of each cation just in its most weatherable source phase, while at the end of phase 1, 5 years of weathering had transferred only about 1.5 and 2.5 mol m^{-2} of total cations to other pools in the NV and RP sandboxes respectively.

[35] The estimated weathering rate ($0.01 \text{ mol m}^{-2} \text{ a}^{-1}$) in RP during this biocycling-dominated interval is within the range estimated in watershed studies ($0.005\text{--}0.08 \text{ mol m}^{-2} \text{ a}^{-1}$) where chemical weathering is taken as equal to chemical denudation [e.g., April *et al.*, 1986; Bain *et al.*, 1994; Hornbeck *et al.*, 1997; Land *et al.*, 1999; Aghamiri and Schwartzman, 2002].

4.3. Denudation-Dominated Nutrient Dynamics Following Tree Harvest (Phase 3)

[36] Phase 3 (1998 harvest-2002) was characterized by a larger denudation flux than weathering flux. This reversal of the relationship observed during phase 1 suggests the term *denudation-dominated* for nutrient dynamics during this period. Loss of biotic regulation in RP was evident in large leaching rates resulting from large drainage flows, accelerated depletion of nutrients from exchange sites and the release of nutrients from biomass decomposition, which caused large cation concentrations in soil and drainage water. Following the harvest, the K^+ concentration increases occurred one season before the Ca^{2+} and Mg^{2+} increases, which dominated the total denudation peak relative to our prediction (Figure 1). Meanwhile K^+ loss dominated the post-harvest exchange-complex dynamics. This suggests that available K^+ resources are more vulnerable to certain kinds of disturbances than Ca^{2+} and Mg^{2+} [Keller *et al.*, 2006a], resulting in delay of the denudation peak relative to our prediction (Figure 1). Meanwhile K^+ loss dominated the post-harvest exchange-complex dynamics. This suggests that available K^+ resources are more vulnerable to certain kinds of disturbances than Ca^{2+} and Mg^{2+} [Keller *et al.*, 2006a], which is perhaps not surprising given the very different biogeochemistry of these cations [Likens *et al.*, 1994, 1998].

[37] We had hypothesized that the anticipated increase in the post-harvest denudation rate would be accompanied and indeed driven by a surge in weathering due to acid production by decomposition (Figure 1). Although CO_2 weathering did continue during this phase [Keller *et al.*, 2006a, 2006b], it was undetectable by the methods of this study; cessation of photosynthesis eliminated weathering directly caused by plant growth and metabolism, so that hydrologic export of available nutrients dominated the nutrient dynamics and weathering became very small, contrary to our model

prediction (Figure 1). The physical soil disturbance which accompanies most natural and managed forest disturbances, and which would tend to spur decomposition and expose fresh weatherable surfaces, was purposefully and artificially eliminated in our experiment. In systems with natural regrowth the duration and amplitude of this phase could be smaller [Romanowicz *et al.*, 1996; Likens *et al.*, 1998]; here the regrowth of vascular vegetation was prevented and this artificially retarded the recovery stage of ecosystem succession.

[38] The reference NV system was not disturbed during this period. Weathering in NV appeared to be zero, but denudation declined less, to 2/3 of its rate in the previous phase ($0.06 \text{ mol m}^{-2} \text{ a}^{-1}$) (Table 2). The decline in weathering was at least partly attributable to the decline in microbial activity, evident in CO_2 respiration rates [Keller *et al.*, 2006b], due to depletion of bioavailable carbon and nitrogen [Sylvia *et al.*, 1999] from the topsoil initially tilled in to the sand. Denudation at a rate greater than weathering (Figure 5) meant that NV was losing its “nutrient capital”, possibly by abiotic processes depleting the soil-extractable pool (Table 2).

[39] Nutrient dynamics in the NV system were similar to those in RP in two important respects: weathering and denudation fluxes were larger at the beginning than later in the study; and early importance of weathering gave way to equivalence or even (slight) dominance of denudation later (Figure 5). However, the changes in NV were relatively smooth over the course of the experiment and they occurred without appreciable photosynthesis and with disturbance only at the beginning, i.e., sandbox construction. Thus while the weathering and denudation dynamics of the NV system appear to have been substantially impacted by its biology, its overall history might be best understood as less biotically regulated and more denudation-dominated via physical-chemical processes.

5. Summary and Conclusions

[40] Chemical weathering and chemical denudation fluxes differed between red pine and reference non-vascular experimental “sandbox” ecosystems and over ecosystem development during our 20-year study. On this timeframe, biotic regulation and its collapse dramatically shifted the relationship between weathering and denudation processes in RP. In the first five years, rapidly growing red pine trees facilitated a large weathering pulse while denudation was limited by rapid nutrient and water uptake to 1/5th of the weathering flux. Contrary to our hypothesis, RP exhibited less than 1/2 of the denudation flux compared to the reference NV. This first phase was characterized by rapid uptake of available organic and “fresh” mineral soil resources by biota, and *weathering-dominated* nutrient dynamics, i.e., rates of weathering that greatly exceeded denudation. Over the next phase, tree growth slowed and weathering and denudation rates became small and not significantly different, such that nutrient dynamics shifted toward being *biocycling-dominated*. This conservative mode of nutrient cycling changed after tree harvest, in phase-3, with RP experiencing significant disruption of biotic regulation. The

denudation flux became large and (contrary to our hypothesis) weathering remained small, i.e., nutrient dynamics shifted to *denudation-dominated*.

[41] If we had adopted the traditional geochemistry perspective for our study and estimated the weathering flux as equal to the denudation flux, we would not have detected the roles of biological regulation and disturbance in dramatically and differentially shifting weathering and denudation rates. In RP system, we would have greatly underestimated the weathering flux in the first phase and greatly overestimated it after disturbance; we would have been correct only in the biocycling-driven interval, when the fluxes were about equal. Neglect of biological and soil pools in transient systems might partly explain why Ca-weathering fluxes are so variable among watershed studies, even on similar timescales of landscape development [e.g., April *et al.*, 1986; Hornbeck *et al.*, 1997; Land *et al.*, 1999].

[42] A body of previous geochemical work suggests that over geologic time, post-mid-Ordovician vascular ecosystems drew down atmospheric CO_2 by more efficiently weathering and denuding Ca-Mg-silicate terrains, relative to their non-vascular predecessors [Basu, 1981; Berner, 1992, 2004]. Our study over ecosystem-development time shows a vascular system rapidly and efficiently mining an artificial Ca-Mg silicate terrain by weathering, but then tenaciously retaining the Ca^{2+} and Mg^{2+} against denudation by storing bioavailable nutrients in various ecosystem pools. Total denudation from this system only approached that of a reference non-vascular system 6 years after a harvest disturbance with suppression of revegetation. In this case the non-vascular system was the more efficacious denuder. While these results are particular to experimental conditions and scaling, they highlight the idea [Berner, 2004] that the rate of chemical denudation of the continents, and its consequences for the regulation of ocean and atmospheric chemistry, may depend critically on the globally averaged frequency and severity of landscape and ecosystem disturbances.

[43] **Acknowledgments.** This work was supported by NSF grant EAR-03-12011 to C. K. Keller. We gratefully acknowledge financial and logistical support by the Northeastern Forest Research Station of the USDA Forest Service, the Long-Term Ecosystem Productivity Program, the Rubenstein School of Environment and Natural Resources at the University of Vermont, and the School of Earth and Environmental Sciences and the Department of Crop and Soil Sciences at Washington State University. This is a contribution of the Hubbard Brook Ecosystem Study and the program of the Institute of Ecosystem Studies. We also thank two anonymous reviewers for their constructive comments.

References

- Aghamiri, R. R., and D. W. Schwartzman (2002), Weathering rates of bedrock by lichens: A mini watershed study, *Chem. Geol.*, **188**, 249–259.
- April, R., R. Newton, and L. T. Coles (1986), Chemical weathering in two Adirondack watersheds: Past and present-day rates, *Geol. Soc. Am. Bull.*, **97**, 1232–1238.
- Bailey, S. W., J. W. Hornbeck, C. T. Driscoll, and H. E. Gaudette (1996), Calcium inputs and transport in base-poor forest ecosystem as interpreted by Sr isotopes, *Water Resour. Res.*, **32**, 707–719.
- Bailey, S. W., D. C. Buso, and G. E. Likens (2003), Implication of sodium mass balance for interpreting the calcium cycle of a northern hardwood ecosystem, *Ecology*, **84**(2), 471–484.
- Bain, D. C., A. Mellor, M. J. Wilson, and M. L. Duthie (1994), Chemical and mineralogical weathering rates and processes in an upland granitic till catchment in Scotland, *Water Air Soil Pollut.*, **73**, 11–27.

- Balogh, Zs. (2006), Chemical hydrology of vascular plant growth: role of root-fungus associations, Ph.D. dissertation, Washington State Univ., Pullman, WA.
- Balogh, Zs., C. K. Keller, J. T. Dickinson, D. Wang, G. Hawley, and T. Coe (2004), Plant effect on chemical weathering and denudation processes: experimental ecosystem studies, in *Water and Rock Interaction Vol. 2*, edited by R. B. Wanty and R. R. Seal II, pp. 1251–1254, A. A. Balkema Publishers, Leiden, The Netherlands.
- Basu, A. (1981), Weathering before the advent of land plants: Evidence from unaltered detrital K-feldspars in Cambrian-Ordovician arenites, *Geology*, *March*, 132–133.
- Berner, R. A. (1992), Weathering, plants, and the long-term carbon cycle, *Geochim. Cosmochim. Acta*, *56*(8), 3225–3231.
- Berner, R. A. (2004), *The Phanerozoic carbon cycle: CO₂ and O₂*, Oxford Univ. Press, New York, NY.
- Berner, R. A., and M. F. Cochran (1998), Plant-induced weathering of Hawaiian basalts, *J. Sed. Res.*, *68*(5), 723–726.
- Berner, R. A., J.-L. Rao, S. Chang, R. O'Brien, and C. K. Keller (1998), Seasonal variability of adsorption and exchange equilibria in soil waters, *Aquatic Geochem.*, *4*, 273–290.
- Blum, J. D., A. Klauke, C. A. Nezat, C. T. Driscoll, C. E. Johnson, T. G. Siccama, C. Eagar, T. J. Fahey, and G. E. Likens (2002), Mycorrhizal weathering of apatite as an important calcium source in base-poor forest ecosystems, *Nature*, *417*, 729–731.
- Bormann, F. H., and G. E. Likens (1979), *Pattern and Process in a forested ecosystem*, Springer-Verlag, New York.
- Bormann, F. H., W. B. Bowden, R. S. Pierce, S. P. Hamburg, G. K. Voigt, R. C. Ingersoll, and G. E. Likens (1987), The Hubbard Brook sandbox experiment, in *Restoration Ecology*, edited by R. Jordan, M. E. Gilpin, and J. D. Aber, pp. 251–256, Cambridge Univ. Press, New York.
- Bormann, B. T., F. H. Bormann, W. B. Bowden, R. S. Pierce, S. P. Hamburg, D. Wang, M. C. Snyder, C. Y. Li, and R. C. Ingersoll (1993), Rapid N₂ fixation in pines, alder, and locust: Evidence from the sandbox ecosystem study, *Ecology*, *74*, 583–598.
- Bormann, B. T., D. Wang, F. H. Bormann, G. Benoit, R. April, and M. C. Snyder (1998), Rapid, plant-induced weathering in an aggrading experimental ecosystem, *Biogeochemistry*, *43*, 129–155.
- Bormann, B. T., C. K. Keller, D. Wang, and F. H. Bormann (2002), Lessons from the sandbox: Is unexplained nitrogen real?, *Ecosystems*, *5*, 727–733.
- Clow, D. W., and J. I. Drever (1996), Weathering rates as a function of flow through an alpine soil, *Chem. Geol.*, *132*, 131–141.
- Dean, A., and D. Voss (1999), *Design and analysis of experiments*, Springer-Verlag, New York.
- Drever, J. I. (1994), The effect of land plants on weathering rates of silicate minerals, *Geochim. Cosmochim. Acta*, *58*, 2325–2332.
- Drever, J. I. (1997), *The geochemistry of natural waters*, 3rd ed. Prentice-Hall, Upper Saddle River, NJ.
- Federer, C. A., J. W. Hornbeck, L. M. Tritton, C. W. Martin, R. S. Pierce, and C. T. Smith (1989), Long-term depletion of calcium and other nutrients in eastern US forests, *Environ. Manage.*, *13*, 593–601.
- Federer, C. A., L. D. Flynn, C. W. Martin, J. W. Hornbeck, and R. S. Pierce (1990), Thirty years of hydrometeorologic data at Hubbard Brook Experimental Forest, New Hampshire. *General Technical Report NE-141*, 44 pp., US Department of Agriculture, Forest Service, Northeastern Forest Experiment Station.
- Gorham, E., P. M. Vitousek, and W. A. Reiners (1979), The regulation of chemical budgets over the course of terrestrial ecosystem succession, *Annu. Rev. Ecol. Syst.*, *10*, 53–84.
- Hedin, L. O., J. J. Armesto, and A. H. Johnson (1995), Patterns of nutrient loss from unpolluted, old-growth temperate forests: Evaluation of biogeochemical theory, *Ecology*, *76*(2), 493–509.
- Holland, H. D., B. Lazar, and M. McCaffrey (1986), Evolution of the atmosphere and oceans, *Nature*, *320*, 27–33.
- Hornbeck, J. W., S. W. Bailey, D. C. Buso, and J. B. Shanley (1997), Stream-water chemistry and nutrient budgets for forested watersheds in New England: Variability and management implications, *For. Ecol. Manage.*, *93*, 73–89.
- Hyman, M. E., C. E. Johnson, S. W. Bailey, R. H. April, and J. W. Hornbeck (1998), Chemical weathering and cation loss in a base-poor watershed, *GSA Bull.*, *110*(1), 85–95.
- Ingersoll, R. C., F. H. Bormann, W. B. Bowen, S. P. Hamburg, and R. D. Bowen (1987), *The sandbox experiment notebook*, School of Forestry and Environmental Studies, Yale Univ.
- Johnson, D. W., D. D. Richter, G. M. Lovett, and S. E. Lindberg (1985), The effect of atmospheric deposition on potassium, calcium, and magnesium cycling in two deciduous forests, *Can. J. For. Res.*, *15*, 773–782.
- Johnson, A. H., A. J. Friedland, E. K. Miller, and T. G. Siccama (1994), Acid rain and soils of the Adirondacks. III. Rates of soil acidification in a montane spruce-fir forest at Whiteface Mountain, New York, *Can. J. For. Res.*, *24*, 663–669.
- Johnson, C. E., R. B. Romanowicz, and T. G. Siccama (1997), Conservation of exchangeable cations after clear-cutting of a northern hardwood forest, *Can. J. For. Res.*, *27*, 859–868.
- Johnson, C. E., C. T. Driscoll, T. G. Siccama, and G. E. Likens (2000), Element fluxes and landscape position in a northern hardwood forest watershed ecosystem, *Ecosystems*, *3*, 159–184.
- Keller, C. K., and B. D. Wood (1993), Possibility of chemical weathering before the advent of vascular land plants, *Nature*, *364*, 223–225.
- Keller, C. K., R. O'Brien, J. R. Havig, J. L. Smith, B. T. Bormann, and D. Wang (2006a), Tree harvest in an experimental sand ecosystem: Hydrogeologic insight into nutrient cycling and solute generation processes, *Ecosystems*, *9*, 634–646.
- Keller, C. K., T. M. White, R. O'Brien, and J. L. Smith (2006b), Soil CO₂ dynamics and fluxes as affected by tree harvest in an experimental sand ecosystem, *J. Geophys. Res.*, *111*, G03011, doi:10.1029/2005JG000157.
- Kelly, E. F., O. A. Chadwick, and T. E. Hilinski (1998), The effect of plants on mineral weathering, *Biogeochem.*, *42*, 21–53.
- Knoll, M. A., and W. C. James (1987), Effect of the advent and diversification of vascular land plants on mineral weathering through geologic time, *Geology*, *15*, 1099–1102.
- Kolka, R. K., D. F. Grigal, and E. A. Nater (1996), Forest soil mineral weathering rates: Use of multiple approaches, *Geoderma*, *73*, 1–21.
- Land, M., J. Ingri, and B. Öhlander (1999), Past and present rates in northern Sweden, *Appl. Geochem.*, *14*, 761–774.
- Likens, G. E. (2004), http://www.hubbardbrook.org/research/data/atmos/psd/psd_all.txt.
- Likens, G. E., and F. H. Bormann (1995), *Biogeochemistry of a forested ecosystem*, 2nd ed., Springer-Verlag, New York.
- Likens, G. E., C. T. Driscoll, D. C. Buso, T. G. Siccama, C. E. Johnson, G. M. Lovett, D. F. Ryan, T. J. Fahey, and W. A. Reiners (1994), The biogeochemistry of potassium at Hubbard Brook, *Biogeochem.*, *25*, 61–125.
- Likens, G. E., et al. (1998), The biogeochemistry of calcium at Hubbard Brook, *Biogeochem.*, *41*, 89–173.
- Lovett, G. M. (1994), Atmospheric deposition of nutrients and pollutants in North America: An ecological perspective, *Ecol. Appl.*, *4*(4), 629–650.
- Lovett, G. M., J. J. Bowser, and E. S. Edgerton (1997), Atmospheric deposition to watersheds in complex terrain, *Hydrol. Processes*, *11*, 645–654.
- Markewitz, D., and D. D. Richter (2000), Long-term soil potassium availability from a Kanhapludult to an aggrading loblolly pine ecosystem, *For. Ecol. Manage.*, *130*, 109–129.
- McIntosh, J. L. (1969), Bray and Morgan soil test extractants modified for testing acid soils from different parent materials, *Agron. J.*, *61*, 259–265.
- Moulton, K. L., J. West, and R. A. Berner (2000), Solute flux and mineral mass balance approaches to the quantification of plant effects on silicate weathering, *Am. J. Sci.*, *300*, 539–570.
- Nahon, D. B. (1991), *Introduction to the petrology of soils and chemical weathering*, Wiley, NY.
- O'Brien, R., C. K. Keller, and D. M. Strobbridge (2004), Plant-cover effects on hydrology and pedogenesis in a sandy vadose zone, *Geoderma*, *118*, 63–76.
- Romanowicz, R. B., C. T. Driscoll, T. J. Fahey, C. E. Johnson, G. E. Likens, and T. G. Siccama (1996), Changes in the biogeochemistry of potassium following a whole-tree harvest, *Soil Sci. Soc. Am. J.*, *60*, 1664–1674.
- Schlesinger, W. H. (1997), *Biogeochemistry, An analysis of global change*, 2nd ed., Academic Press, San Diego.
- Stallard, R. F., and J. M. Edmond (1987), Geochemistry of the Amazon, 3. Weathering chemistry and limits to dissolved inputs, *J. Geophys. Res.*, *92*(C8), 8293–8302.
- Sverdrup, H., and K. Rosen (1998), Long-term base cation mass balances for Swedish soils and the concept of sustainability, *For. Ecol. Manage.*, *110*, 221–236.
- Sylvia, D. M., J. J. Fuhrmann, P. G. Hartel and D. A. Zuberer (1999), *Principles and applications of soil microbiology*, Prentice Hall, Inc.
- Valet, H. M., C. L. Crenshaw, and P. F. Wagner (2002), Stream nutrient uptake, forest succession, and biogeochemical theory, *Ecology*, *83*(10), 2888–2901.
- Van Breemen, N., R. Finlay, U. Lundstrom, A. G. Jongmans, R. Giesler, and M. Olsson (2000), Mycorrhizal weathering: A true case of mineral plant nutrition?, *Biogeochemistry*, *49*, 53–67.
- Vitousek, P. M., and W. A. Reiners (1975), Ecosystem succession and nutrient retention: A hypothesis, *Bioscience*, *25*, 376–381.
- Vitousek, P. M., O. A. Chadwick, T. E. Crews, J. H. Fownes, D. M. Hendricks, and D. Herbert (1997), Soil and ecosystem development across the Hawaiian Islands, *GSA Today*, *7*(9), 1–8.
- Wang, X., D. A. Burns, R. D. Yanai, R. D. Briggs, and R. H. Germain (2006), Changes in stream chemistry and nutrient export following a

- partial harvest in the Catskill Mountains, New York, USA, *For. Ecol. Manage.*, 223, 103–112.
- Watmough, S. A., and P. J. Dillon (2003), Base cation and nitrogen budget for seven forested catchments in central Ontario, 1983–1999, *For. Ecol. Manage.*, 177, 155–177.
- B. T. Bormann, Forest Service, PNW, 3200 SW Jefferson way, Corvallis, OR, 97331, USA.
- G. Hawley and D. Wang, Rubenstein School of Environment and Natural Resources, University of Vermont, 332 Aiken Center, Burlington, VT, 05405, USA.
- R. O'Brien, Department of Geology, Allegheny College, 520 North Main Street, Meadville, PA, 16335, USA.
-
- Z. Balogh-Brunstad and C. K. Keller, School of Earth and Environmental Sciences, Washington State University, PO Box 642812, Pullman, WA, 99164-2812, USA. (zsuzsa@wsu.edu)