Forest calcium depletion and biotic retention along a soil nitrogen gradient

Citation	Steven S. Perakis, Emily R. Sinkhorn, Christina E. Catricala, Thomas D. Bullen, John A. Fitzpatrick, Justin D. Hynicka, and Kermit Cromack, Jr. 2013. Forest calcium depletion and biotic retention along a soil nitrogen gradient. Ecological Applications 23:1947–1961. doi:10.1890/12-2204.1
DOI	10.1890/12-2204.1
Publisher	Ecological Society of America
Version	Version of Record
Citable Link	http://hdl.handle.net/1957/46931
Terms of Use	http://cdss.library.oregonstate.edu/sa-termsofuse

Ecological Applications, 23(8), 2013, pp. 1947–1961

Forest calcium depletion and biotic retention along a soil nitrogen gradient

Steven S. Perakis,[1,4] Emily R. Sinkhorn,[2] Christina E. Catricala,[1] Thomas D. Bullen,[3] John A. Fitzpatrick,[3] Justin D. Hynicka,[2] and Kermit Cromack, Jr.[2]

[1]*U.S. Geological Survey, Forest and Rangeland Ecosystem Science Center, Corvallis, Oregon 97331 USA*
[2]*Oregon State University, Department of Forest Ecosystems and Society, Corvallis, Oregon 97331 USA*
[3]*U.S. Geological Survey, National Research Program, Menlo Park, California 94025 USA*

Abstract. High nitrogen (N) accumulation in terrestrial ecosystems can shift patterns of nutrient limitation and deficiency beyond N toward other nutrients, most notably phosphorus (P) and base cations (calcium [Ca], magnesium [Mg], and potassium [K]). We examined how naturally high N accumulation from a legacy of symbiotic N fixation shaped P and base cation cycling across a gradient of nine temperate conifer forests in the Oregon Coast Range. We were particularly interested in whether long-term legacies of symbiotic N fixation promoted coupled N and organic P accumulation in soils, and whether biotic demands by non-fixing vegetation could conserve ecosystem base cations as N accumulated. Total soil N (0–100 cm) pools increased nearly threefold across the N gradient, leading to increased nitrate leaching, declines in soil pH from 5.8 to 4.2, 10-fold declines in soil exchangeable Ca, Mg, and K, and increased mobilization of aluminum. These results suggest that long-term N enrichment had acidified soils and depleted much of the readily weatherable base cation pool. Soil organic P increased with both soil N and C across the gradient, but soil inorganic P, biomass P, and P leaching loss did not vary with N, implying that historic symbiotic N fixation promoted soil organic P accumulation and P sufficiency for non-fixers. Even though soil pools of Ca, Mg, and K all declined as soil N increased, only Ca declined in biomass pools, suggesting the emergence of Ca deficiency at high N. Biotic conservation and tight recycling of Ca increased in response to whole-ecosystem Ca depletion, as indicated by preferential accumulation of Ca in biomass and surface soil. Our findings support a hierarchical model of coupled N–Ca cycling under long-term soil N enrichment, whereby ecosystem-level N saturation and nitrate leaching deplete readily available soil Ca, stimulating biotic Ca conservation as overall supply diminishes. We conclude that a legacy of biological N fixation can increase N and P accumulation in soil organic matter to the point that neither nutrient is limiting to subsequent non-fixers, while also resulting in natural N saturation that intensifies base cation depletion and deficiency.

Key words: aluminum; base cation depletion; calcium; Douglas-fir; magnesium; nitrate leaching; nitrogen saturation; phosphorus; potassium; temperate forest.

Introduction

Biogeochemical theory emphasizes slow rates of N input and persistent N losses as mechanisms that prevent N accumulation in temperate ecosystems, leading to widespread N limitation of primary productivity (Vitousek and Howarth 1991, Hedin et al. 1995, LeBauer and Treseder 2008). As soil N accumulates and N availability increases, it is thought that nutrient limitation most often shifts from N to phosphorus (P), or to co-limitation by N and P (Elser et al. 2007, Vitousek et al. 2010). Shifts to P limitation are most common in subtropical and tropical regions, which support warm climates favorable to symbiotic biological N fixation (Houlton et al. 2008) and which contain highly weathered, P-depleted soils (Walker and Syers 1976, Porder and Hilley 2011). In contrast, relatively few boreal and temperate ecosystems naturally accumulate sufficient N to overcome N limitation. However, elevated atmospheric N deposition can in some cases lead to emergence of P limitation (or N and P co-limitation) in ecosystems that were historically N-limited (Vitousek et al. 2010, Crowley et al. 2012).

In temperate regions, elevated N inputs from deposition or fertilization could promote P deficiency, but are more generally thought to cause depletion of soil base cations (i.e., calcium [Ca], magnesium [Mg], and potassium [K]) (Aber et al. 1998, Lucas et al. 2011). Base cations are essential plant nutrients that are relatively abundant in N-limited forests, but increased N availability can promote base cation loss by accelerating nitrification and nitrate leaching, which produces acidic H^+ ions that displace base cations from soil exchange sites and promotes coupled nitrate and

Manuscript received 19 December 2012; revised 3 April 2013; accepted 1 May 2013. Corresponding Editor: E. Hinckley.
[4] E-mail: steven.perakis@oregonstate.edu

base cation leaching (Reuss and Johnson 1986, Homann et al. 1994, Aber et al. 1998). As a result, base cation depletion has emerged as an issue of concern in many forests receiving elevated N inputs, with evidence for deficiencies in Ca, Mg, and K (Aber at al. 1989, Hüttl and Schaaf 1997, Tripler et al. 2006). Forest harvest has also been implicated in base cation depletion by accelerating removals in biomass and leaching faster than replenishment by atmospheric deposition and weathering (Federer et al. 1989, Huntington 2000). Under conditions of severe base cation depletion and low soil pH, there is increased mobilization of aluminum and manganese into soil solution, leading to plant toxicity and interference with base cation uptake (McLaughlin and Wimmer 1999).

Despite evidence that N from forest fertilization and atmospheric deposition can accelerate base cation leaching and depletion from soil (Lucas et al. 2011), it is unclear whether base cation losses continue after N inputs cease, particularly where added N accumulates to cause sustained increases in N cycling. Reductions of N and other acidic inputs can improve base cation status in some cases (Beier et al. 1998, Högberg et al. 2006), but in others base cation depletion is so severe that recovery is slow (Likens et al. 1996). Remeasurement studies in areas affected by acid deposition also suggest that base cation uptake by aggrading biomass can be more important than acidic deposition in driving soil base cation depletion (Johnson and Todd 1990, Johnson et al. 1994). Historical changes in the deposition of acidic sulfur and nitrogen species, as well as base cations (Hedin et al. 1994), further complicate assessments of how long-term changes in soil N fertility may shape soil base cation depletion and associated ecosystem response.

Nutrient conservation through uptake and storage in plant biomass is an important mechanism restricting the loss of essential nutrients from aggrading ecosystems (Vitousek and Reiners 1975). Plant uptake of both P and base cations can be an order of magnitude greater than their release from weathering (Sollins et al. 1980, Watmough and Dillon 2003, Pett-Ridge 2009), but differences in P and base cation biogeochemistry in soils may lead to their differential limitation in high-N sites. Phosphorus is readily retained in soils by both permanent and variable charge clays, whereas base cations are easily displaced from soil exchange sites by hydrogen ions and lost to solution in high-N sites (Sollins et al. 1988). In trees, P and K are both readily resorbed from senescent foliage and redistributed within plants to meet P demands, whereas Mg resorption is lower, and Ca resorption is minimal (Vergutz et al. 2012). Plants and associated microbial communities can use excess available N to produce phosphatase enzymes that liberate P from soil organic matter, but analogous enzymes that target base cation acquisition are unknown outside of general root-mycorrhizal foraging of primary minerals (van Schöll et al. 2008). These factors may preferentially increase P retention and availability relative to base cations (especially Ca, due to minimal resorption) as N accumulates in terrestrial ecosystems, thus intensifying plant demands for base cations from decomposing leaf litter. However, there remains limited evidence as to whether biotic recycling of base cations through litterfall and uptake pathways responds to variations in soil base cation availability, as occurs with N and P.

Regional gradients of soil fertility provide opportunities to evaluate interactions among biogeochemical cycles in ecosystems while minimizing variation in climate, biota, and soil parent material. Across the Pacific Northwest, Douglas-fir forests occupy a highly diverse biogeochemical landscape, ranging from N-limited forests with high P and base cation availability (e.g., Sollins et al. 1980) to N-rich forests with low base cation availability on andic soils of high P sorption capacity (Perakis et al. 2006). Atmospheric N deposition is relatively low across much of this region, but soils can accumulate considerable N under early-successional symbiotic N fixing red alder, which is capable of adding 100–200 kg $N \cdot ha^{-1} \cdot yr^{-1}$ over 50–75 years (Binkley et al. 1994). In the short-term, N fixing red alder often adds sufficient N to accelerate nitrate and base cation loss from soils (Van Miegroet and Cole 1984, Compton et al. 2003), though these changes may reverse rapidly when red alder is removed from low-N soils (Van Miegroet et al. 1992, Homann et al. 1994). Over the long-term, however, recurring disturbances followed by red alder N fixation can cumulatively promote such high N accumulation that internal N availability exceeds biotic demands, leading to natural N saturation that persists even after succession to non-fixing coniferous trees (Perakis and Sinkhorn 2011, Perakis et al. 2011). The consequences of long-term ecosystem N enrichment on soil and ecosystem base cation balances may depend, in part, on the ability of biotic mechanisms to retain essential base cations as nitrate loss increases. In coastal Oregon forests, Ca is of particular interest because annual demands by plants often exceed supplies from weathering and atmospheric deposition (Bockheim and Langley-Turnbaugh 1997, Perakis et al. 2006). High N availability in such areas may stimulate plant growth and biotic Ca retention, resulting in preferential accumulation of Ca in biomass and surface soil at the expense of deeper mineral soil. Yet, high N availability may also cause such intense nitrification and nitrate loss that Ca is also lost via soil solutions, regardless of plant demands. Resolving these interactions can help maintain long-term forest productivity in areas where N enrichment results from biological fixation, atmospheric deposition, or fertilization, and is also important for understanding the degree to which biomass removal and other forest practices may influence long-term site fertility.

The objective of this study was to examine P, Ca, Mg, and K pools and dynamics in plants, soil, and soil water

leaching losses across a soil N gradient of nine young Douglas-fir forests in the Oregon Coast Range. Our prior work at these study sites has shown how long-term cycles of wildfire disturbance and symbiotic N fixation shape broad variation in soil N accumulation across the landscape (Perakis et al. 2011), and has evaluated how soil N legacies shape ecosystem N dynamics and N saturation (Perakis and Sinkhorn 2011, Perakis et al. 2012). Here, we expand these studies of N biogeochemistry to consider multi-element interactions built around the following questions: (1) How do plant and soil pools of P and base cations change with soil N accumulation from N-limited to N-saturated forests? (2) Do increases in nitrate leaching and soil acidification associated with high soil N also drive increased P and base cation loss? (3) Do ecosystem distribution patterns of P and base cations at high-N sites suggest preferential biotic conservation of potential non-N limiting nutrients? The wide soil N gradients studied here provide a glimpse into the potential long-term effects of atmospheric N deposition on temperate forests, and can test ideas most often evaluated for tropical forests of how high soil N availability from symbiotic N fixation shapes coupled biogeochemical cycling.

Methods

Study area description

We studied nine Douglas-fir forests in the north-central Coast Range of Oregon (Table 1), selected as a subset of sites that span a soil N gradient characteristic of the region (Perakis et al. 2006). Climate in the study area is temperate maritime with cool, wet winters and warm, dry summers. Most precipitation falls from October–April as rainfall, and ranges from approximately 180 to 300 cm/yr across the area (National Atmospheric Deposition Program [NADP] OR02 watershed, averaged annual data from 1980–2004). January mean minimum and July mean maximum temperatures range from −2° to +2°C and from 20° to 28°C, respectively. At the time of study, all sites were fully stocked plantations dominated by Douglas-fir (*Pseudotsuga menziesii*; average of 93.4% of basal area greater than 5 cm) ranging from 22–31 years of age, with minor contributions of western hemlock (*Tsuga heterophylla*; average of 2.1% of basal area), and Sitka spruce (*Picea sitchensis*), cascara buckthorn (*Rhamnus purshiana*), bitter cherry (*Prunus emarginata*), red alder (*Alnus rubra*), and bigleaf maple (*Acer macrophyllum*) (<2% basal area).

Our study sites occur on soils formed from Tertiary sedimentary geologic formations. Sedimentary deposits throughout the Oregon Coast Range during this time period accumulated in extensive fore-arc basins, with sediment derived from the Idaho batholith and/or proximal volcanic rock fragments and ash (Heller et al. 1987). Most of our sites occur on the Tyee (5, 22, 58, 76, 77) and Yamhill (16) formations, which are differentiated by the thickness of interbedded sandstone layers; both formations consist of lithic to arkosic or basaltic wackes, and dominant minerals include quartz, andesine, and lithic fragments, with trace potassium feldspars, smectite, calcite, and micas (Snavely et al. 1964, McWilliams 1973, Heller et al. 1985). One site occurs on the Nestucca formation (7), described as thin-bedded tuffaceous siltstone and arkosic sandstone (Bukry and Snavely 1988). Another occurs on the Hamlett formation (20), a fossiliferous basaltic conglomerate and sandstone geochemically identical to the Tillamook volcanic formation from which the clasts are thought to originate; >50% basaltic rock fragments, 3–25% plagioclase, and lesser amounts of augite, opaque minerals, and quartz (Rarey 1985), although road cuts near our site reveal only sandstone and not conglomerate locally. The final site occurs on the Alsea formation (39), which consists predominately of fossiliferous massive to medium-bedded tuffaceous siltstone and very fine-grained sandstone, with minerals including plagioclase, quartz, alkali feldspar, and glauconite, and with volcanic glass shards embedded within the matrix all cemented by secondary carbonates (Snavely et al. 1975). Bulk geochemical data from the references above suggest that the Hamlett formation (20) may contain higher levels of Ca (2–4×), Mg (1.5–2×), and P (2–10×) and less K (0.2–0.5×) than the other parent materials, reflecting its primary basaltic origin. The development of andic properties in soils at our sites reflects both the weathering of igneous materials that contribute to these sedimentary formations, and the presence of poorly characterized humus-metal compounds, and suggests tens of thousands of years of parent material weathering in contrast to Ultisols that form here over hundreds of thousands of years (Franklin 1970, Lindeburg et al. 2013). Highly advanced stages of pedogenic nutrient depletion associated with Ultisols are unlikely at our sites, however, given their classification as andic Inceptisols (eight sites) and Andisols (one site; Table 1).

The development and expression of the wide soil N gradient characterizing our study sites has been described previously (Perakis and Sinkhorn 2011, Perakis et al. 2011). Briefly, high N content in these soils results from long-term cycles of episodic wildfire disturbance and colonization by N fixing red alder, which can add about 7500 kg N/ha (100–200 $kg \cdot ha^{-1} \cdot yr^{-1}$; Binkley et al. 1994) over the lifetime of a 75-year stand. Variation in soil N content across the Oregon Coast Range reflects historic landscape variation in long-term disturbance frequency, the number of accumulated disturbances, and/or the colonization density and associated N fixation by red alder; at some sites, these factors together promote the highest soil N accumulations ever reported worldwide, including those described for tropical forests (Perakis and Sinkhorn 2011). Soil N contents (and natural abundance $\delta^{15}N$ stable isotope values) are greatest near the coast, where red alder is most favored after disturbance, yet soil N is not correlated with elevation, slope, aspect, clay, mean annual temperature,

TABLE 1. Site characteristics, arranged in order from low to high surface soil percent N.

Site	Temp. (°C)	Ppt (cm/yr)	Stand age (yr)	ANPP ($Mg \cdot ha^{-1} \cdot yr^{-1}$)	Soil type (USDA)	Soil C (%)	Soil N (%)	Sand (%)	Silt (%)	Clay (%)	pH (0–10 cm)	pH (0–100 cm)
7	11.3	180	31	8.91	Andic Dystrudept	6.04	0.29	33	20	48	5.83	5.89
20	9.5	231	22	9.09	Alic Hapludand	6.59	0.31	30	44	26	5.22	5.35
76	11.6	172	26	14.90	Andic Dystrudept	5.37	0.33	38	26	36	4.99	5.07
5	11.4	173	29	21.46	Andic Dystrudept	6.25	0.33	53	23	25	5.50	5.62
77	11.2	158	28	19.27	Andic Dystrudept	5.49	0.34	29	31	40	5.30	5.32
58	11.2	175	23	17.02	Andic Dystrudept	6.65	0.38	40	28	33	4.79	4.88
22	10.8	155	29	18.19	Andic Dystrudept	8.24	0.56	46	25	29	5.61	5.65
16	11.2	169	26	14.32	Andic Dystrudept	9.22	0.57	30	31	39	4.61	4.63
39	10.7	200	27	13.63	Andic Dystrudept	16.43	0.78	33	29	39	4.13	4.27

Notes: Surface soil is defined as 0–10 cm depth. Abbreviations are Temp., temperature; Ppt, precipitation; ANPP, aboveground net primary productivity. Soil pH was determined using 2:1 H_2O : soil, with pH (0–100 cm) calculated as a weighted average of all six sampling depths.

nor mean annual precipitation (Perakis and Sinkhorn 2011). We have used surface soil N (0–10 cm) as a predictor variable in our prior analyses from these sites because of its ease of measurement, direct comparability to other studies, relevance as the major rooting zone for forest trees, and its widespread use in ecology, forestry, and soil science. Across our nine study sites, surface mineral soil N (0–10 cm) ranges nearly threefold, from 0.29% to 0.78% N, which correlates with annual net N mineralization ($r = 0.93$, $P < 0.001$) and total soil N pools to 1 m depth ($r = 0.88$, $P = 0.002$; Perakis and Sinkhorn 2011). The percentage of silt + clay in surface soil (0–10 cm) does not correlate with surface soil percent N ($r = 0.07$, $P = 0.86$), net N mineralization ($r = -0.29$, $P = 0.48$), nor total N stocks to 100 cm depth ($r = 0.09$, $P = 0.82$). Weak and nonsignificant correlations between soil bulk density and N pools in all 9 of our soil sampling depths to 100 cm (all $P > 0.37$, Pearson correlation with uncorrected probabilities), and the similarity in soil taxonomic classification across sites, further suggest that subtle parent material differences among some sites are unlikely to explain the large N-related changes in biogeochemistry that we report.

Vegetation and soil sampling

Details of plant and soil sampling for biomass, nutrient content, and nutrient leaching are described previously in a study of ecosystem N dynamics across these sites (Perakis and Sinkhorn 2011). Briefly, foliage and branch samples were collected in July 2005 from the upper canopy of three randomly selected trees per site. Stemwood was sampled by coring three trees per site. Bulk litterfall was collected monthly using 10 traps (0.26 m^2 each) per site. All stems >5 cm diameter were inventoried in 0.02-ha plots in 2006 and Douglas-fir was converted to aboveground biomass using the Douglas-fir hybrid growth system model, an allometry-based growth model developed at these sites (Weiskittel et al. 2010). Biomass estimates were converted to nutrient pools by multiplying against measured concentrations in foliage, branches, and stems. For western hemlock, the next most abundant tree on these sites (average 2.1% of basal area), we estimated biomass using standard allometric equations (Ter-Mikaelian and Korzukhin 1997) and used literature values of nutrient concentrations (Binkley et al. 1992) to scale to nutrient pools.

Forest floor and mineral soil were sampled at four locations per site. Forest floor was collected in 30 × 30 cm frames, and dried at 65°C for 48 h for mass determination. Mineral soil (0–100 cm depth) was sampled using a combination of quantitative pits (30 × 30 cm) in 0–10 cm, 10–20 cm, and 20–30 cm depth intervals, followed by coring (4 cm diameter) for 30–50 cm, 50–70 cm, and 70–100 cm depth intervals. Mineral soil samples were sieved to 2 mm, and soil bulk density was calculated for each depth as the total dry mass of <2 mm soil divided by the volume sampled (Appendix A). Subsamples were dried at 105°C for 48 h to determine moisture content and at 65°C for 48 h prior to grinding for C and N analysis on a Costech ECS-4010 elemental combustion analyzer (Costech Analytical Technologies, Valencia, California, USA). Subsamples from 0–10 cm depth were analyzed for soil texture (percent clay, silt, and sand) by the hydrometer method (Central Analytical Laboratory, Oregon State University, Corvallis, Oregon, USA).

Soil inorganic P (P_i) and organic P (P_o) were determined on air-dry soil subsamples by extraction with NaOH/EDTA, which removes both labile and moderately labile forms of iron and aluminum associated P_i and microbial P_i, and soil organic matter P_o and microbial P_o (Bowman and Moir 1993, Turner 2004). Analysis of P_i was performed colorimetrically via Lachat QuikChem 8000 flow-injection auto-analyzer (Lachat Instruments, Loveland, Colorado, USA), and analysis of total dissolved P via inductively coupled plasma optical emission spectrometer at the W. M. Keck Collaboratory at Oregon State University, with P_o calculated by difference. Exchangeable soil cations, calcium (Ca), magnesium (Mg), and potassium (K), were determined on moist subsamples of soil by ammonium acetate extraction (Bullen and Bailey 2005) with analysis by inductively coupled plasma mass emission spectrometer at the USGS Metal Isotope Laboratory (Menlo Park, California, USA). Soil solution pH (2 water : 1 soil) was assayed using fresh soil

with an Accumet pH probe meter. Forest floor, litter, foliage, branch, and bolewood concentrations of C and N were determined by Costech ECS-4010 elemental combustion analyzer, and concentrations of Ca, Mg, K, and P were determined by nitric acid microwave digestion and analysis by ICP, as above. Nutrient capital of the forest floor and soil to 100 cm was calculated using forest floor or soil layer thickness, nutrient concentrations, and bulk density.

Lysimeter installation and soil water sampling

Soil solution nutrient concentrations were monitored using three pairs of Prenart low-tension lysimeters (Prenart Equipment ApS, Frederiksberg, Denmark) installed at 20 cm (shallow) and 1 m (deep) depths at each site, which were installed and allowed to equilibrate for 2–4 months before sampling. Lysimeters were sampled monthly by applying 35 kPa of vacuum for 2 days. One replicate sample per lysimeter was immediately capped, and another preserved with 0.2 mL of chloroform. Samples were analyzed for nitrate (NO_3^--N) and ammonium (NH_4^+-N) colorimetrically using cadmium reduction on a Lachat QuikChem 8000 flow-injection auto-analyzer, and for total dissolved N and dissolved organic carbon (DOC) by catalytic oxidation combustion using a Shimadzu TOC-V CSH total organic carbon analyzer with total N module. Dissolved organic N (DON) was calculated as total dissolved N minus NO_3^--N minus NH_4^+-N. Samples were also analyzed for total dissolved P by persulfate digestion and analysis as P_i colorimetrically via Lachat QuikChem 8000 flow-injection auto-analyzer, for Ca, Mg, K, sodium (Na), and total aluminum (Al) by ICP, and for chloride (Cl) and sulfate (SO_4^{2-}) by ion chromatography using a Dionex-600. We also normalized fluxes of sulfate and base cations to calculate non-sea-salt (NSS) contributions based on Cl : ion ratios (Hedin et al. 1995) measured in precipitation in the Oregon Coast Range (NADP OR02, averaged annual data from 1980–2007).

We scaled monthly lysimeter nutrient concentrations to fluxes using water yield estimates derived as precipitation minus evapotranspiration for each of our sites. We obtained precipitation for each site from spatially resolved PRISM modeling (data *available online*),[5] and used these data to drive 3-PG (Physiological Processes for Predicting Growth), a forest process model that uses the Penman-Monteith equation to estimate evapotranspiration (Lansberg and Waring 1997). We estimated the volume of water leaching past 100 cm as the difference between precipitation and evapotranspiration, and used the depth distribution of fine roots from a nearby Coast Range site (M. Johnson, *unpublished data*) to partition soil water leaching into 0–20 and 20–100 cm increments (Appendix B). Soil water nutrient fluxes were calculated monthly as nutrient concentration times the water leaching at 20 cm and 100 cm.

[5] http://www.prismclimate.org

Statistics

We used least-squares linear and nonlinear (form $y = A/[x - B]$) regression to evaluate relationships between predictor variables (soil percent N and nitrate leaching) and response variables. We analyzed subsamples for most variables at all sites, but only variable means are used in regression analyses, as entire study sites were not replicated along the gradient (Hurlbert 1984). Slopes of linear regressions were compared using homogeneity of slopes tests. Pearson correlation was used where dependent and independent variables could be interchanged. Paired t tests were used to compare nutrient leaching at 20 cm vs. 100 cm depths. SYSTAT 11 (Richmond, California, USA) was used for all statistical analyses. Significance levels were set at $P \leq 0.05$.

Results

Nutrients in biomass and soil

Calcium was the only nutrient that displayed decreasing concentrations in biomass components along the soil N gradient, with significant declines detected in foliage, branches, litterfall and forest floor (Fig. 1). Concentrations of N and K increased in foliage across the gradient, Mg concentrations increased in branches, and P showed no significant trends (Fig. 1). Stemwood did not display any significant nutrient concentration trends along the N gradient (data not shown). Annual Ca fluxes in litterfall exhibited a weak linear decline along the N gradient ($r^2 = 0.41$, $P = 0.06$, not shown), but litterfall N, P, Mg, and K did not exhibit trends with soil N (all $P > 0.18$). Calcium fluxes in litterfall also varied more than other litterfall fluxes across the gradient (3.5-fold for Ca vs. 2-fold variation for other nutrients).

For total nutrient pools in aboveground biomass, Ca was the only nutrient that decreased significantly across the soil N gradient ($r^2 = 0.45$, $P = 0.048$; Fig. 2A). Biomass pools of N, Mg, and K increased from the two lowest-N sites to relatively constant values at higher-N sites (Table 2), but did not display significant linear trends across the full N gradient.

Forest floor nutrient pools varied less than mineral soil nutrients across the N gradient, and Ca varied more than other elements overall. The forest floor Ca pool varied 2.7-fold across sites, followed by K (2.1-fold), Mg and N (1.8-fold), and C and P (1.5-fold; Table 2). Only Ca declined in forest floor as soil N increased ($r^2 = 0.66$, $P = 0.005$; Fig. 2B). In mineral soil (0–100 cm), the exchangeable Ca pool varied 35-fold across sites, followed by exchangeable Mg (25-fold) and K (4-fold), extractable P_i and P_o (3-fold, excluding one outlier for P_i) and total C and N (2.6-fold; Table 3). Mineral soil (0–100 cm) exchangeable pools of Ca and Mg both declined nonlinearly across the soil N gradient (Ca $r^2 = 0.82$, $P < 0.001$; Mg $r^2 = 0.73$, $P = 0.017$), whereas

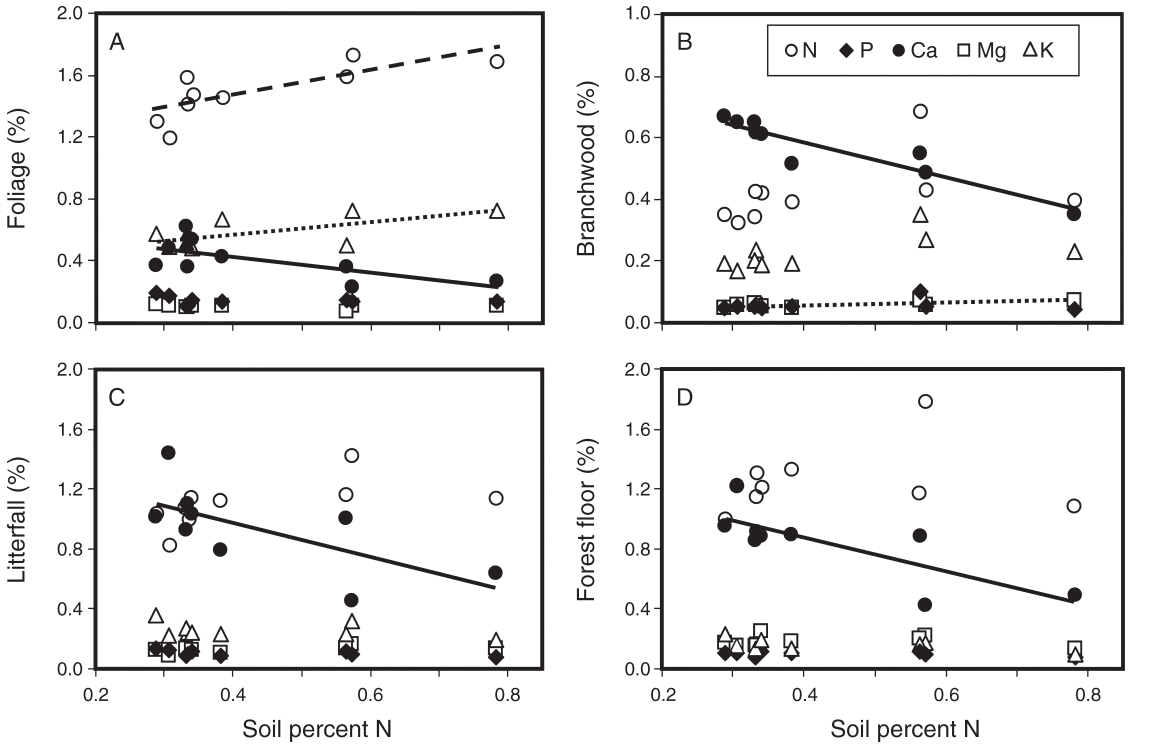

FIG. 1. Concentrations of N, P, Ca, Mg, and K in (A) foliage, (B), branches, (C) litterfall, and (D) forest floor plotted against soil percent N (0–10 cm depth). Linear regressions are shown for (A) N ($r^2 = 0.59$, $P = 0.01$), Ca ($r^2 = 0.45$, $P = 0.05$) and K ($r^2 = 0.39$, $P = 0.08$); (B) Ca ($r^2 = 0.86$, $P < 0.001$) and Mg ($r^2 = 0.57$, $P = 0.02$), (C) Ca ($r^2 = 0.45$ $P = 0.05$); and (D) Ca ($r^2 = 0.61$, $P = 0.01$).

exchangeable K exhibited a weak linear decline ($r^2 = 0.45$, $P = 0.07$), extractable P_i showed no trend, and extractable P_o increased linearly ($r^2 = 0.72$, $P = 0.004$; Fig. 2C).

Surface soil nutrient pools (0–10 cm) were positively linearly correlated with pools at depth (10–100 cm) for all nutrients. Surface to deep correlations of nutrient pools were especially strong for exchangeable base cations (Ca $r = 0.98$, $P < 0.0001$; Mg $r = 0.84$, $P = 0.005$; K $r = 0.85$, $P = 0.004$; all $n = 9$), and were also significant for total pools of C ($r = 0.67$, $P = 0.05$) and N ($r = 0.78$, $P = 0.01$), and for extractable P_i ($r = 0.54$, $P = 0.02$) and P_o ($r = 0.77$, $P = 0.002$).

We used nutrient pool data to calculate how nutrient partitioning among ecosystem compartments and soil depths varied across the N gradient. Total ecosystem nutrient content was estimated as the sum of nutrient pools in aboveground biomass, forest floor, and mineral soil (0–100 cm). In mineral soil, we calculated pools based on values for total N, total extractable P ($P_i + P_o$), and exchangeable Ca, Mg, and K. We found that aboveground biomass contained a decreasing percentage of total ecosystem N as soil N increased ($r^2 = 0.75$, $P < 0.01$), with no analogous trend observed for P ($P = 0.29$; Fig. 3A). In contrast, aboveground biomass contained an increasing percentage of total ecosystem Ca ($r^2 = 0.65$, $P < 0.01$), Mg ($r^2 = 0.57$, $P = 0.02$), and K ($r^2 = 0.79$, $P = 0.001$) as soil N increased, and the slope was steeper for Ca than for Mg ($P = 0.05$) or K ($P = 0.07$; homogeneity of slopes test). Likewise, forest floor contained an increasing percentage of total ecosystem Ca ($r^2 = 0.54$, $P = 0.02$) and Mg ($r^2 = 0.47$, $P = 0.05$), a decreasing percentage for N ($r^2 = 0.52$, $P = 0.03$), and no pattern for P or K ($P > 0.12$) as soil N increased (Fig. 3B). In mineral soil, both Ca and Mg were increasingly concentrated in the top 10 cm (Ca $r^2 = 0.76$, $P = 0.002$; Mg $r^2 = 0.58$, $P = 0.02$) as soil N increased, with no trend observed for K, P_i, or P_o (all $P > 0.66$; Fig. 3C)

We calculated weighted average element ratios in mineral soil (0–100 cm) across all sites of C:N = 16.4 ± 0.6 (mean ± SE), C:P_o = 197 ± 18, and N:P_o = 12.0 ± 0.8. Neither C:N, C:P_o, nor N:P_o ratios in mineral soil varied predictably with 0–10 cm soil percent N across the gradient (all $P > 0.65$, not shown). However, 0–100 cm mineral soil pools of C, N and P_o were interrelated, with significant positive correlations between C and N ($r = 0.93$), C and P_o ($r = 0.77$), and N and P_o ($r = 0.87$; all $P < 0.02$).

Exchangeable Ca and Mg in both 0–20 cm and 0–100 cm depths and K in the 0–20 cm depth declined with increasing nitrate leaching at these respective depths (Fig. 4A and B). Leaching of total and non-sea-salt Ca and Mg were unrelated to exchangeable pools at either 0–20 cm or 0–100 cm depths. The pool of soil

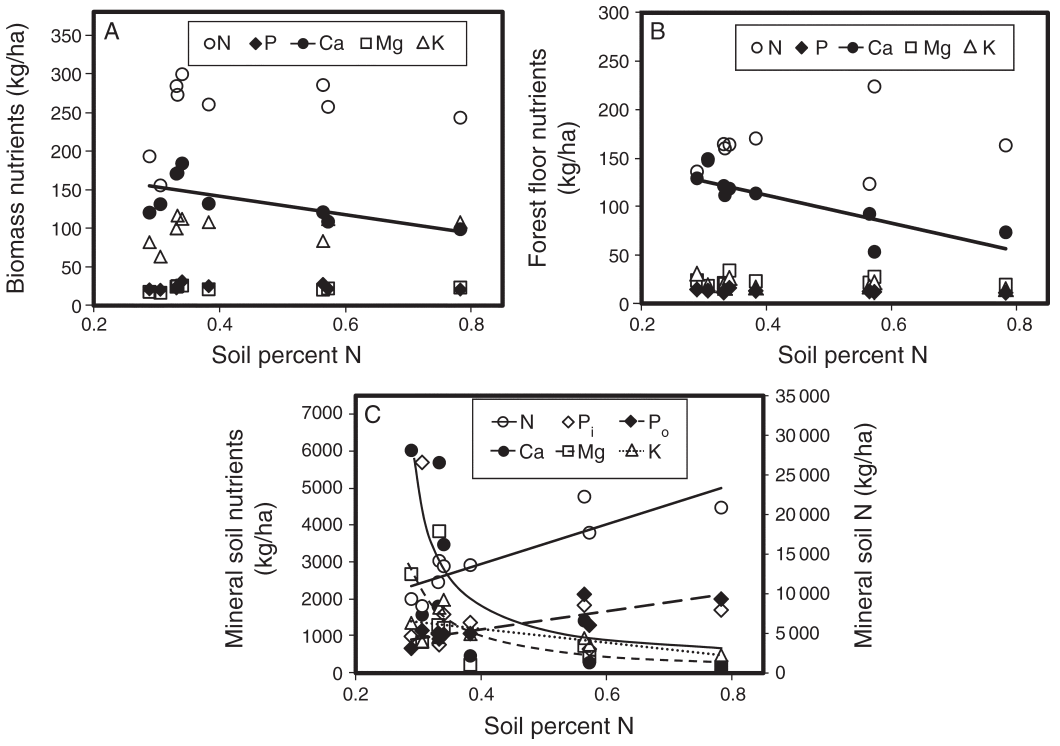

FIG. 2. Pools of N, P, Ca, Mg, and K plotted against surface soil (0–10 cm depth) percent N for (A) aboveground biomass, (B) forest floor, and (C) mineral soil (0–100 cm depth). Mineral soil pools are for total N, extractable inorganic P (P_i) and organic P (P_o), and exchangeable Ca, Mg, and K. Significant linear regressions are shown for (A) Ca ($r^2 = 0.44$, $P = 0.05$), (B) Ca ($r^2 = 0.70$, $P = 0.005$), and (C) N ($r^2 = 0.77$, $P = 0.002$), P_o ($r^2 = 0.72$, $P = 0.004$), Ca ($r^2 = 0.82$, $P < 0.001$), Mg ($r^2 = 0.73$, $P = 0.017$), and K (marginally significant, $r^2 = 0.45$, $P = 0.07$).

exchangeable K to 100 cm depth was positively correlated to both total (abs) and non-sea-salt (nss) K leaching at 100 cm depth (K_{abs} $r = 0.75$, $P = 0.02$; K_{nss} $r = 0.81$, $P < 0.01$), but no relationships occurred at 20 cm depth. Mean soil profile pH ranged over roughly 1 unit across sites (Table 1), and declined logarithmically with nitrate leaching at both 20 cm ($r^2 = 0.69$, $P = 0.006$) and 100 cm ($r^2 = 0.67$, $P = 0.007$; Fig. 4C). In addition, the sum of exchangeable Ca, Mg, and K was positively correlated with soil pH over both 20 cm ($r = 0.82$, $P < 0.01$) and 100 cm ($r = 0.85$, $P < 0.01$) depths (not shown). The sum of exchangeable Ca, Mg, and K pools to 20 cm was not correlated significantly with either soil organic carbon (SOC; $P = 0.30$) or percent clay ($P = 0.55$).

Nutrient leaching

Na was the most abundant base cation in soil solution leachates across all sites and sampling depths, except for shallow lysimeters at site 20 (the most N-poor site), where Ca was the most abundant base cation in soil solution (Table 4). Total leaching fluxes at 20 cm vs. 100

TABLE 2. Nutrient pools in aboveground biomass and in annual litterfall.

	Aboveground biomass						Litterfall					
Site	C (Mg/ha)	N (kg/ha)	P (kg/ha)	Ca (kg/ha)	Mg (kg/ha)	K (kg/ha)	C (Mg·ha^{-1}·yr^{-1})	N (kg·ha^{-1}·yr^{-1})	P (kg·ha^{-1}·yr^{-1})	Ca (kg·ha^{-1}·yr^{-1})	Mg (kg·ha^{-1}·yr^{-1})	K (kg·ha^{-1}·yr^{-1})
7	61.1	193.3	21.0	120.4	17.9	82.1	1.21	24.3	3.2	23.7	2.8	8.3
20	33.4	155.6	20.5	131.3	16.6	63.4	1.19	19.0	2.8	33.2	2.1	5.1
76	84.7	284.1	22.3	170.8	24.6	99.8	1.43	30.0	2.5	25.7	3.7	7.6
5	81.6	272.8	25.2	171.6	25.3	116.5	1.09	21.0	2.0	23.0	2.7	4.9
77	95.4	299.5	31.4	184.0	25.9	112.2	1.52	33.0	3.2	29.7	3.5	7.0
58	63.0	260.3	25.2	132.0	21.2	108.0	1.42	30.7	2.4	21.2	2.9	6.3
22	80.2	285.5	28.1	120.9	20.7	83.6	1.45	33.0	3.3	28.0	3.8	6.4
16	49.2	257.2	21.8	108.7	22.3	111.8	1.14	30.3	2.0	9.6	3.4	6.8
39	60.8	243.2	20.7	98.9	23.5	108.1	1.24	26.6	1.7	14.7	3.0	4.6

Notes: Sites are arranged in order of increasing surface soil (0–10 cm) percent N.

TABLE 3. Nutrient pools in forest floor and mineral soil (0–100 cm).

	Forest floor						Mineral soil					
Site	C (Mg/ha)	N (kg/ha)	P (kg/ha)	Ca (kg/ha)	Mg (kg/ha)	K (kg/ha)	C (Mg/ha)	N (kg/ha)	P (kg/ha)	Ca (kg/ha)	Mg (kg/ha)	K (kg/ha)
7	6.2	136.1	14.5	129.3	24.0	30.7	170	9 349	1658	6022	2654	1357
20	5.6	148.9	13.3	147.5	18.1	18.9	142	8 460	6846	1573	823	855
76	6.9	164.6	11.3	121.4	21.2	19.3	164	11 463	2140	1805	1278	972
5	5.8	160.2	13.1	111.8	20.1	16.1	267	14 152	1686	5689	3817	1764
77	5.3	164.0	16.1	118.6	34.0	26.4	196	13 483	2632	3473	1189	1981
58	5.9	170.4	13.1	113.6	23.0	16.4	219	13 624	2430	464	201	1053
22	4.8	123.5	12.5	92.5	21.6	17.4	314	22 255	3962	1415	713	943
16	5.1	224.0	11.9	53.4	27.6	22.0	291	17 707	1939	280	418	765
39	7.3	163.2	11.1	73.5	19.3	14.8	379	20 880	3705	171	155	484

Notes: Sites are arranged in order of increasing surface soil (0–10 cm) percent N. Soil C and N pools are total values from Perakis et al. (2011). Ca, Mg, and K are total digests in forest floor and exchangeable in mineral soil. P is a total digest for forest floor and total NaOH extractable (inorganic and organic) in mineral soil.

cm were positively correlated for Na (slope = 0.75, $r^2 = 0.87$, $P < 0.001$) and Mg (slope = 0.54, $r^2 = 0.82$, $P < 0.001$), weakly correlated for Ca (slope = 0.16, $r^2 = 0.39$, $P = 0.07$), and uncorrelated for K (slope = 0.29, $r^2 = 0.16$, $P = 0.29$). Leaching fluxes were significantly greater at 20 cm than 100 cm depth for Ca ($P = 0.01$) and Mg ($P < 0.01$), but did not vary by depth for Na ($P = 0.10$) or K ($P = 0.13$). After correcting for sea-salt inputs (Appendix C), non-sea-salt contributions to lysimeter fluxes were significantly higher at 20 cm than at 100 cm for Ca (77% at 20 cm, 68% at 100 cm, paired t test, $P = 0.04$), marginally higher at 20 cm than 100 cm for Mg (52% at 20 cm, 42% at 100 cm, paired t test, $P = 0.07$), and not different by depth for Na (<1% at 20 cm, 7% at 100 cm, paired t test, $P = 0.25$) or K (44% at 20 cm, 46% at 100 cm, paired t test, $P = 0.91$). Non-sea-salt contributions to lysimeter SO_4^{2-} fluxes were consistently negative, indicating net retention, with no significant differences by depth (–42% at 20 cm, –26% at 100 cm, paired t test, $P = 0.45$)

Nitrate leaching (Table 5) increased with soil N, particularly at high-N sites. Nitrate fluxes in shallow and deep lysimeters were significantly related near 1:1, indicating high nitrate mobility through soil (slope = 1.18, $r^2 = 0.91$, $P < 0.001$). However, we observed few significant relationships across sites between nitrate leaching and either absolute or non-sea-salt leaching fluxes of base cations, Cl, and SO_4^{2-}. Volume weighted concentrations of Cl, Mg, and Na in 100 cm deep lysimeters, and Na in 20 cm deep lysimeters, did decrease with distance (km) from the coast (Cl $y = -1.31\ln x + 6.27$, $r^2 = 0.48$, $P = 0.04$; Mg $y = -0.15\ln x + 0.716$, $r^2 = 0.52$, $P = 0.03$; Na_{deep} $y = -0.88\ln x = 3.99$, $r^2 = 0.66$, $P = 0.008$; $Na_{shallow}$ $y = -0.78\ln x + 3.74$, $r^2 = 0.48$, $P = 0.04$), but this pattern was not seen for Ca, K, or P. Fluxes of total Al increased with NO_3^- in both 20 cm ($r^2 = 0.82$, $P < 0.001$) and 100 cm deep lysimeters ($r^2 = 0.88$, $P < 0.001$), primarily due to high values at sites with soil pH < 5 (Table 4). Total Al and DOC were not correlated at either lysimeter depth (20 cm, $P = 0.78$; 100 cm, $P = 0.72$). Lysimeter TP fluxes (Table 6) at 20 and 100 cm were unrelated to total extractable soil P and P_o over these depths (all $P > 0.18$). A single P-rich site (20) strongly influenced a positive relationship between soil extractable P_i and TP leaching to 20 cm ($r^2 = 0.56$, $P = 0.02$).

DISCUSSION

Our results support a hierarchical model of coupled N and base cation cycles across gradients of soil N enrichment; over the long-term at the ecosystem-level, symbiotic N fixation promotes high N accumulation, N saturation, and persistent nitrate loss that depletes soil base cations, and within this context biotic processes increase base cation conservation as overall pools diminish. Soil pools of Ca, Mg, and K and soil pH declined sharply with increased soil N and nitrate leaching across sites, yet measured leaching losses of nitrate and base cations were unrelated, suggesting that readily weatherable base cations had already been mobilized and depleted by long-term nitrate loss. As base cation availability declined across the N gradient, vegetation became a progressively more important reservoir for remaining base cations, particularly for Ca. Vegetation played a stronger role in conserving Ca than other base cations, most likely because Ca is in shortest supply relative to plant demands in these forests, where atmospheric nutrient sources predominate (Perakis et al. 2006). Surface mineral soil (0–10 cm) was also an increasingly important reservoir for Ca across the gradient of soil Ca depletion, suggesting efficient biotic Ca recycling through litterfall, decomposition, and plant uptake pathways. Overall, the patterns we observed in coupled N–Ca cycles along our N gradient are consistent with the broader idea that ultimate ecosystem and soil biogeochemical constraints on nutrient availability can shape proximal plant physiological strategies for nutrient conservation, as reported previously along gradients of soil age (Treseder and Vitousek 2001) and climate (Schuur and Matson 2001). We also note that while biotic retention may slow losses of essential nutrients, such retention appears incapable of reversing whole-ecosystem nutrient depletion where the cause of depletion persists, such as the unusually

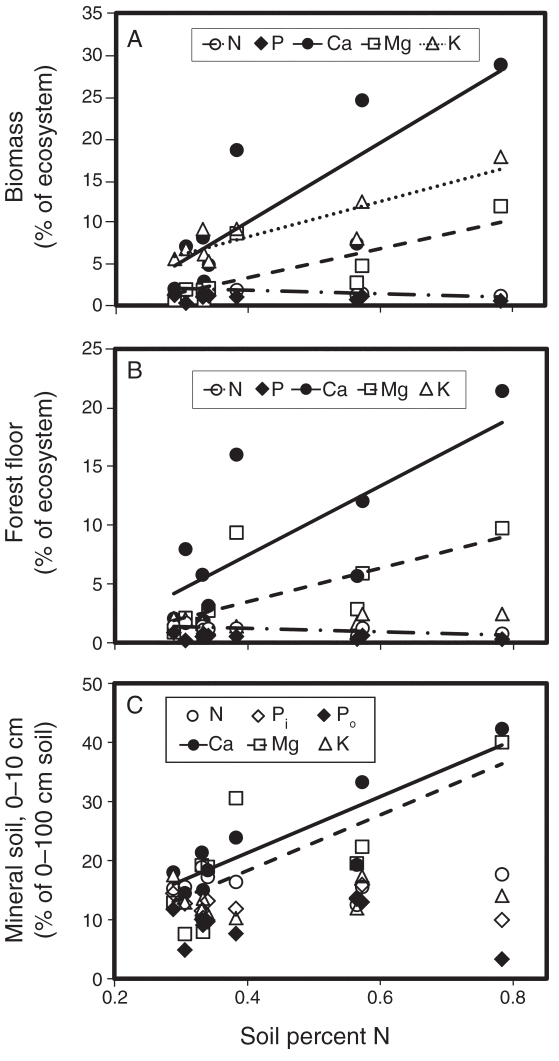

FIG. 3. The percentage of nutrients contained in (A) aboveground biomass relative to the entire ecosystem, (B) forest floor relative to entire ecosystem, and (C) surface 0–10 cm mineral soil relative to 0–100 cm mineral soil, all plotted against surface 0–10 cm soil percent N. Significant linear regressions are shown for (A) N ($r^2 = 0.75$, $P = 0.003$), Ca ($r^2 = 0.65$, $P = 0.008$), Mg ($r^2 = 0.57$, $P = 0.02$), and K ($r^2 = 0.79$, $P = 0.001$); (B) N ($r^2 = 0.51$, $P = 0.03$), Ca ($r^2 = 0.54$, $P = 0.02$), and Mg ($r^2 = 0.47$, $P = 0.04$), and (C) Ca ($r^2 = 0.76$, $P = 0.002$) and Mg ($r^2 = 0.58$, $P = 0.02$).

high N accumulation that drives chronic nitrate leaching and base cation depletion across our sites.

We did not find support for the idea that P was deficient and/or limiting as N availability increased. In vegetation, neither pools nor concentrations of biomass P changed significantly across the N gradient. Foliar N:P increased from 6.5 to 12.5 (by mass) as foliar N increased across the gradient, yet foliar N:P remained well below the ratio (N:P = 20) that is suggested to indicate potential P limitation (Güsewell 2004). In mineral soil, P_i did not vary with soil N across sites, and P_i content in both 0–10 and 0–100 cm soil (median = 106 kg P/ha and 1300 kg P/ha, respectively) greatly exceeded the P content of aboveground biomass (median = 22.3 kg P/ha) and of annual aboveground P demands (median = 2.54 kg $P \cdot ha^{-1} \cdot yr^{-1}$, data not shown), suggesting ample soil P_i relative to plant demands (Johnson et al. 2003, Yang and Post 2011). The insensitivity of soil P_i to low pH at high-N sites is surprising, and is true for both the basic (NaOH) soil extractant used in this study, and an acidic soil extractant (Bray-1) used in a prior survey of surface soils across 24 coastal Oregon forests (Perakis et al. 2006). The insensitivity of soil P_i to low pH may instead be due to P_i sorption by variably charged clays in these Andisols, which are less pH sensitive for P_i sorption than permanently charged clays (Sollins et al. 1988). Regardless, the relatively constant and high levels of foliar P

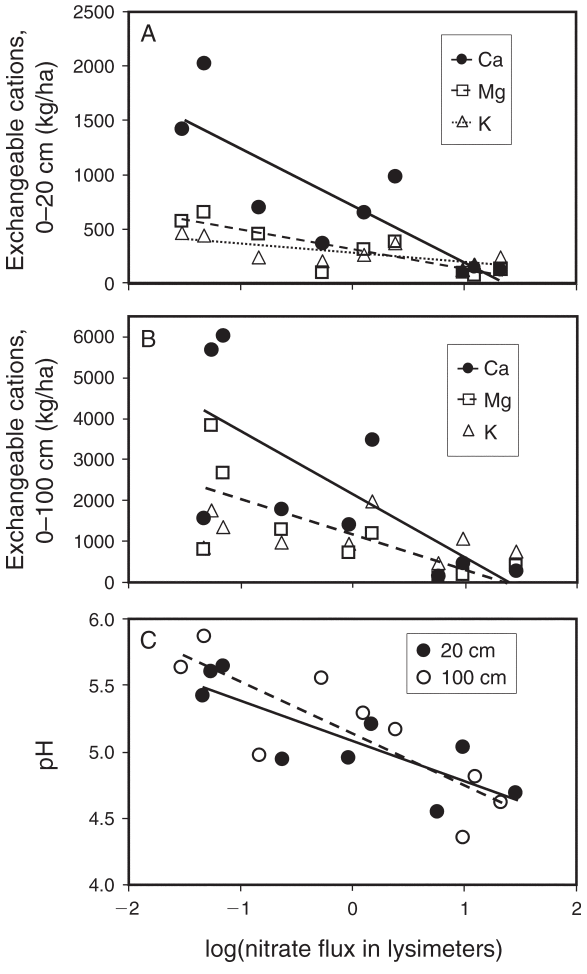

FIG. 4. Exchangeable Ca, Mg, and K pools in mineral soil at (A) 20 cm and (B) 100 cm, and (C) soil pH at 20 cm and 100 cm, plotted against log(NO_3^- leaching in lysimeters) (measured as kg $N \cdot ha^{-1} \cdot yr^{-1}$) at 20 and 100 cm depth. Significant linear regressions are shown for (A) Ca ($r^2 = 0.69$, $P = 0.006$), Mg ($r^2 = 0.73$, $P = 0.003$), and K ($r^2 = 0.52$, $P = 0.03$); (B) Ca ($r^2 = 0.51$, $P = 0.03$) and Mg ($r^2 = 0.52$, $P = 0.03$); and (C) 20 cm ($r^2 = 0.69$, $P = 0.006$) and 100 cm ($r^2 = 0.67$, $P = 0.007$).

TABLE 4. Cation fluxes in soil water at 20 cm and 100 cm.

Site	20 cm						100 cm					
	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+-N	Al_{tot}	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+-N	Al_{tot}
7	8.74	6.45	4.09	31.83	0.23	0.38	5.39	5.01	1.81	22.43	0.17	0.14
	(0.39)	(0.24)	(0.87)	(1.97)	(0.01)	(0.09)	(0.34)	(0.19)	(0.37)	(2.06)	(0.02)	(0.02)
20	32.08	11.34	14.95	22.76	0.19	0.31	10.46	8.38	2.97	33.10	0.20	0.18
	(4.07)	(1.08)	(2.91)	(2.49)	(0.01)	(0.06)	(1.51)	(0.55)	(0.09)	(1.09)	(0.01)	(0.03)
76	8.36	6.39	4.33	36.65	0.21	0.42	6.79	4.83	3.62	32.80	0.23	0.08
	(0.05)	(0.15)	(0.36)	(0.21)	(0.02)	(0.09)	(1.14)	(0.42)	(0.79)	(1.03)	(0.02)	(0.01)
5	20.05	21.94	20.75	76.62	0.17	0.51	7.19	12.16	9.67	60.81	0.13	0.17
	(2.52)	(2.83)	(0.93)	(15.38)	(0.01)	(0.07)	(0.56)	(0.70)	(1.66)	(6.76)	(0.01)	(0.02)
77	13.03	8.65	11.26	37.89	0.19	0.13	8.55	3.59	18.12	24.55	0.15	0.18
	(2.69)	(1.67)	(2.25)	(3.92)	(0.03)	(0.01)	(1.88)	(0.39)	(0.63)	(0.20)	(0.01)	(0.02)
58	20.34	10.23	20.44	32.01	0.22	1.05	11.54	6.10	6.28	31.22	0.13	0.17
	(4.38)	(1.89)	(3.31)	(2.18)	(0.03)	(0.10)	(2.65)	(1.37)	(1.33)	(1.96)	(0.01)	(0.01)
22	7.62	6.54	7.39	31.07	0.18	0.24	7.79	6.88	5.90	31.34	0.13	0.11
	(0.45)	(48%)	(0.82)	(1.03)	(0.03)	(0.03)	(0.72)	(0.26)	(0.82)	(1.28)	(0.01)	(0.01)
16	13.80	16.62	8.29	63.84	0.21	3.89	6.80	12.11	8.45	62.79	0.16	4.26
	(2.18)	(1.34)	(1.56)	(6.78)	(0.01)	(0.39)	(1.35)	(0.90)	(1.44)	(4.57)	(0.01)	(0.46)
39	14.67	16.66	1.09	84.65	0.25	1.03	9.67	11.42	1.01	70.19	0.21	0.22
	(1.05)	(1.07)	(0.19)	(2.54)	(0.02)	(0.15)	(0.47)	(0.98)	(0.16)	(5.33)	(0.01)	(0.05)

Notes: Values ($kg \cdot ha^{-1} \cdot yr^{-1}$) are the average of three lysimeters per site per depth, with standard errors in parentheses. Al fluxes are for total Al. NH_4^+ data are from Perakis and Sinkhorn (2011).

and soil P_i across our gradient suggest that P deficiency did not emerge as N accumulated.

To understand how nutrient accumulation shapes long-term nutrient limitation, it is noteworthy that soil P_o increased significantly with both soil N and C across our gradient. Soil P_o often increases with soil C, and provides a large reservoir of potentially mineralizable and enzymatically accessible P for plant uptake (McGill and Cole 1981, Sitters et al. 2013). Symbiotic N fixing red alder, which is the primary source of soil N across our gradient, can accelerate weathering to access P from primary minerals and recycle P through litterfall, thus leading to increased soil P_o accumulation (Compton and Cole 1998). In this way, N accumulation from symbiotic N fixing trees may increase soil P reservoirs as soil P_o, potentially delaying P deficiency and limitation as N accumulates. Such increased P availability could also delay the onset of N saturation until some element other than N or P becomes limiting. Once produced, the long-term ecosystem importance of P_o ultimately depends on its availability for plant uptake vs. susceptibility to loss (Hedin et al. 2003, Perring et al. 2008). The sandstone-derived soils where we worked are relatively young (2000–6000 years; Anderson et al. 2002), yet our rates of P leaching loss at 1 m depth (range 0.01–0.04, average = 0.02) were at the low end of loss rates from other temperate (e.g., 0.8 kg $P \cdot ha^{-1} \cdot yr^{-1}$ [Sollins et al. 1980], 0.05 kg $P \cdot ha^{-1} \cdot yr^{-1}$ [Yanai 1991]) and tropical (e.g., <0.08 kg $P \cdot ha^{-1} \cdot yr^{-1}$ [Hedin et al. 2003, Pett-Ridge 2009]) forests, and P leaching did not vary systematically along the gradient. Andic soil properties at our sites may be especially important in retaining P, with high content of amorphous minerals that promote both organic matter (i.e., P_o) and P_i sorption (Franklin 1970). These properties may enhance retention of P that is cycled by symbiotic N fixers, leading to a large internal P reservoir that delays P limitation of successional non-fixing vegetation. This contrasts with highly weathered Oxisols and Ultisols, more common in subtropical and tropical regions, which exhibit intense P occlusion and terminal P depletion (Walker and Syers 1976). Whereas accumulated P_o may be a significant long-term reservoir for

TABLE 5. Anion fluxes in soil water at 20 cm and 100 cm depths.

Site	20 cm			100 cm		
	NO_3^--N	Cl^-	SO_4^{2-}-S	NO_3^--N	Cl^-	SO_4^{2-}-S
7	0.05 (0.01)	60.12 (0.88)	2.67 (0.30)	0.07 (0.01)	34.54 (3.93)	3.99 (0.09)
20	0.53 (0.02)	36.14 (4.65)	3.81 (0.07)	0.05 (0.01)	43.17 (1.50)	4.69 (0.32)
76	0.15 (0.03)	64.56 (1.82)	4.16 (0.25)	0.23 (0.04)	76.67 (5.05)	3.04 (0.18)
5	0.03 (0.01)	164.52 (31.72)	18.88 (2.64)	0.05 (0.01)	114.62 (10.36)	9.14 (1.51)
77	2.40 (0.27)	68.26 (10.73)	3.41 (0.06)	1.50 (0.15)	40.37 (2.92)	2.50 (0.15)
58	12.50 (2.43)	52.90 (3.77)	2.49 (0.42)	9.66 (1.56)	42.26 (1.35)	3.70 (0.55)
22	1.26 (0.11)	51.95 (2.29)	7.42 (0.88)	0.92 (0.16)	55.91 (3.93)	7.52 (0.33)
16	21.20 (3.67)	103.00 (7.36)	4.68 (0.45)	28.33 (5.09)	90.32 (1.77)	3.71 (0.43)
39	9.76 (1.48)	147.71 (7.41)	7.14 (0.30)	5.76 (0.83)	105.03 (13.53)	6.94 (0.95)

Notes: Values ($kg \cdot ha^{-1} \cdot yr^{-1}$) are the average of three lysimeters per site per depth, with standard errors in parentheses. NO_3^- data are from Perakis and Sinkhorn (2011).

TABLE 6. DOC, total N, and total P fluxes in soil water at 20 cm and 100 cm depths

Site	20 cm			100 cm		
	DOC	TN	TP	DOC	TN	TP
7	21.55 (4.32)	1.34 (0.10)	0.04 (0.02)	6.55 (0.24)	0.74 (0.09)	0.02 (0.00)
20	24.04 (4.34)	2.24 (0.34)	0.05 (0.01)	8.36 (0.56)	0.91 (0.07)	0.04 (0.01)
76	17.54 (0.63)	3.55 (0.56)	0.02 (0.00)	5.87 (0.75)	0.86 (0.12)	0.01 (0.00)
5	25.78 (2.31)	1.43 (0.18)	0.02 (0.01)	14.00 (0.21)	0.87 (0.03)	0.01 (0.00)
77	17.02 (2.10)	3.83 (0.85)	0.02 (0.00)	9.12 (0.63)	2.56 (0.69)	0.01 (0.00)
58	15.80 (3.60)	16.54 (4.03)	0.01 (0.00)	5.09 (0.88)	10.45 (6.61)	0.01 (0.00)
22	19.69 (2.74)	2.43 (0.68)	0.02 (0.00)	9.13 (1.17)	1.50 (0.46)	0.01 (0.00)
16	22.24 (1.56)	23.54 (4.22)	0.02 (0.01)	7.35 (0.52)	28.98 (4.92)	0.04 (0.01)
39	16.53 (0.47)	10.91 (2.08)	0.01 (0.00)	10.69 (0.77)	6.63 (1.17)	0.02 (0.01)

Notes: DOC, TN, and TP fluxes are per unit C, N, and P, respectively. Values ($kg \cdot ha^{-1} \cdot yr^{-1}$) are the average of three lysimeters per site per depth, with standard errors in parentheses.

P in forest soils, the lack of substantial organic phases for Ca and other base cations in mineral soil precludes their retention and recycling by these mechanisms.

A legacy of long-term nitrate leaching and soil acidification, driven by unusually high N accumulation from historic symbiotic N fixation, is responsible for the substantial decline in soil base cations observed across our N gradient. Disturbance in moist Pacific Northwest forests promotes colonization of N fixing red alder, which increases soil N availability and coupled nitrate and base cation leaching, but such changes are reversible on low-N soils when N fixing red alder is removed (Van Miegroet et al. 1992, Homann et al. 1994). However, multiple cycles of disturbance and red alder N fixation can foster such high soil N accumulation that a legacy of elevated N cycling and loss can persist for centuries to millenia after red alder is no longer present, particularly where surface 0–10 cm soil exceeds ~0.4% N (Perakis and Sinkhorn 2011). Sustained nitrate loss and soil acidification can deplete readily weatherable base cations to such a degree that further base cation loss becomes decoupled from acidification sources, with limited potential for recovery (Likens et al. 1996, Peltzer et al. 2010). Such a legacy effect may explain why we found weak relationships between contemporary nitrate and base cation leaching in lysimeters, yet strong cumulative depletion of soil exchangeable base cations, intensified soil acidification, and increased Al mobilization at high-N sites. Given that our sites have not had significant N inputs for at least three decades, we conclude that the base cation depletion we observed is not reversible on decadal timescales. Consequently, the naturally high-N forests of the Oregon Coast Range may be more sensitive to additional N from atmospheric N deposition than suggested by current critical N loads estimates (Pardo et al. 2011), and may exhibit rapid biogeochemical responses that are characteristic of N-rich tropical forests (Matson et al. 1999, Lu et al. 2009).

A legacy of chronic N saturation due to soil N accumulation appears more important than parent material in driving low base cation availability across our sites. We previously surveyed 22 coastal Oregon forests across both sedimentary and igneous soil parent materials, and reported for surface 0–10 cm soil that base cation concentrations were consistently very low where soil exceeded ~0.4% N, regardless of soil parent material (Perakis et al. 2006). This level of soil N also corresponds with the saturation of biotic N sinks and emergence of elevated nitrate leaching from soils (Perakis and Sinkhorn 2011). Here, we further show that base cation depletion is even more intense in deeper soils than indicated by our earlier survey of surface soils, as we found that exchangeable base cations were increasingly concentrated in surface soil at high-N sites. Indeed, even weakly developed soils of the Oregon Coast Range can lose up to 50% of Ca and 25% of Mg and Na relative to stocks of these elements in soil parent materials, suggesting that weathering of very deep soil and bedrock occurs below our 1 m sampling depth (Anderson et al. 2002, Lindeburg et al. 2013), which in turn contributes to positive correlations between nitrate and base cations in watershed streams of this region (Compton et al. 2003). We did, however, detect a potential signal of parent material on soil chemistry at one site; soil at site 20 developed on sedimentary rock derived primarily from basaltic material, with potentially higher original Ca, Mg, and P content. Indeed, extractable P_i was noticeably elevated in soil at this site, yet base cations were not, suggesting that soil parent material may be more important in shaping P than base cation availability under strongly leaching conditions. Exchangeable base cations decline to low terminal levels within ~20 000 years on soil parent materials typical of our study sites (Lindeburg et al. 2013), remarkably similar to the ~22 000 years required for N balances to achieve steady-state in these forests (Perakis et al. 2011). These patterns overall highlight how rapid N accumulation and accelerated nitrate leaching may contribute to base cation depletion from relatively young, poorly developed soils. Even without additional disturbance and N accumulation from N fixing red alder, it is likely that soil acidification and base cation depletion would continue as forest succession proceeds to dominance by shade-tolerant, soil-acidifying, western hemlock (Cross and Perakis 2011).

Several lines of evidence point to Ca as the base cation that is most likely deficient as N increases across our sites. Calcium was the only base cation that declined in biomass along our gradient, reaching deficiency levels in foliage. In addition, atmospheric deposition rates relative to tree demands is lower for Ca than for other base cations in these forests (Perakis et al. 2006). Efficient recycling of Ca between plants and soils appears necessary, but inadequate, to satisfy plant Ca requirements as Ca declines across our N gradient. Plants do not appreciably resorb Ca before leaf senescence, and Ca in litterfall exceeded foliar concentrations at our sites, presumably due to mobilization of starches and other leaf constituents before abscission. Overall, coniferous trees are less able physiologically to recycle Ca internally compared to other nutrients such as N or P (McLaughlin and Wimmer 1999, Vergutz et al. 2012). Biotic Ca recycling therefore depends on efficient retention of litterfall Ca in surface soil and subsequent root uptake, before leaching loss of weakly adsorbed Ca can occur. Surface 0–10 cm soil contained a progressively larger percentage of total (0–100 cm) mineral soil exchangeable Ca as soil N increased, indicating elevated Ca recycling through surface soils as overall soil Ca declined. This contrasts with previous work in more base-rich Pacific Northwest forests showing that short-term increases in N availability redistribute base cations to deeper in the soil profile (Van Miegroet and Cole 1984). We also found that non-sea-salt (i.e., internally generated) contributions to soil water Na fluxes were greater in deep than shallow lysimeters, yet the reverse pattern was observed for Ca, Mg, and K, suggesting preferential recycling of nutrient base cations through surface soils. On the other hand, base cation leaching overall was dominated by non-sea-salt sources at several sites, indicating that at least some base cations mobilized from soil exchangeable or weatherable pools had escaped plant uptake. It is likely that high N conditions across our gradient impaired the foraging ability of roots and mycorrhizae due to diminished plant C allocation belowground (Dybzinski et al. 2011). This may be intensified in western Oregon Douglas-fir by native pathogenic fungi on high-N sites (Mulvey et al. 2013; Luoma and Eberhart, *in press*), consistent with declines in plant Ca concentrations and pools at high-N sites. Low plant Ca availability can also directly reduce C allocation to roots and mycorrhizae, which may further impede plant Ca uptake from soil (Schulte-Baukloh and Fromm 1993). Overall our results are consistent with the idea that annual plant cation demands can depend strongly on internal recycling within ecosystems, particularly for Ca in Ca-poor forests (Watmough and Dillon 2003, Blum et al. 2008).

The coupled gradients in soil N-Ca status that we observed across sites can inform forestry practices to promote sustainable management of Ca nutrition across the Oregon Coast Range. Most forests across our study area have experienced one or two harvest cycles. Assuming slash is minimal or removed to piles, one whole-tree harvest rotation at these sites would remove on average 137 kg Ca/ha (range 99–184 kg Ca/ha, $n = 9$ sites), making it implausible that even several cycles of prior logging and biomass removal could account for the ~6000 kg Ca/ha difference in soil Ca we observed across sites. However, at our most Ca-poor sites aboveground biomass accounts for 25–30% of readily available ecosystem Ca (biomass + forest floor + exchangeable soil to 1 m), making it plausible that removal of this Ca pool could intensify Ca deficiency. Recent interest in whole-tree harvest to support biomass-based energy production is also more likely to deplete site nutrients when compared to bole-only harvest for wood products. The foliar and bolewood Ca concentrations across our sites were at the low end of reported values for Douglas-fir in the Pacific Northwest (Walker and Gessel 1991, Binkley et al. 1992, Homann et al. 1994, Cross and Perakis 2011), and the three highest-soil-N sites possessed foliar Ca concentrations at or below deficiency levels (Walker and Gessel 1991). We also found that aboveground productivity increased as N accumulated to roughly the mid-point of our soil N gradient, then plateaued or declined thereafter (Table 1), raising the possibility that Ca depletion exacerbates the impacts of foliar pathogens in suppressing forest growth on the most N-rich sites (Mulvey et al. 2013). Ongoing fertilization experiments in coastal Oregon forests show that Ca can limit growth of Douglas-fir on high-N sites, with growth response related to background Ca:N ratios in soil (D. B. Mainwaring, D. A. Maguire, and S. S. Perakis, *unpublished manuscript*). Whereas low N and P can induce root growth and foraging for these nutrients, Ca deficiency is relatively ineffective at inducing root growth (Dauer et al. 2007), which may limit the ability of trees to fully meet Ca requirements in naturally high-N, low-Ca sites. To sustain productivity in low-Ca sites, it may be beneficial to keep logging slash on site, delay control of competing vegetation, plant tree species with low Ca requirements, use direct Ca fertilization, and/or foster longer rotations that minimize opportunities for Ca loss in biomass removal and leaching.

Conclusions

Our findings show that a legacy of symbiotic N fixation in coastal Oregon forests can promote N and P accumulation in soil organic matter while fostering base cation loss from available soil pools, leading to the emergence of Ca rather than P limitation as N accumulates. This trajectory of nutrient limitation differs from biogeochemical theory based on longer-term soil development, which emphasizes a transition from N to P limitation as N accumulates and P is lost during soil weathering (Walker and Syers 1976, Hedin et al. 2003, Vitousek et al. 2010). It also differs somewhat from nutrient limitation concepts based in N saturation theory, which predominantly emphasize the emergence of potentially reversible Ca or Mg limitation resulting

from soil acidification and nitrate leaching (Aber et al. 1998, Högberg et al. 2006), yet without increased soil organic P storage at high N. We instead suggest that symbiotic N fixers with high N and P recycling through litterfall can promote a net storage of N and P in soil organic matter over millennial scales that exceed rates of hydrologic N and P loss, with the accumulated reservoir of soil organic N and P sufficient to alleviate limitation by these nutrients when N fixers are replaced by non-fixers. Longer-term soil development, if allowed to proceed well beyond the 2000–6000-year residence time of soils that we studied (Anderson et al. 2002), could eventually lead to terminal P depletion and P or Ca-P co-limitation. However, over shorter intervals characteristic of our field sites, high N accumulation instead results in preferential soil Ca depletion, which is intensified by low precipitation inputs of Ca (vs. Mg or K) relative to plant demands (Perakis et al. 2006). As soil N increases and Ca is lost, remaining ecosystem Ca is increasingly concentrated in vegetation and surface soils, suggesting a tightening of biotic Ca retention and recycling in response to Ca deficiency. However, biotic mechanisms of Ca conservation may be inefficient relative to those for N and P, because Ca is neither appreciably resorbed from senescing plant tissues nor stored in soil organic matter. Consequently, Ca is particularly susceptible to leaching loss from high-N sites during recycling through uptake–litterfall–decomposition pathways. In regions where disturbance or other factors favor high rates of symbiotic N fixation, our findings suggest that patterns of nutrient limitation and deficiency may proceed from N to base cations (especially Ca in coastal regions) where long-term soil development has not yet depleted ecosystem P to a terminal steady state.

Acknowledgments

We thank Melissa McCartney for field and laboratory assistance, and Jana Compton, Jeff Hatten, and three anonymous reviewers for comments on the manuscript. This research was supported by NSF DEB-0346837. Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Literature Cited

Aber, J., W. McDowell, K. Nadelhoffer, A. Magill, G. M. Berntson, M. Kamakea, S. McNulty, W. Currie, L. Rustad, and I. Fernandez. 1998. Nitrogen saturation in temperate forest ecosystems: hypotheses revisited. BioScience 48:921–934.

Anderson, S. P., W. E. Dietrich, and G. H. Brimhall, Jr. 2002. Weathering profiles, mass-balance analysis, and rates of solute loss: Linkages between weathering and erosion in a small, steep catchment. Geological Society of America Bulletin 114:1143–1158.

Beier, C., K. Blanck, M. Bredemeir, N. Lamersdorf, and L. Rasmussen. 1998. Field-scale "clean rain" treatments to two Norway spruce stands within the EXMAN project—effects on soil solution chemistry, foliar nutrition and tree growth. Forest Ecology and Management 101:111–123.

Binkley, D., K. Cromack, Jr., and D. D. Baker. 1994. Nitrogen fixation by red alder: biology, rates, and controls. Pages 57–72 *in* D. E. Hibbs, D. S. DeBell, and R. F. Tarrant, editors. The biology and management of red alder. Oregon State University Press, Corvallis, Oregon, USA.

Binkley, D., P. Sollins, R. Bell, D. Sachs, and D. Myrold. 1992. Biogeochemistry of adjacent conifer and alder–conifer ecosystems. Ecology 73:2022–2033.

Blum, J., A. A. Dasch, S. P. Hamburg, R. D. Yanai, and M. A. Arthur. 2008. Use of foliar Ca/Sr discrimination and $^{87}Sr/^{86}Sr$ ratios to determine soil Ca sources to sugar maple foliage in a northern hardwood forest. Biogeochemistry 87:287–296.

Bockheim, J. G., and S. Langley-Turnbaugh. 1997. Biogeochemical cycling in coniferous ecosystems on different aged marine terraces in coastal Oregon. Journal of Environmental Quality 26:292–301.

Bowman, R. A., and J. O. Moir. 1993. Basic EDTA as an extractant for soil organic phosphorus. Soil Science Society of America Journal 57:1516–1518.

Bukry, D., and D. Snavely, Jr. 1988. Coccolith zonation for Paleogene strata in the Oregon Coast Range. Pages 251–264 *in* M. V. Filewicz and R. L. Squires, editors. Paleogene stratigraphy, west coast of North America. Pacific Section, Society for Sedimentary Geology, West Coast Paleogene Symposium, Los Angeles, California, USA.

Bullen, T. D., and S. W. Bailey. 2005. Identifying calcium sources at an acid deposition-impacted spruce forest: a strontium isotope, alkaline earth element multi-tracer approach. Biogeochemistry 74:63–99.

Compton, J. E., M. R. Church, S. T. Larned, and W. E. Hogsett. 2003. Nitrogen export from forested watersheds in the Oregon Coast Range: the role of N_2-fixing red alder. Ecosystems 6:773–785.

Compton, J. E., and D. W. Cole. 1998. Phosphorus cycling and soil P fractions in Douglas-fir and red alder stands. Forest Ecology and Management 110:101–112.

Cross, A., and S. S. Perakis. 2011. Tree species and soil nutrient profiles in old-growth forests of the Oregon Coast Range. Canadian Journal of Forest Research 41:195–210.

Crowley, K. F., et al. 2012. Do nutrient limitation patterns shift from nitrogen to phosphorus with increasing nitrogen deposition across the northeastern United States? Ecosystems 15:940–957.

Dauer, J. M., J. Chorover, O. A. Chadwick, J. Oleksyn, M. G. Tjoelker, S. E. Hobbie, P. B. Reich, and D. M. Eissenstat. 2007. Controls over leaf and litter calcium concentrations among temperate trees. Biogeochemistry 86:175–187.

Dybzinski, R., C. Farrior, A. Wolf, P. B. Reich, and S. W. Pacala. 2011. Evolutionarily stable strategy carbon allocation to foliage, wood, and fine roots in trees competing for light and nitrogen: an analytically-tractable, individual-based model and quantitative comparisons to data. American Naturalist 177:153–166.

Elser, J. J., M. E. S. Bracken, E. E. Cleland, D. S. Gruner, W. S. Harpole, H. Hillebrand, J. T. Ngai, E. W. Seabloom, J. B. Shurin, and J. E. Smith. 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. Ecology Letters 10:1135–1142.

Federer, C. A., J. W. Hornbeck, L. M. Tritton, C. W. Martin, and R. S. Price. 1989. Long-term depletion of calcium and other nutrients in eastern US forests. Environmental Management 13:593–601.

Franklin, W. T. 1970. Mineralogical and chemical characteristics of western Oregon andic soils. Dissertation. Oregon State University, Corvallis, Oregon, USA.

Güsewell, S. 2004. N:P ratios in terrestrial plants: variation and functional significance. New Phytologist 164:243–266.

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 76:493–509.

Hedin, L. O., L. Granat, G. E. Likens, T. A. Buishand, J. N. Galloway, T. J. Butler, and H. Rodhe. 1994. Steep declines in atmospheric base cations in regions of Europe and North America. Nature 367:351–354.

Hedin, L. O., P. M. Vitousek, and P. A. Matson. 2003. Nutrient losses over four million years of tropical forest development. Ecology 84:2231–2255.

Heller, P. L., Z. E. Peterman, J. R. O'Neil, and M. Shafiqullah. 1985. Isotopic provenance of sandstones from the Eocene Tyee Formation, Oregon Coast Range. Bulletin of the Geological Society of America 96:770–780.

Heller, P. L., R. W. Tabor, and C. A. Suczek. 1987. Paleogeographic evolution of the United States Pacific Northwest during Paleogene time. Canadian Journal of Earth Sciences 24:1652–1667.

Högberg, P., H. B. Fan, M. Quist, D. Binkley, and C. O. Tamm. 2006. Tree growth and soil acidification in response to 30 years of experimental nitrogen loading on boreal forest. Global Change Biology 12:489–499.

Homann, P. S., D. W. Cole, H. Van Miegroet, and J. E. Compton. 1994. Relationships between cation and nitrate concentrations in soil solutions from mature and harvested red alder stands. Canadian Journal of Forest Research 24:1646–1652.

Houlton, B. Z., Y. P. Wang, P. M. Vitousek, and C. B. Field. 2008. A unifying framework for dinitrogen fixation in the terrestrial biosphere. Nature 454:327–330.

Huntington, T. G. 2000. The potential for calcium depletion in forest ecosystems of southeastern United States: Review and analysis. Global Biogeochemical Cycles 14:623–638.

Hurlbert, S. H. 1984. Pseudoreplication and the design of ecological field experiments. Ecological Monographs 52:187–211.

Hüttl, R. F., and W. Schaaf. 1997. Magnesium deficiency in forest ecosystems. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Johnson, A. H., S. B. Anderson, and T. G. Siccama. 1994. Acid rain and soils of the Adirondacks. I. Changes in pH and available calcium, 1930–1984. Canadian Journal of Forest Research 24:39–45.

Johnson, A. H., J. Frizano, and D. R. Vann. 2003. Biogeochemical implications of labile phosphorus in forest soils determined by the Hedley fractionation procedure. Oecologia 135:487–499.

Johnson, D. W., and D. E. Todd. 1990. Nutrient cycling in forests of Walker Branch watershed, Tennessee: roles of uptake and leaching in causing soil changes. Journal of Environmental Quality 19:97–104.

Lansberg, J. J., and R. H. Waring. 1997. A generalized model of forest productivity using simplified concepts of radiation-use efficiency, carbon balance and partitioning. Forest Ecology and Management 95:209–228.

LeBauer, D. S., and K. K. Treseder. 2008. Nitrogen limitation of net primary productivity in terrestrial ecosystems is globally distributed. Ecology 89:371–379.

Likens, G. E., C. T. Driscoll, and D. C. Buso. 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. Science 272:244–246.

Lindeburg, K., P. Almond, J. J. Roering, and O. A. Chadwick. 2013. Pathways of soil genesis in the Oregon Coast Range, USA. Plant and Soil 367:57–75.

Lu, X. K., J. M. Mo, P. Gundersern, W. X. Zhu, G. Y. Zhou, D. J. Li, and X. Zhang. 2009. Effects of simulated N deposition on soil exchangeable cations in three forest land-use types in subtropical China. Pedosphere 19:189–198.

Lucas, R. W., J. Klaminder, M. N. Futter, K. H. Bishop, G. Egnell, H. Laudon, and P. Högberg. 2011. Nitrogen additions and base cations: implications for plants, soils, and streams. Forest Ecology and Management 262:95–104.

Luoma, D., and J. Eberhart. *In press*. Response of ectomycorrhizal fungi to Swiss needle cast disease. Mycologia.

Matson, P. A., W. H. McDowell, A. R. Townsend, and P. M. Vitousek. 1999. The globalization of N deposition: ecosystem consequences in tropical environments. Biogeochemistry 46:67–83.

McGill, W. B., and C. V. Cole. 1981. Comparative aspects of cycling of organic C, N, and P through soil organic matter. Geoderma 26:267–286.

McLaughlin, S. B., and R. Wimmer. 1999. Calcium physiology and terrestrial ecosystem processes. New Phytologist 142:373–417.

McWilliams, R. G. 1973. Stratigraphic and biostratigraphic relationships of the Tyee and Yamhill Formations in central-western Oregon. Oregon Department of Geology and Mineral Industries, The Ore Bin 35(11):169–186.

Mulvey, R. L., D. C. Shaw, and D. A. Maguire. 2013. Fertilization impacts on Swiss needle cast severity in western Oregon. Forest Ecology and Management 287:147–158.

Pardo, L. H., et al. 2011. Effects of nitrogen deposition and empirical critical loads for nitrogen for ecoregions of the United States. Ecological Applications 21:3049–3082.

Peltzer, D. A., et al. 2010. Understanding ecosystem retrogression. Ecological Monographs 80:509–529.

Perakis, S. S., D. A. Maguire, T. D. Bullen, K. Cromack, R. H. Waring, and J. R. Boyle. 2006. Coupled nitrogen and calcium cycles in the forests of the Oregon Coast Range. Ecosystems 9:63–74.

Perakis, S. S., J. J. Matkins, and D. E. Hibbs. 2012. Interactions of tissue and fertilizer nitrogen on decomposition dynamics of lignin-rich conifer litter. Ecosphere 3:art54.

Perakis, S. S., and E. R. Sinkhorn. 2011. Biogeochemistry of a temperate forest nitrogen gradient. Ecology 92:1481–1491.

Perakis, S. S., E. R. Sinkhorn, and J. E. Compton. 2011. $\delta^{15}N$ constraints on long-term nitrogen balances in temperate forests. Oecologia 167:793–807.

Perring, M. P., L. O. Hedin, S. A. Levin, M. McGroddy, and C. de Mazancourt. 2008. Increased plant growth from nitrogen addition should conserve phosphorus in terrestrial ecosystems. Proceedings of the National Academy of Sciences USA 105:1971–1976.

Pett-Ridge, J. 2009. Contributions of dust to phosphorus cycling in tropical forests of the Luquillo Mountains, Puerto Rico. Biogeochemistry 94:63–80.

Porder, S., and G. E. Hilley. 2011. Linking chronosequences with the rest of the world: predicting soil phosphorus content in denuding landscapes. Biogeochemistry 102:153–166.

Rarey, P. J. 1985. Geology of the Hamlet-North Fork of the Nehalem River area, southern Clatsop and northernmost Tillamook Counties, northwest Oregon. Thesis. Oregon State University, Corvallis, Oregon, USA.

Reuss, J. O., and D. W. Johnson, editors. 1986. Acid deposition and the acidification of soils and waters. Springer-Verlag, New York, New York, USA.

Schulte-Baukloh, C., and J. Fromm. 1993. The effect of calcium starvation on assimilate partitioning and mineral distribution of the phloem. Journal of Experimental Botany 44:1703–1707.

Schuur, E. A. G., and P. A. Matson. 2001. Aboveground net primary productivity and nutrient cycling across a mesic to wet precipitation gradient in Hawaiian montane forest. Oecologia 128:431–442.

Sitters, J., P. J. Edwards, and H. Olde Venterink. 2013. Increases in soil C, N, and P pools along an *Acacia* tree density gradient and their effects on trees and grasses. Ecosystems 16:347–357.

Snavely, P. D., N. S. MacLeod, and W. W. Rau. 1975. Alsea formation, an Oligocene marine sedimentary sequence in the Oregon Coast Range. Bulletin 1395-F. U.S. Geological Survey, Reston, Virginia, USA.

Snavely, P. D., H. C. Wagner, and N. S. MacLeod. 1964. Rhythmic-bedded eugeosynclinal deposits of the Tyee

Formation, Oregon Coast Range. Kansas Geological Survey Bulletin 169:461–480.
Sollins, P., C. C. Grier, F. M. McCorison, K. Cromack, Jr., R. Fogel, and R. L. Fredriksen. 1980. The internal element cycles of an old-growth Douglas-fir ecosystem in western Oregon. Ecological Monographs 50:261–285.
Sollins, P., G. P. Robertson, and G. Uehara. 1988. Nutrient mobility in variable-and permanent-charge soils. Biogeochemistry 6:181–189.
Ter-Mikaelian, M. T., and M. D. Korzukhin. 1997. Biomass equations for sixty-five North American tree species. Forest Ecology and Management 97:1–24.
Treseder, K. K., and P. M. Vitousek. 2001. Effects of soil nutrient availability on investment in acquisition of N and P in Hawaiian rain forests. Ecology 82:946–954.
Tripler, C. E., S. S. Kaushal, G. E. Likens, and M. T. Walter. 2006. Patterns in potassium dynamics in forest ecosystems. Ecology Letters 9:451–466.
Turner, B. L. 2004. Optimizing phosphorus characterization in animal manures by solution phosphorus-31 nuclear magnetic resonance spectroscopy. Journal of Environmental Quality 33:757–766.
Van Miegroet, H., and D. W. Cole. 1984. The impact of nitrification on soil acidification and cation leaching in a red alder ecosystem. Journal of Environmental Quality 13:586–590.
Van Miegroet, H., P. S. Homann, and D. W. Cole. 1992. Soil nitrogen dynamics following harvesting and conversion of red alder and Douglas-fir stands. Soil Science Society of America Journal 56:1311–1318.
van Schöll, L., T. W. Kuyper, M. M. Smits, R. Landeweert, E. Hoffland, and N. van Breemen. 2008. Rock-eating mycorrhizas: their role in plant nutrition and biogeochemical cycles. Plant and Soil 303:35–47.
Vergutz, L., S. Manzoni, A. Porporato, R. F. Novais, and R. B. Jackson. 2012. Global resorption efficiencies and concentrations of carbon and nutrients in leaves of terrestrial plants. Ecological Monographs 82:205–220.
Vitousek, P. M., and R. W. Howarth. 1991. Nitrogen limitation on land and in the sea: How can it occur? Biogeochemistry 13:87–115.
Vitousek, P. M., S. Porder, B. Z. Houlton, and O. A. Chadwick. 2010. Terrestrial phosphorus limitation: mechanisms, implications and nitrogen-phosphorus interactions. Ecological Applications 20:5–15.
Vitousek, P. M., and W. A. Reiners. 1975. Ecosystem succession and nutrient retention: a hypothesis. BioScience 25:376–381.
Walker, R. B., and S. P. Gessel. 1991. Mineral deficiencies of coastal northwest conifers. University of Washington Institute of Forest Resources, Seattle, Washington, USA.
Walker, T. W., and J. K. Syers. 1976. The fate of phosphorus during pedogenesis. Geoderma 15:1–19.
Watmough, S. A., and P. J. Dillon. 2003. Base cation and nitrogen budgets for seven forested catchments in central Ontario, 1983-1999. Forest Ecology and Management 177:155–177.
Weiskittel, A. R., D. A. Maguire, R. A. Monserud, and G. P. Johnson. 2010. A hybrid model for intensively managed Douglas-fir plantations in the Pacific Northwest, USA. European Journal of Forest Research 129:325–338.
Yanai, R. D. 1991. Soil solution phosphorus dynamics in a whole-tree-harvested northern hardwood forest. Soil Science Society of America Journal 55:1746–1752.
Yang, X., and W. M. Post. 2011. Phosphorus transformations as a function of pedogenesis: a synthesis of soil phosphorus data using Hedley fractionation method. Biogeosciences 8:2907–2916.

Supplemental Material

Appendix A

Soil bulk density for each sampling depth (*Ecological Archives* A023-095-A1).

Appendix B

Soil water fluxes at 20 cm and 100 cm for the nine study sites (*Ecological Archives* A023-095-A2).

Appendix C

Percentages of non-sea-salt fluxes in soil water at 20 cm and 100 cm for the nine study sites (*Ecological Archives* A023-095-A3).