

Tropical tree species traits drive soil cation dynamics via effects on pH: a proposed conceptual framework

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Abstract. Humid tropical forests are major players in the global carbon cycle, despite evidence that cations (rock-derived, positively charged ions) can limit or co-limit net primary productivity (NPP). In mature forests, tight cation cycling, i.e., without leaching losses, could maintain cation stocks on site. That mechanism does not explain how regenerating tropical secondary forest trees start from seeds and accrue large cation stocks in biomass, when growing on soils depleted in available cations. We propose a new mechanism that links tree species' traits to soil cation availability via impacts on soil pH, a master biogeochemical driver. We tested plot-level effects of tree species on soil pH, soil extractable cations, and cation accrual in biomass in a unique, 25-yr-old, randomized-complete-block experiment in which climate, soil, and previous land-use history were similar across four native tree species grown in mono-dominant plantations in Costa Rica. Surface-soil pH in this Oxisol, initially 4.52 ± 0.02 (mean \pm SE (standard error)), declined to 4.14 ± 0.02 under *Pentaclethra macroloba*, a nodulated legume, and increased to 4.71 ± 0.08 under *Vochysia guatemalensis*, an aluminum (Al) accumulator. The range in pH corresponds to a five-fold difference in proton concentrations, which is sufficient to alter dispersion of organo-mineral colloids. Cation stocks in biomass differed across species by 1.7-, 1.9-, 2.8-, 2.9-, 3.1-, 3.5-, and 17.2-fold for iron (Fe), calcium (Ca), potassium (K), manganese (Mn), strontium (Sr), magnesium (Mg), and Al, respectively. Differential acquisition of available soil cations was an unlikely explanation for measured differences among species because changes in extractable soil cation stocks were unrelated to cation accrual in biomass. Soil pH and biomass cation stocks were highly correlated, however. By our proposed conceptual framework, species traits that strongly increase proton concentrations and decrease pH in soil, e.g., support of N fixation, increase colloid aggregation, reducing cation availability. Traits that reduce soil protons and increase pH, e.g., Al³⁺ accumulation, disperse colloids, thereby releasing cations occluded during pedogenesis. This highlights a novel biogeochemical role for the Al-accumulation trait, i.e., liberation of occluded soil cations. Further studies would clarify effects of soil pH on cation supply via colloid dispersion, and its importance for nutrient acquisition in cation-depleted soils.

Key words: Al accumulation; carbon cycling; cation cycling; fine roots; soil pH; stoichiometry; tree species effects; tropical forest regeneration.

INTRODUCTION

Humid tropical forests are “engines” of the global climate system, and impact the water and carbon (C) cycles far afield from the tropics (Malhi et al. 2008). In particular, regrowing forests comprise a rapidly increasing proportion of humid tropical forests (Asner et al. 2009), and constitute an important C sink in the global cycle, 1.6 ± 0.5 Pg C/yr (mean \pm SE (standard error); Pan et al. 2011). Paradoxically, these ecosystems are also often highly depleted in rock-derived nutrients that frequently limit or co-limit plant growth: phosphorus (P), and cations such as potassium (K), calcium (Ca), and magnesium (Mg; Vitousek and Sanford 1986, Cuevas and Medina 1988, Kaspari et al. 2008, Cleveland et al.

2011, Wright et al. 2011, Condit et al. 2013). Thus, understanding the biogeochemical mechanisms that sustain cation acquisition by trees in weathered humid tropical soils contributes critically to understanding processes that influence C accumulation in tropical forests. Currently, the inability to predict the complex effects of multiple element limitations to tropical forest growth is a gap that hinders our capacity to model tropical C cycling and the consequences for global climate change (Townsend et al. 2011).

Under the current paradigm, primary minerals are the dominant ecosystem sources of available cations in young soils. As primary minerals and 2:1 layer aluminosilicate phases are progressively depleted during millennia of soil development, cations and P are leached or become co-precipitated with, or occluded within, Fe and Al (hydr)oxide secondary mineral phases (Walker and Syers 1976). Cations can also be associated with Fe and Al phases via mineral substitution, co-precipitation,

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and association with exchange sites on sorbed or co-precipitated organic matter (OM; Taylor and Graley 1967, McBride 1978, 1989, Kleber et al. 2015). Thus, in highly weathered soils depleted of primary minerals, plants are generally thought to rely on exchangeable or biogeochemically “labile” mineral nutrient pools, including nutrient release from decaying OM, to meet growth requirements (Proctor 1987, Crews et al. 1995, Markewitz et al. 2001, 2004, Condit et al. 2013). Nutrients sorbed to or occluded within Fe and Al phases are generally thought to be unavailable to plants over ecological timescales (Walker and Syers 1976, Tiessen and Moir 1993, Crews et al. 1995, Johnson et al. 2003, Yang et al. 2013).

By this paradigm, “tight” nutrient cycling, i.e., without erosional or leaching losses, is the primary means by which tropical rainforests conserve available cation nutrients that are in short supply on highly weathered soils, and thereby maintain their productivity. Secondary forests on highly weathered soils, however, can start regrowth with near-zero cations in biomass. Nevertheless, their rates of aboveground biomass recovery are rapid, with particularly high rates in humid forests, and rates of forest regrowth are not well correlated with soil cation exchange capacity (Poorter et al. 2016). Thus, a critical question for tropical ecosystem ecology is: How do trees in re-growing forests meet their cation requirements, when situated on highly weathered soils?

We addressed this question using a more focused conceptual framework that builds upon the current paradigm, which explains how nutrient limitation for plants changes over the course of soil development. Specifically, we aimed to integrate the effects of species-specific traits of trees with biogeochemical mechanisms that could drive soil cation availability and uptake. Our objectives were to evaluate the trait-based effects of single tree species on two aspects of cation cycling: (1) the regulation of cation availability in soil by mechanisms involving alteration of soil pH and (2) the relationship between the trait of leaf C cation molar stoichiometry and accrual of cations in biomass, relative to other traits likely to influence cation uptake and accrual in biomass (Fig. 1). Hereafter, the term “species effects” refers to species-specific effects of overstory trees on plot-level attributes, and thus includes their effects on the under-story, forest floor, and soils. For this study, “traits” refers to tree species.

Variability across the landscape in abiotic state factors such as climate, parent material, topography, and time, and human factors (*sensu* Jenny 1941) affects soil development and thereby gives rise to variability in nutrient supply to plants. To control for these factors, our studies were conducted in replicated, 25-yr-old mono-dominant plantations in an experiment containing four native, broad-leaved, evergreen, tropical tree species in lowland Costa Rica. As such, these state factors were similar across the study site and only the planted tree species varied among plots at the onset of the experiment. This

provided a robust means for evaluating the effects of individual tree species across a common soil, a highly weathered Oxisol with negligible primary minerals (Kleber et al. 2007). This study took advantage of inherent differences among the four species in traits that could influence biogeochemical cycles, including productivity, litterfall, decomposition, and tissue chemistry, as documented during previous studies of these species in this experiment (Table 1; Fisher 1995, Raich et al. 2007, Russell et al. 2007, 2010). “Available” soil nutrients are notoriously difficult to quantify in tropical forests (Denslow et al. 1987, Silver et al. 1994, Johnson et al. 2003). We quantified cations accumulated in biomass after 25 yr of growth, as an integrative measure of dynamic cation bioavailability over time. We also measured extractable soil cations for comparison.

Species effects on soil cation availability

Alteration of soil pH.—Tree species can alter soil pH differentially, as documented at the level of individual tree canopies (Zinke 1962, Finzi et al. 1998), clumps of trees (Muller 1887, as cited by Zinke 1962), and monodominant experimental stands (Hobbie et al. 2007, Russell et al. 2007, Bauters et al. 2016a). Several traits of plants (and their associated microbial communities) can strongly alter soil pH (Mueller et al. 2012), especially in poorly buffered Oxisols. Tree species traits associated with variability in this capacity include CO₂ production in soil (soil respiration), exudation, organic acid production and release to soil, and the quantity and chemistry of detritus produced in bark, litterfall, and fine roots (Zinke 1962, Finzi et al. 1998, Hobbie et al. 2007, Russell et al. 2007). The resulting variation in proton (H⁺) release or consumption generates differences in soil acidification among species, as in Fig. 1a. Alteration of soil pH by a tree species could affect cation availability via at least two mechanisms, which are not mutually exclusive.

- 1) By the current main mechanism as in Fig. 1a, H⁺ concentrations affect replacement of cations on soil cation exchange sites. Soil pH thus influences cation exchange capacity (CEC), base saturation, mineral speciation, and particle surface charge (Sollins et al. 1988, Chorover and Sposito 1995, Thompson et al. 2006). As pH declines in variable-charge soils, base cations (Ca⁺², Mg⁺², K⁺, Mn⁺²) may be replaced with H⁺ and Al⁺³ on exchange sites, such that exchangeable acidity increases and base saturation declines. This replacement temporarily increases base cation concentrations in soil solution, but those free cations are subject to loss, such that soil acidification promotes ecosystem cation leaching over annual to decadal timescales (Likens et al. 1996, Cheng et al. 2010). By this mechanism, hereafter referred to as “cation loss from acidification,” we would expect decreased pH to reduce soil exchangeable cation stocks over the long term, over the course of our

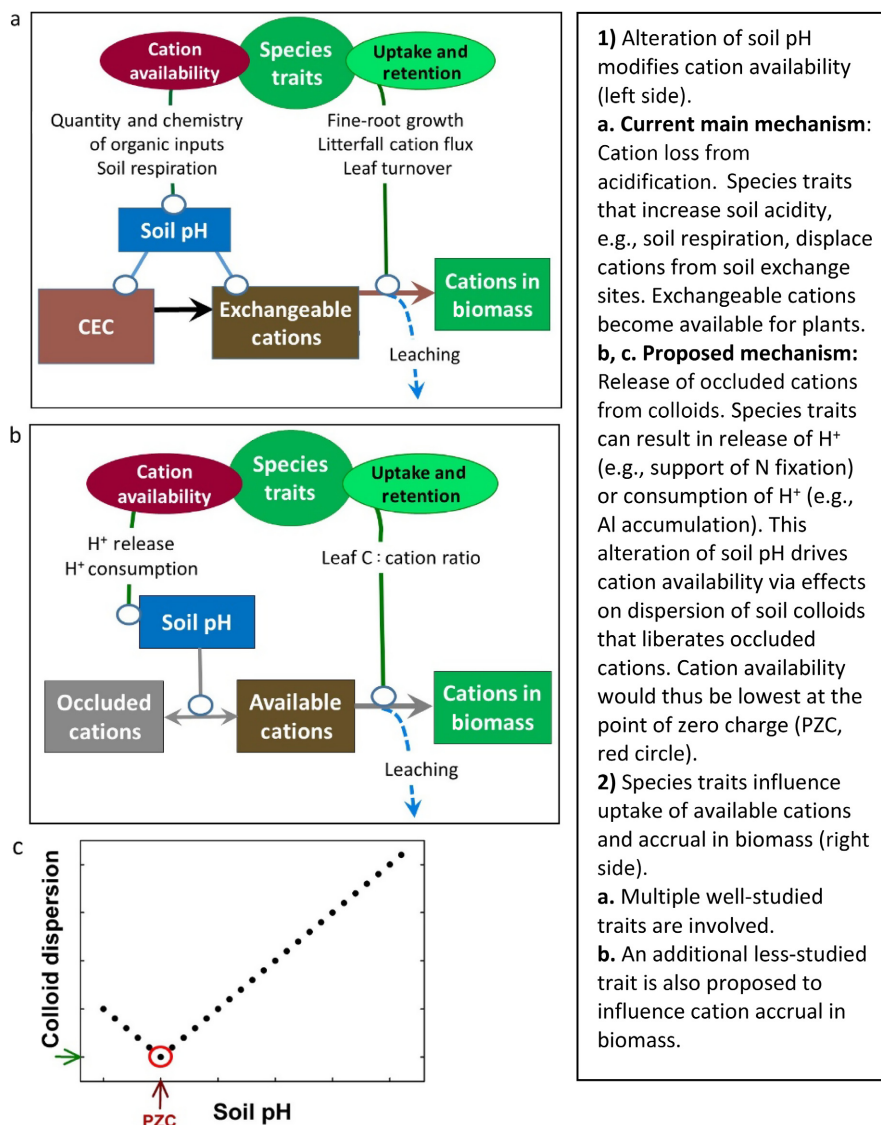


FIG. 1. Conceptual framework showing how tree species differ in traits (listed below ovals) that influence (1) cation availability in soil and (2) cation accrual in biomass. (a) Current mechanism, (b) proposed mechanism, and (c) specific effect of soil pH under proposed mechanism. The connections between species traits and cation stocks in soil and biomass (boxes, kg/ha) are represented as curved lines terminating in circles. Fluxes of cations lost via leaching ($\text{kg} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$) are in dashed curves.

study, although short-term increases could also have occurred (Johnson et al. 1977, Fujii 2014).

- 2) By our proposed mechanism in Fig. 1b, species traits that strongly influence either release or consumption of H^+ , and thereby alter soil pH, influence the liberation of occluded cations associated with colloids. In leguminous plants, nodulation that supports microbial N_2 fixation increases ammonification and subsequent nitrification that releases H^+ within soil (Van Miegroet and Cole 1984). In contrast, the trait of Al accumulation results in consumption of Al that significantly alters the equilibrium between Al minerals and soluble Al, consuming H^+ (Essington 2004):



Aluminum accumulators thereby reduce soil acidity and increase soil pH, a “master” soil variable that influences a variety of biochemical, geochemical and biological processes.

By the proposed mechanism (Fig. 1b), soil pH influences dispersion of colloids in the acidic, variable-charge soils that typify highly weathered tropical ecosystems. Soil colloids comprise heterogeneous assemblages of minerals, OM, and associated nutrients with diameters between 0.01 and 10 μm (Sposito 2008). Colloids can combine to form larger soil aggregates. Nutrients can become physically occluded, adsorbed, or co-precipitated within

TABLE 1. Study species and select traits relevant for biogeochemical processes.

Species	Family	Acronym	Basal area (m ² /ha)	Height (m)	Leaf area index (m ² /m)	Fine-root growth (Mg C·ha ⁻¹ ·yr ⁻¹)	Surface litter (Mg C·ha ⁻¹ ·yr ⁻¹)	Other
<i>Hteronyma alchorneoides</i> Allemao	Phyllanthaceae	Hial	15.7 ± 0.9	22.4 ± 1.1	3.8 ± 0.3	3.9 ± 0.5	3.5 ± 0.4	early-mid
<i>Pentaclethra macraloba</i> (Willd.) Kunth	Fabaceae	Pema	21.6 ± 4.8	14.6 ± 1.9	5.2 ± 1.2	2.0 ± 0.2	2.3 ± 0.3	nodulated legume; mid-late
<i>Virola koschnyi</i> Warb.	Myristicaceae	Viko	20.4 ± 3.6	19.6 ± 1.8	3.8 ± 0.7	1.9 ± 0.3	1.7 ± 0.2	late
<i>Vochysia guatemalensis</i> Donn. Sm	Vochysiaceae	Vogu	41.3 ± 3.8	24.2 ± 0.8	3.3 ± 0.4	3.3 ± 0.7	2.8 ± 0.4	Al accumulator early

Notes: Means (±SE) are from experimental plots at La Selva, Costa Rica, in 2005 (Raich et al. 2007, Russell et al. 2007, Valverde-Barrantes et al. 2007). Early, early-mid, and late refer to the successional stage at which the species tends to occur.

colloidal assemblages, and thus poorly available to plants. For simplicity, we will henceforth refer to these poorly accessible nutrients as “occluded.” Variable-charge soils exhibit a characteristic point of zero charge (PZC), the pH value at which the net electrical charge on particle surfaces is zero. Colloids and OM are most aggregated (least dispersed) at the PZC, with dispersion increasing as pH increases above or decreases below the PZC (Chorover and Sposito 1995, Chorover et al. 2004, Thompson et al. 2006, Henderson et al. 2012, Buettner et al. 2014). As colloids disperse, cations that were occluded may be exchanged or released to the soil solution. These dynamics have been previously assessed primarily from the perspective of soil weathering and material transport (Chorover and Sposito 1995, Chorover et al. 2004, Thompson et al. 2006, Henderson et al. 2012, Buettner et al. 2014), but not with respect to sorbed or occluded soil cations. We propose that this effect of pH on dispersion and aggregation of soil colloids could have important consequences for cation availability; theory predicts that it would be lowest at the PZC as in Fig. 1c. This proposed mechanism is hereafter referred to as “Release of occluded cations from colloids.”

Other mechanisms.—We also examined other mechanisms that could explain differences among species in their access to available cations. These included differential (1) capture of primary mineral inputs from rainfall or erosion, (2) depletion of extractable cations, and (3) cation uptake from deep soil. Soil microbial processes and their relationships with plant species could also mediate cation cycling, but extensive recent studies conducted in this study site demonstrated that measurable variation in microbial community composition and function was insufficient to explain differences in biomass nutrient accumulation among the dominant tree species (Kivlin and Hawkes 2016a,b). Differences in bacterial community composition were only weakly related to tree species ($R^2 = 0.06$), and much of that variation was driven by soil pH, as supported by other studies (Fierer and Jackson 2006, Prober et al. 2015). Similarly, fungal taxonomic richness and phylogenetic diversity were unrelated to tree species composition, and were only weakly related to fungal community composition ($R^2 = 0.152$; Kivlin and Hawkes 2016a,b). These findings were echoed by another comprehensive study at Barro Colorado Island, Panama, where plant species composition and functional traits were poor predictors of microbial community composition (Barberán et al. 2015). Another potential mechanism, differential mineral weathering by mycorrhizae, was unlikely to be important in this study because all of the tree species present have arbuscular mycorrhizal associations. These fungi are not known to produce organic acids or chelators or otherwise directly contribute to mineral weathering (Taylor et al. 2009), in contrast to ectomycorrhizal fungi (Landeweert et al. 2001, Koele et al. 2014).

Species traits and cation accrual in biomass

Soil cations liberated by any of the above mechanisms are subject to leaching at this high-rainfall site. Hence, the fate of available soil cations likely varies with species traits that modulate cation uptake and retention in biomass. Multiple physiological, biochemical, and morphological traits that vary among species are likely involved, as are differential symbiotic relationships with microbes and fungi (Marschner 2012). Traits regarding leaf C, N, and P stoichiometry have been analyzed for their variability and relationships to biomass and production (McGroddy et al. 2004) and widely integrated into biogeochemical models (e.g., Parton et al. 1994, Herbert et al. 2004) and trait-based ecology (e.g., Westoby and Wright 2006). Carbon–cation leaf stoichiometry variability and the relationships with ecosystem properties has not been nearly so well studied, however. For C:N:P ratios, molar stoichiometry was similar within biomes, but varied across them (McGroddy et al. 2004). For heavier elements such as cations, however, molar stoichiometry might vary among plant species as a result of differences in traits associated with absorption, metabolism, and partitioning among woody and non-woody tissues (Lambers et al. 2008). Jobbágy and Jackson (2004) found that Mn and Fe leaf and litter concentrations differed significantly between grasslands and plantations. Our study presented a unique opportunity to evaluate C:cation variability among species and its correlation with accrual of cations in biomass. Thus, we included leaf C:cation ratios in the proposed additions to the

conceptual framework (Fig. 1b). Three other more widely studied traits were evaluated for comparison purposes, with traits selected based on their documented variability among species, their role in nutrient uptake and/or retention in biomass, and/or their frequent use in biogeochemical models. The rationale for selecting these three traits (Fig. 1a) is the following: (1) Fine-root growth allows for exploration of the soil volume; thus differences among species in this trait could result in differential uptake of available soil cations. Rooting depth differences could also affect uptake, given the potential importance of nutrient capture from deep soil (Stone and Kalisz 1991, Dijkstra and Smits 2002, Richter and Billings 2015). (2) Cation fluxes in fine litterfall can also vary among species (Cuevas and Lugo 1998), reflecting physiological differences, e.g., in growth rate or resorption of cations prior to leaf abscission, and thus result in differential cation use efficiency. (3) Leaf turnover time can also differ among species (Reich 1998), resulting in variation in cation use. Faster turnover times could result in greater leaching losses if cation uptake is not well-coupled with decomposition of litter, and more rapid leaf turnover would provide more frequent opportunities for cation loss.

We evaluated the current and proposed mechanisms regarding the effect of soil pH on cation availability, and the possible effects of C:cation molar stoichiometry on accrual of cations in biomass as in Fig. 1. The connections between the biogeochemical mechanisms and focal species traits, hypotheses to be tested and other means of inference, which are stated as predictions, and variables to be evaluated are provided in Table 2.

TABLE 2. Mechanisms, species traits, hypotheses tested, and variables quantified in the evaluations of hypotheses.

Trait, ecosystem property, or mechanism and hypothesis	Variables
Objective 1: Alteration of cation availability	
Proton release or consumption	
H1a: species alter soil pH	
H1b: soil pH decreases with increasing soil respiration	soil pH, soil respiration, nodulation, Al accumulation
Cation stocks in biomass	
H2: cation stocks differ among species	biomass stocks, cation concentrations
Current main mechanism: cation loss from acidification	
H3a: soil pH is positively correlated with base saturation	soil pH, effective CEC, base saturation
H3b: extractable soil cations are positively correlated with soil pH	soil pH, extractable cations
H3c: extractable soil cations are negatively correlated with cations in biomass, i.e., decline as forest grows	extractable cations, change in extractable soil cation stocks over 8 yr
Cation biomass stocks \leq [Extractable soil cations + external inputs]	simple cation budgets
Proposed mechanism: release of occluded cations from colloids	
H4: cation biomass stocks increase as soil pH increases above the PZC	biomass : cation stocks, soil pH
Cation biomass stocks $>$ [extractable soil cations + external inputs]	simple cation budgets
Other potential processes	
Capture of primary mineral inputs in rainfall, depletion of extractable soil cations, uptake from deep soil	simple cation budgets, extractable soil cations, fine-root biomass at five depths to 1 m
Objective 2: Traits and cation accrual in biomass	
C:cation stoichiometry	
H5: C–cation stoichiometry is correlated with cations stocks in biomass, in comparison with three other well-studied traits that influence cation uptake and retention in biomass.	biomass : C and cation stocks, leaf C:cation, fine-root growth, cations in litterfall, turnover time

METHODS

Soil

Study site

The experimental plots are situated at La Selva Biological Station (10°26' N, 83°59' W) in the Atlantic lowlands of Costa Rica. In this humid tropical environment, mean annual temperature is 25.8°C and mean annual rainfall is 4,000 mm, with rainfall averaging >100 mm in any month (Sanford et al. 1994). The soil, classified as a Andic Haploperox (M. L. Thompson, *personal communication*), is acidic and relatively high in OM in the mature forest in our study site, with a mean surface soil (0–15 cm) C concentration of 48.0 g/kg. The mature evergreen broad-leaved rainforest had been felled and burned in 1955 to establish pasture in this site, which was then grazed until abandonment in 1987 (Russell et al. 2010). The experiment was initiated in 1988, with trees planted in a randomized complete block design containing four blocks. By 2011, one plot of *Vochysia* had been killed by a stand-level lightning event, so only three blocks were used for that species, however. The site is hilly, with elevation ranging from 44 to 89 m. To ensure that topographic effects did not create a bias, each block was centered on a hilltop, and randomization of plot assignment to a species was stratified such that, across the four blocks, each species was represented in each topographic position (hilltop, slope, and slope bottom).

Each plot was 50 × 50 m (0.25 ha). For the purpose of sub-sampling within plots, all plots were divided into four quadrants. Trees were planted at a spacing of 3 × 3 m. Understory vegetation in all plots was manually cleared over the first 3 yr, until canopy closure was attained, except in the control treatment (described in next paragraph). The planted trees dominated C cycling even though the understory had not been managed for the last 20 yr (Russell et al. 2010). For more information about the original design and management see Russell et al. (2010). At the onset of the experiment, the soil pH averaged 4.5 across all plots (Fisher 1995).

The experiment contained the four species listed in Table 1: *Hieronyma alchorneoides*, *Pentaclethra macroloba*, a nodulated legume, *Virola koschnyi*, and *Vochysia guatemalensis*, an Al accumulator. We also measured soil properties and litterfall, but not biomass, in two types of reference vegetation to provide a basis of comparison for the four tree species. (1) The original experimental design contained a control, with plots identical to the other plots, except that no trees were planted. (2) Mature forest was situated in a fifth block (150 × 200 m in size) established <150 m from the experimental site, such that soils, climate, and historical vegetation were similar to the adjacent experiment. *Pentaclethra* is the most dominant species in La Selva mature forest, accounting for 36–38% of the estimated aboveground biomass of trees (Clark and Clark 2000). Thus, these reference plots provided a basis for comparison with the *Pentaclethra* treatment. We sampled in four 50 × 50 m plots randomly selected from within this block.

We sampled mineral soil at five depth intervals to 1 m for measurements of pH and concentrations of total C and extractable Al, Ca, Mg, and K. Stocks of elements were calculated as the product of bulk density, soil depth of the interval, and element concentration. Soil was sampled in the 0–15 and 15–30 cm depth intervals as in the sampling in 2003 (Russell et al. 2007). Briefly, we sampled soil at 80 randomly selected points within each plot (20 per quadrant), using a 3.2 cm diameter soil core in the 0–15-cm layer, and a 1.9 cm diameter core for the 15–30 cm depth. Samples were bulked within quadrants for further processing as in Russell et al. (2007). To sample element concentrations in deeper layers (30–50, 50–75, and 75–100 cm), one 0.75 × 1.0 m, 1 m deep, soil pit per plot was excavated at a randomized location between trees in 2013. Bulk density was determined from the mass of the entire layer excavated from the soil pit for 0–15 and 15–30 cm layers only; we assumed that it had not changed for layers below 30 cm since the last sampling in 2005.

Soil respiration (CO₂ flux) was measured approximately every three weeks in one quadrant/plot for a total of four measurements per plot at each sample time, using a LI-8100A automated soil CO₂ flux system with 20-cm diameter chamber (LI-COR Biosciences, Lincoln, Nebraska, USA). Fluxes were calculated based on the final 100 s of the 120-s measurement period as in Valverde-Barrantes et al. (2007). Previous studies in these plots indicated that there was no meaningful diel variation in soil respiration (Raich 2017). Nevertheless, the order of measurements was changed at every sample time. All measurements were taken between ~8:00 and 14:00.

Biomass and surface litter: cation stocks

Aboveground biomass.—To encompass all strata in the vegetation, three sets of measurements were done. During annual inventories, we measured the diameter at breast height (dbh) and height for (1) all trees ≥ 10 cm dbh (both planted and natural regeneration) in each plot and (2) understory trees 2.5 to <10 cm in diameter of a single 3 × 15 m transect in each plot. (3) For herbaceous vegetation, saplings (<2.5 cm diameter), shrubs (<1.5 m tall), vines, and palms, we conducted destructive biomass harvests in 2013 in four randomly located 0.5 × 1.0 m quadrats per plot. Data from all three strata were summed on an aerial basis, to determine total plot-level biomass and element stocks. Sample sizes for vines and palms were too small, so they were not included in the plot-level element stocks.

Belowground biomass.—Fine-root biomass was sampled in 2012 at two depths (0–15 and 15–30 cm) in five randomly selected points within a plot, one in each of three quadrants and two in the fourth, using a hammer-driven metal corer (5.35 cm inner diameter). For deeper depth increments (30–50, 50–75, and 75–100 cm), fine roots

were sampled from the face of the soil pits that were sampled for mineral soil. This was done by taking five horizontal soil cores, evenly spaced along the vertical range of the depth interval, to sample a total volume of 505 cm³ per depth interval. All fine-root samples were processed within two days as in Valverde-Barrantes et al. (2007). Briefly, samples were soaked overnight, then elutriated using a hydropneumatic system (Smucker et al. 1982) with 530- μ m mesh filters, and then sorted by status (live or dead). Coarse-root, stump, and stump-root biomass within a 1 m radius of trees was determined, based on the biomass regressions described in the next paragraph. Coarse-root biomass beyond the 1 m radius (i.e., between trees) was sampled in 2013 by harvesting all suberized roots >2 mm diameter from the 1 m deep soil pits from which mineral soil was sampled. Roots were separated into three size categories (2 mm–1 cm, 1–10 cm, and >10 cm diameter) by depth interval (0–15, 15–30, 30–50, 50–75, and 75–100 cm).

Species-specific biomass-regression.—These equations were developed by tissue component (listed in the following paragraph) by harvesting nine trees of each species encompassing the range of tree sizes across all four blocks in 2004, 2005, and 2011. For each tree, we determined dry mass (organic matter) by tissue component (Appendix S1: Table S1). The harvests included excavating large coarse roots, stumps, and stump-roots to 1-m depth within the 1-m radius around the boles of the nine trees per species harvested for the aboveground biomass regressions. Fresh masses of all materials were obtained in the field using an electronic hanging balance, and samples were processed as described in Russell et al. (2010). The linear regressions of components of tree biomass were based on $d^2 \times h$ (diameter² \times height, in m³) and yielded R^2 values of >0.75 for each of the planted tree species (Appendix S1: Table S1). The same approach was used for non-planted tree species (>2.5 cm diameter) that colonized the plots, for which sample sizes varied (Appendix S1: Table S1). Samples were dried at 65°C and then ground prior to elemental analyses, first with a Wiley mill and then with a high-energy ball mill (8000M Mixer/mill; SPEX Metuchen, New Jersey, USA).

For element concentration analyses, live biomass from harvested plants was divided into the following components: (1) aboveground overstory (planted) tree species, divided into canopy (leaves, flowers, fruits), twigs (≤ 1 cm diameter), branches (1–10 cm diameter), and larger branches and bolewood (≥ 10 cm diameter); (2) aboveground understory (non-planted species), divided into herbs, shrubs (< 1.5 m tall), saplings (≤ 2.5 cm diameter), and (d) trees (>2.5 cm diameter) (in all categories, tissues were divided into the same tissue categories as for the planted tree species); (3) belowground biomass categories, including fine roots (unsuberized roots generally <2 mm diameter), small and medium coarse (suberized) roots (2 mm–1 cm and 1–10 cm diameter, respectively), and large woody roots and stumps (>10 cm diameter).

Surface litter.—Litter mass, including branches ≤ 1 cm in diameter, was measured three times in 2013–2014 from four 0.11-m² square locations as in Raich et al. (2007). Larger woody debris was based on sampling in a single 3.0 \times 3.0 m quadrat per plot at one time. Dead roots were quantified during the root biomass sampling described below. Only C concentrations were quantified for dead root samples, however, as masses were small.

Stocks of elements.—C, Al, Ca, Fe, K, Mg, Mn, and Sr were calculated by tissue component on an individual basis for trees and shrubs >2.5 cm dbh, using the species-specific biomass regressions, applied to the annual inventory data. Stocks in herbaceous vegetation, shrubs, and saplings <2.5 cm diameter dbh were determined directly from the biomass harvests. In all cases, vegetation (or surface litter) was separated into tissue components and stocks were calculated by tissue component as the product of dry mass and its respective elemental concentration determined from the harvested plants. Data were summed across tissues and across individuals within a plot to yield total element stocks on a plot basis.

Species traits

Stoichiometry, i.e., C:cation molar ratios, were calculated based on analyses of overstory (planted) tree tissue components from the biomass harvests. Fine-root growth was measured in 2012–2013 using 2-mm mesh ingrowth cores as in Valverde-Barrantes et al. (2007) and Russell et al. (2010), with one difference. We measured growth over two depth intervals, 0–15 and 15–30 cm, with cores for the two depth intervals situated in the same hole. Root ingrowth on a length basis was determined by elutriating the sample, separating roots from detritus, and quantifying root length with a WinRHIZO image analysis system (Regent Instruments, Quebec City, Quebec, Canada). Mass was determined for the same sample. Fine litter production was measured using four 1.3 \times 0.4 m litter traps per plot as in Raich et al. (2007). Litterfall was classified by four categories: overstory leaves (of planted species), leaves of other species, twigs (diameters ≤ 1 cm, including bark), and other materials (fruits, flowers, frass). These and all other OM samples were dried at 65°C soon after collection. The dried samples were weighed and then ground as described for other plant tissues prior to elemental analyses. Turnover time of the overstory trees was calculated based on measurements of leaf litterfall and leaf biomass.

Laboratory analyses

Total C for both vegetation and soil were measured by dry combustion, using a ThermoFinnigan Flash EA 1112 elemental analyzer (Thermo Fisher Scientific, Waltham, Massachusetts, USA). Other elements (Al, Ca, Fe, K, Mg, Mn, Sr) in vegetation were measured by

microwave-assisted acid digestion and analyzed using inductively coupled plasma optical emission spectroscopy (Kingston and Haswell 1997). In total, 2,704 plant samples were analyzed for C and cations. Plant tissues were composited within plots, tissue types, and studies across sample times in proportion to their total OM contribution over the time period.

A total of 230 soil samples were analyzed for C concentration and 115 soil samples were analyzed for pH in water, exchangeable acidity and cations. Soil pH was measured using a stirred slurry of 10 mL sieved, air-dried soil in 25 mL deionized water (Thomas 1996). Extractable Al, Ca, and Mg and exchangeable acidity were determined by extraction with a salt solution, 1 mol/L KCl. Extractable K was measured by Olsen's method, displacement with 1 mol/L ammonium acetate. The Olsen's reactant contained NaHCO₃ (sodium bicarbonate) and EDTA, (ethylenediaminetetraacetic acid), adjusted to pH 8.5 using 5 mol/L NaOH (sodium hydroxide). For both methods, the soil : solution ratio was 2.5:25, soil was shaken in a vertical shaker at 400 rpm for 10 min, and then filtered through Whatman #2 paper. Extractable cations were then measured by atomic absorption spectrometry. Changes over time in extractable cations were calculated using published 2005 data from these plots; extractable Al was not measured in 2005, however, so changes could not be calculated. Effective CEC (cmol(+)/kg) was calculated as the sum of exchangeable acidity and extractable Ca, Mg, and K. Base saturation (%) was determined as $[(Ca^{+2} + Mg^{+2} + K^{+})/CEC] \times 100$.

Statistical analyses

For all statistical tests, the experimental unit was the plot. For variables with multiple measurements per plot, the plot mean was used in the analysis. Means are presented with standard errors. For analyses involving only the four planted species, the study design was considered to be randomized complete block; for analyses including the mature forest, it was a randomized incomplete block design. Blocks were treated as a random effect. We tested for homogeneity of variances and normality of distributions. For Al, the variances were heterogeneous, so tests were performed on ln-transformed data. Comparisons among the four planted tree treatments are more precise than comparisons with the mature forest because the first are within-block comparisons but the second are between-block comparisons. Computations were done using the SAS MIXED procedure and for comparisons including the mature forest, we used the Satterthwaite adjustment for degrees of freedom. Pairwise comparisons for significant overall *F* tests were performed using *P* values adjusted by Tukey's Honestly Significant Difference method.

ANOVA was used to evaluate differences among tree species in soil pH and biomass stocks in cations (see Table 2, H1a, H2). For H2, we first conducted a

MANOVA. In all tests, the interactions among cations were significant, so individual ANOVAs were done for each cation. To assess redistribution of cations within the soil profile, we analyzed changes in extractable Ca, Mg, and K (but not Al) at five depth intervals (0–1 m) over an 8-yr period. This ANOVA model included terms for depth and vegetation type \times depth interaction. Procedures were conducted in SAS (Littell et al. 1996).

For tests of correlations, Pearson analyses were conducted (H1b, H3); linear regression was used to test H4. To assess the effects of the four species traits on cation stocks in total live biomass (H5), we used a multiple regression model that included one response variable, the stock of the cation in total biomass (kg/ha). The four predictor (explanatory) variables tested were (1) overstory-leaf C:cation ratio, (2) fine-root growth (length basis, 0–15 cm depth, $\text{cm}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$), (3) cation flux in fine litterfall ($\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) for the corresponding cation stock in biomass, e.g., Ca in litterfall ($\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) in the model for Ca in total biomass (kg Ca/ha), and (4) overstory leaf turnover time (yr). With $n = 15$ plots for these analyses, it would not be appropriate to include more variables. Partial regression residual analysis, which quantifies the effect of a particular explanatory variable after the effects of all the other explanatory variables in the model have been taken into consideration, was used to evaluate the strength of the four explanatory variables (Neter et al. 1996).

RESULTS

Soil pH and biomass stocks of elements

Soil pH.—Tree species differed in their effects on mineral soil pH at all depth intervals ($P < 0.0001$; Fig. 2; Appendix S1: Table S2). (H1a). The lowest soil pH in the surface 15 cm, 4.08 (mean \pm SE 4.14 ± 0.02), was in *Pentaclethra*, the only nodulated legume species in our study and the dominant tree species in the mature forest. Soil pH was highest, 4.85 (4.71 ± 0.08), in *Vochysia*, the Al-accumulating species and next highest in the control, which is dominated by *V. guatemalensis* and *V. ferruginea* (also an Al accumulator) that may have colonized from surrounding plots in the experiment. The effect of species declined with depth, but was still significant in all layers.

Soil respiration, a soil-acidifying process, was significantly higher in *Vochysia* than in the other vegetation types in both years of this study period (Appendix S1: Table S11). Soil pH was not significantly correlated with soil respiration, however, contrary to the hypothesized relationship (H1b; Fig. 3).

Biomass stocks of elements.—After 25 yr of growth, the differences among species in OM, C, and cation stocks in total live biomass (above- plus belowground) were significant (Fig. 4; Appendix S1: Tables S3–S10) (H2). The specific results differed by element (MANOVA, $P \leq 0.005$).

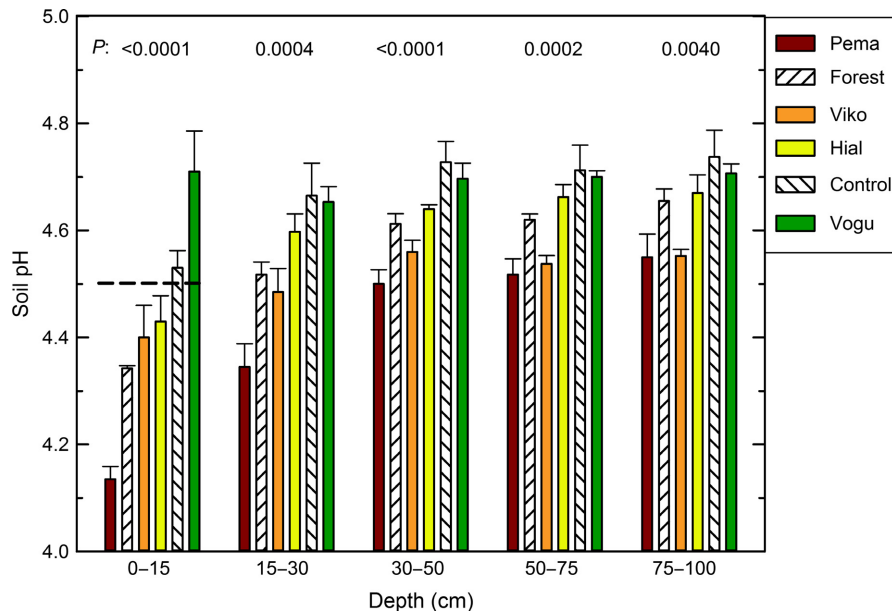


FIG. 2. Soil pH by depth interval in experimental plots at La Selva, Costa Rica. Species are identified by acronyms as in Table 1. Surface soil pH at onset of experiment is denoted by dashed line.

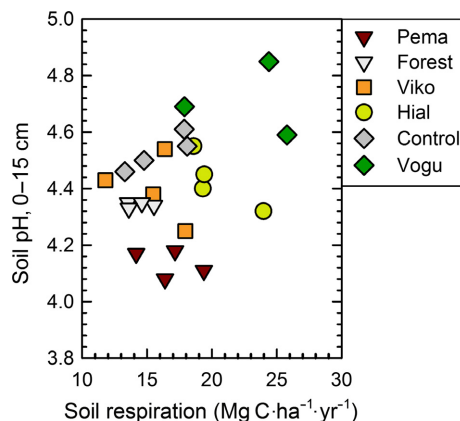


FIG. 3. Soil pH as a function of soil respiration in experimental plots at La Selva.

Species effects on soil cation availability

1. Cation loss from acidification.—Effective CEC differed among species in surface soil only ($P < 0.0406$; Appendix S1: Table S13); it was highest in the mature forest and *Pentaclethra*, and lowest in *Virola* and *Vochysia*. The significantly higher effective CEC at lower soil pH (Fig. 5) reflected the greater exchangeable acidity at lower pH (Appendix S1 Table S2). As such, base saturation increased with soil pH, as hypothesized (H3a; Fig. 5).

Extractable cation concentrations within mineral soil layers did not differ among species, except for Mg in the surface layer, where concentrations were >4.6 times higher in *Vochysia* than in *Pentaclethra* ($P = 0.0220$;

Appendix S1: Table S2). Extractable Al concentrations were negatively correlated with pH, consistent with Eq. 1 (Fig. 5). We hypothesized that extractable base cations would correlate positively with soil pH (H3b), given that soil acidification would release cations that would be either leached or taken up into biomass. Neither Ca nor K were significantly correlated with pH, but Mg had a significant positive correlation with pH (Fig. 5).

Surface-soil extractable cations were significantly correlated with their respective cation stocks in biomass for Mg and K, but both correlations were positive ($P < 0.0001$, $r = 0.86$) and ($P = 0.0141$, $r = 0.62$, respectively), the opposite of the hypothesized relationship (H3c).

Changes in soil extractable cation stocks did not differ significantly among species over an 8-yr period, when trees were aged 17–25 yr post-planting (Table 3) (Appendix S1: Table S12). This result is contrary to the hypothesis of reduction of extractable soil cations over time as uptake into vegetation occurred (H3c). Moreover, for data pooled across vegetation types within soil layers, the only significant changes in extractable cations were subtle increases, rather than decreases, in surface soil K and Mg ($P > 0.05$; Appendix S1: Table S12).

2. Release of occluded cations from colloids and other mechanisms.—All stocks of cations in total biomass, except Mn, were strongly and positively correlated with surface soil pH (Fig. 6, Table 4), as hypothesized (H4). For all cations except Al, the minimum biomass stock occurred at a pH of ~ 4.1 – 4.4 , with stocks greater above and below this pH range. These trends are consistent with the hypothesis that occluded cations are released as a result of alteration of soil pH.

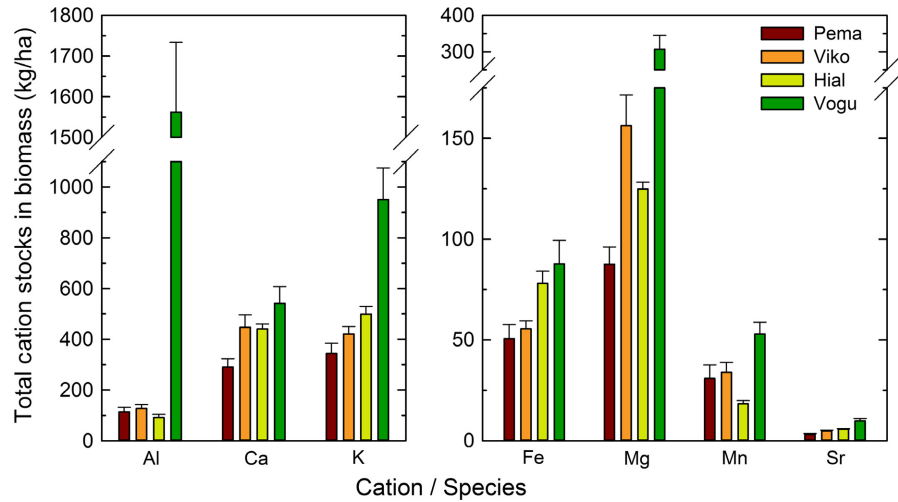


FIG. 4. Stocks of cations (kg/ha) in biomass. Species are identified by acronyms as in Table 1.

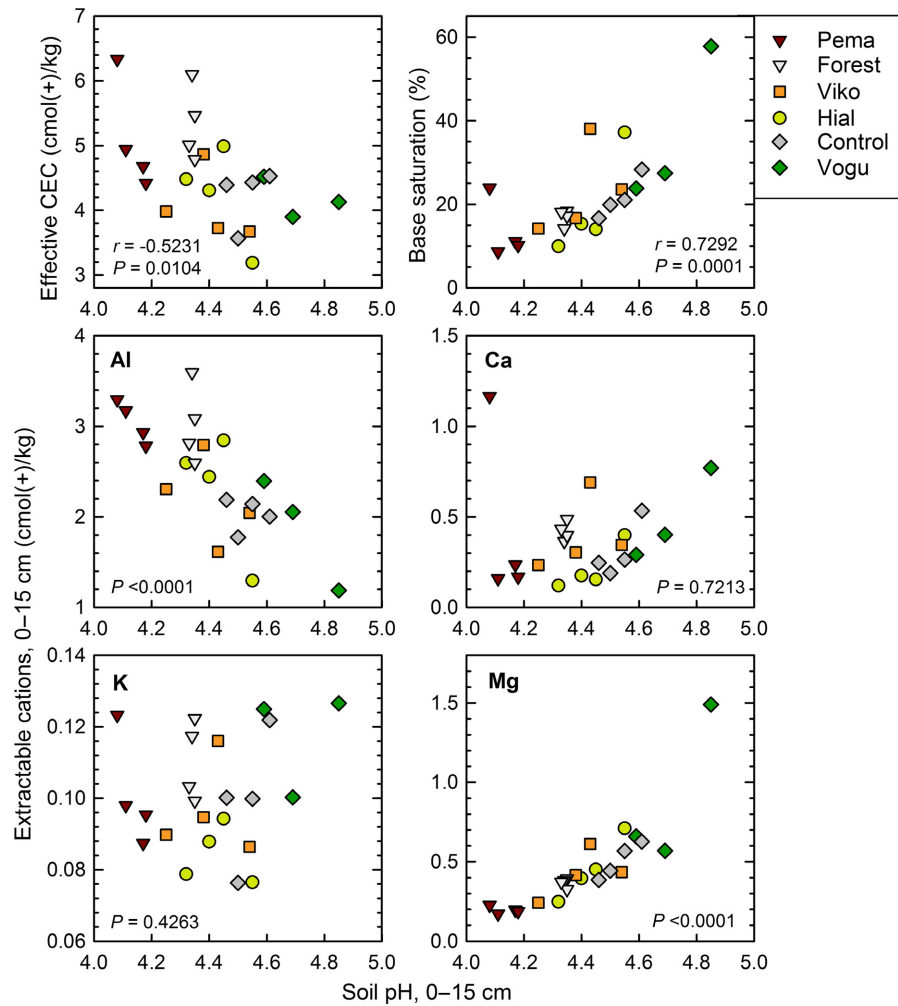


FIG. 5. Effective cation exchange capacity (CEC) (top left), base saturation (top right), and extractable cations as a function of pH in surface soil in experimental plots at La Selva. Species acronyms are defined in Table 1.

TABLE 3. Cation budgets include deposition in precipitation (mean annual), changes in extractable soil cations, and changes in total cations in biomass and surface litter at La Selva.

Cation	Species			
	<i>Hieronyma</i>	<i>Pentaclethra</i>	<i>Virola</i>	<i>Vochysia</i>
Ca (kg·ha ⁻¹ ·yr ⁻¹)				
Precipitation (Eklund et al. 1997)	5.7 ± 1.6	5.7 ± 1.6	5.7 ± 1.6	5.7 ± 1.6
Δ Soil Extr. Cations, 0–100	−4.3 ± 4.8	8.4 ± 4.5	−2.8 ± 7.2	6.7 ± 5.2
Δ Biomass + surface litter	19.5 ± 2.7	12.3 ± 4.4	19.6 ± 5.7	24.6 ± 9.4
K (kg·ha ⁻¹ ·yr ⁻¹)				
Precipitation	3.2 ± 0.9	3.2 ± 0.9	3.2 ± 0.9	3.2 ± 0.9
Δ Soil Extr. Cations, 0–100	2.9 ± 0.6	1.5 ± 0.8	−1.2 ± 3.5	0.8 ± 2.1
Δ Biomass + surface litter	20.2 ± 3.8	14.0 ± 5.3	17.0 ± 3.7	38.4 ± 15.7
Mg (kg·ha ⁻¹ ·yr ⁻¹)				
Precipitation	3.9 ± 0.5	3.9 ± 0.5	3.9 ± 0.5	3.9 ± 0.5
Δ Soil Extr. Cations, 0–100	6.7 ± 7.1	−6.4 ± 2.0	−8.9 ± 7.0	−1.3 ± 3.3
Δ Biomass + surface litter	5.6 ± 0.5	3.7 ± 1.1	6.7 ± 1.6	13.2 ± 5.2

Notes: Full species names are in Table 1. Values are means ± SE. Precipitation data are for 1992–1995; samples were taken at La Selva near, but not within, the study site. Mean annual change in soil extractable cations (Δ Soil Extr. Cations) are calculated from data taken in the study site in 2005 (Russell et al. 2007) and 2013; changes in concentration were not significantly different from zero below 15 cm in all species (see Appendix S1: Table S12). Mean annual changes in the sum of total biomass (overstory + understory, above- and belowground), surface fine litter, and surface branches (Δ Biomass + surface litter), also from this site, are calculated from totals measured in 2013 (Appendix S1: Tables S6–S8) divided by 25, the age of the planted trees.

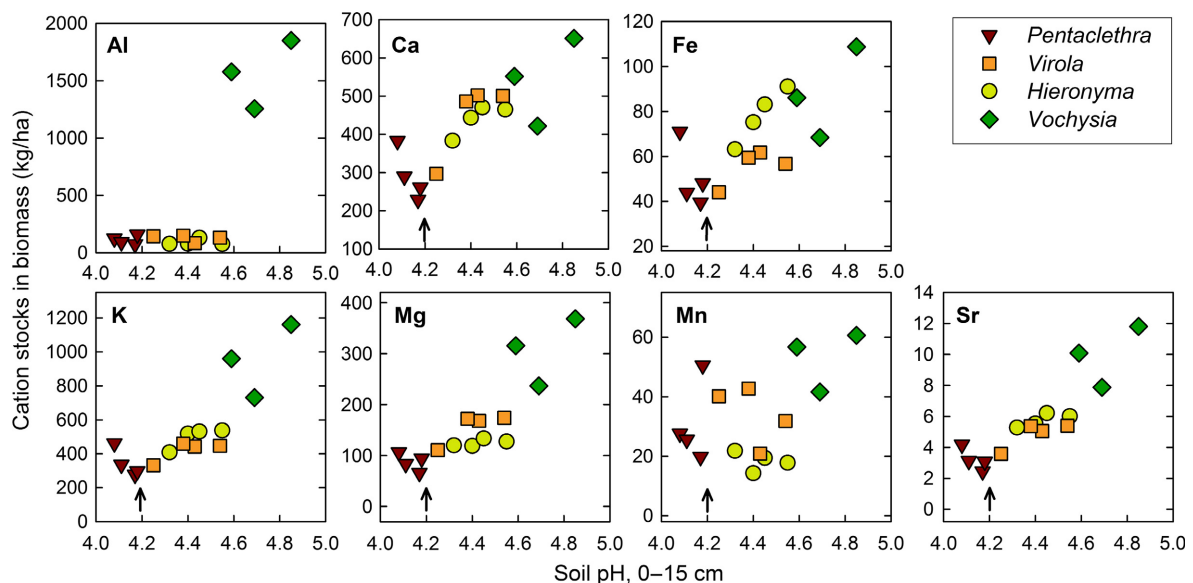


FIG. 6. Cation stocks in total biomass as a function of surface soil pH in experimental plots at La Selva. Full species names are in Table 1. Arrows indicate the hypothesized value for the point of zero charge (PZC), the pH at which expected nutrient availability is lowest by the release of occluded cations from colloids mechanism.

3. *Differential depletion of soil cations.*—This mechanism is not supported by the data reported above for surface-soil extractable cations (Appendix S1: Table S2). Consistent with this, in deeper soil (30–100 cm), changes in extractable Ca, K, and Mg were not significantly different from zero ($P = 0.40, 0.14$, and 0.08 , respectively).

4. *Uptake from deep soil.*—Live fine-root biomass was concentrated in the surface 15 cm of soil, which

contained 78.5–83.2% of the total to 1-m depth (*Vochysia* and *Hieronyma*, respectively; Appendix S1: Table S14). The 15–30 cm layer essentially made up the balance, 16.8–21.5%, given that the 30–100 cm layer accounted for only 0.002% in all species. Given that cation concentrations decreased significantly with depth ($P < 0.0001$; Appendix S1: Table S2), and a depth to bedrock of >4 m, the data do not provide strong support for this mechanism in this site.

TABLE 4. Results of statistical analyses for cation stocks in biomass (kg/ha) as a function of surface soil pH.

Element	Slope estimate	SE	<i>t</i>	<i>P</i>	<i>R</i> ²
Al	2,028	522	3.89	0.0019	0.54
Ca	440	80	5.47	0.0001	0.70
Fe	66	16	4.05	0.0014	0.56
K	932	171	5.44	0.0001	0.69
Mg	332	56	5.93	<0.0001	0.73
Mn	27	17	1.58	0.1390	0.16
Sr	10	1	7.13	<0.0001	0.80

Notes: Linear regression results for *n* = 15 plots. Age of overstory trees is 25 yr.

Soil respiration, a soil-acidifying process, was significantly higher in *Vochysia* than in the other vegetation types in both years of this study period (Appendix S1: Table S11). Soil pH was not significantly correlated with soil respiration, however, contrary to the hypothesized relationship (H1b; Fig. 3).

Species traits and cation accrual in biomass

The molar stoichiometry of the overstory (planted trees) varied by tissue and cation, with significant differences among species (Fig. 7; Appendix S1: Table S15, as calculated from concentrations in Appendix S1: Table S16). Fine-root growth differed among species. On a mass basis, rates were similarly highest in *Hieronyma* and *Vochysia* (Appendix S1: Table S17). On a length basis, fine-root growth was highest in *Vochysia* alone (*P* = 0.0072). Litterfall fluxes differed significantly among vegetation types for all cations except Fe (Fig. 8; Appendix S1: Table S18). For all cations, *Pentaclethra* had the lowest fluxes in litterfall. Leaf turnover time in *Pentaclethra*, 1.68 ± 0.40 yr, was significantly longer than that of 0.64 ± 0.07 yr in *Hieronyma* (Appendix S1: Table S19).

Of these four traits evaluated, the significance of a particular trait as an explanatory variable depended on the specific cation stock modeled (Table 5). C:cation molar stoichiometry was a significant variable for two of the seven cations modeled (H5). This single trait explained 51%, 47%, and 33% of the variability among species in Mg, K, and Mn in biomass stocks, respectively (Appendix S1: Table S20). Two other traits, flux of cations in litterfall and turnover time of leaves, were also significant factors for two cations, while fine-root growth was a slightly more predictive trait in that it was a significant factor in three of the cation stocks modeled.

DISCUSSION

Tight nutrient cycling alone cannot explain how vegetation in this experiment started with near-zero cation stocks in biomass and accumulated up to 1,561, 542, 951, 307, and 53 kg/ha of Al, Ca, K, Mg, and Mn, respectively (at the plot level) over the course of 25 yr. Moreover, transfer of extractable cations from the soil, i.e., depletion of extractable soil stocks, did not account for accrual of cation stocks in biomass among four native tropical tree species over their first 25 yr of growth in a common site, on the same Oxisol. These data suggest that tropical tree species can significantly and differentially mobilize cations from the soil, despite very low extractable soil cation availability. Thus, our results challenge the current idea that the primary mechanism by which soil cations become bioavailable is through loss from soil exchange sites as a result of acidification (Fig. 1a). We evaluated proposed new mechanisms that explicitly integrate species traits with soil biogeochemistry, and specifically cation availability, in a highly weathered tropical soil (Fig. 1b, c). These mechanisms concern the connections between species traits and two main aspects of cation cycling: (1) soil pH and its regulation of cation availability and (2) plant cation uptake from soil into and retention within biomass.

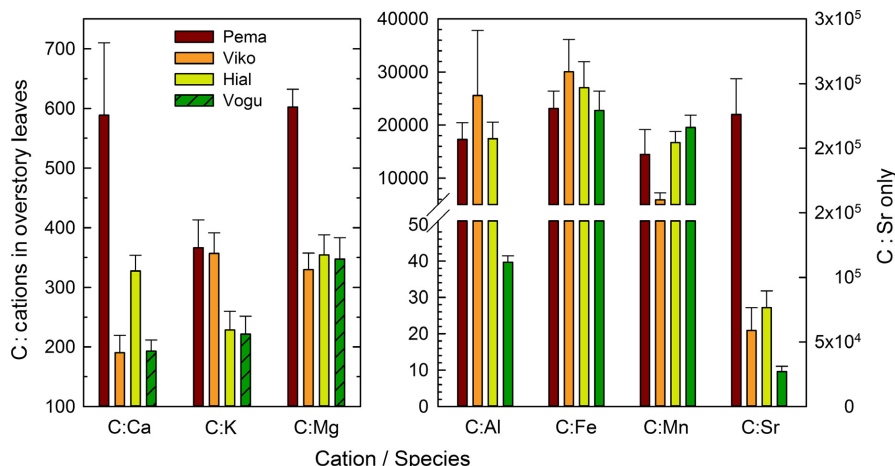


FIG. 7. C-cation stoichiometry of overstory (planted) tree species in experimental plots at La Selva.

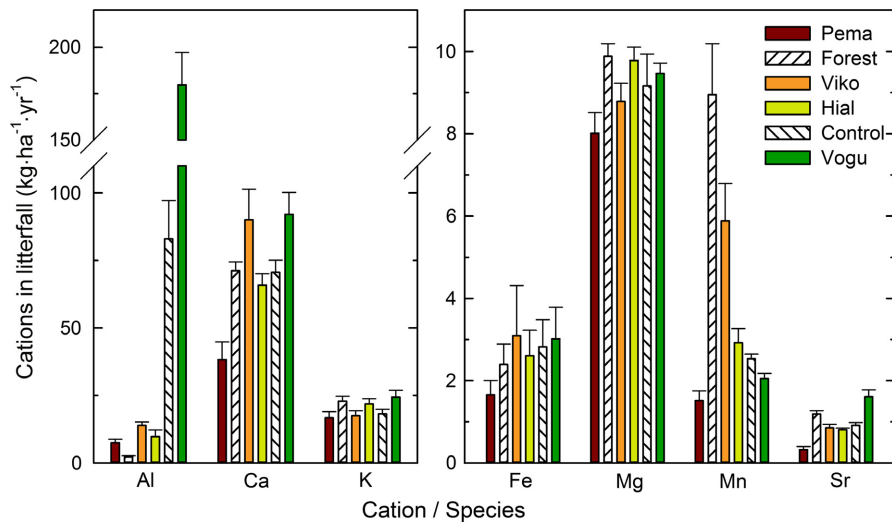


FIG. 8. Cations in fine litterfall in experimental plots at La Selva. Species are identified by acronyms as in Table 1.

TABLE 5. Multiple regression model statistical results: species traits and cation stocks in biomass.

Explanatory variables	<i>P</i> values of response variable, cation stocks in total biomass						
	Al	Ca	Fe	K	Mg	Mn	Sr
Stoichiometry	0.7563	0.4418	0.8429	0.5275	0.0294	0.0064	0.1379
Fine-root growth	0.1691	0.1601	0.0589	0.0014	0.8697	0.0005	0.0179
Litterfall	<0.0001	0.0728	0.1463	0.0080	0.4409	0.5640	0.0911
Leaf turnover	0.7181	0.1721	0.8460	0.8924	0.0227	0.0310	0.1034
All variables	<0.0001	0.0468	0.1435	0.0004	0.0069	0.0004	0.0027
<i>R</i> ²	0.96	0.37	NS	0.84	0.71	0.85	0.56

Notes: A single model was analyzed for each cation. The response variable was the cation stock in total live biomass, in kg/ha. Regressions were based on $n = 15$ plots. The *P* values (Type II sums of squares) refer to significance of the reduction in the sum of squared error when adding a parameter to the model that already has the other three parameters in it. The explanatory variables (followed by their label) were C:cation ratios in overstory (planted tree) leaves (stoichiometry); fine-root growth on a length basis, 0–15 cm depth, in $\text{cm}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ (fine-root growth); cation flux in total fine litterfall for the respective cation stock (litterfall); and overstory leaf turnover time in yr (leaf turnover). Bold values were significant at $P = 0.05$.

Regulation of cation availability

Release of occluded cations from colloids.—Soil pH has a strong influence on colloidal dispersion in the acidic, variable-charge soils characteristic of this study site and many other tropical forests. Detrimental effects of acidification on cation stocks resulting from increased exchangeable acidity and decreased base saturation and Al^{3+} replacement have been widely studied. Effects of pH on nutrient supply via colloid dispersion have received very little attention, and may be critical for understanding how large increases or decreases in pH that are mediated by plants could release occluded nutrients.

Across all plots, cation stocks in biomass were lowest at soil pH ~ 4.2 (except for Mn; note arrows in Fig. 6; H4). This pH value is similar to the PZC of other Oxisols in other tropical forests (Chorover and Sposito 1995). Thus, our measured trends are strikingly similar to results from soil weathering and material transport

studies in which colloids and OM were increasingly dispersed as pH changed relative to the PZC (Chorover and Sposito 1995, Chorover et al. 2004, Thompson et al. 2006). Our data in Fig. 6 are consistent with, but do not confirm, the hypothesized relationship between soil pH and cation availability depicted in Fig. 1c. Given that data in Fig. 6 represent a field study with only 15 plots, and that the lower limit of natural soil pH was so close to the hypothesized PZC, the similarity between observed and predicted trends is remarkable. The V-shaped relationship between soil pH and biomass cation stocks is consistent with our hypothesis that the release and occlusion of cations is mediated by soil pH (Fig. 1b).

This relationship between biomass nutrient stocks and soil pH cannot be readily explained by CEC, or by replacement of cations by H^+ and Al^{3+} (Fig. 1a). The reasoning is that extractable soil cation concentrations in surface soil did not correlate positively with pH, even

though this soil layer contained 79–83% of fine root biomass. The one exception was Mg (Fig. 5, H3b), which is known to associate specifically with short-range-ordered Al phases, which co-vary with pH (McBride 1978). Furthermore, extractable soil cations did not decline with cation accrual in biomass (Appendix S1: Table S12; H3c; Table 3).

Other mechanisms.—The interception and uptake of cations in precipitation is one possible source of new plant nutrients, but at La Selva, these inputs do not account for the magnitude of cations accrued in biomass (Eklund et al. 1997; Table 3). Precipitation inputs of K, for example, can account for a maximum of only 16–20% of biomass K accrual among species, without accounting for potential leaching losses. Erosion and dust deposition can also supply primary minerals and rock-derived nutrients to highly weathered tropical landscapes (Chadwick et al. 1999, Vitousek et al. 2003, Porder et al. 2006). However, these mechanisms cannot explain the dramatic variation in rock-derived nutrient stocks in biomass among different tree species growing on a common soil in our replicated experiment, in that any dust or erosive inputs would be expected to affect species similarly. The mechanism of “differential depletion of extractable cations” was similarly not supported by our results, given that soil extractable cations increased under some species, even while they accrued cations in biomass (Table 3; Appendix S1: Table S2). Increases in extractable soil cation stocks are consistent with the proposed mechanism of “release of occluded cations from colloids,” however. “Uptake from deep soil” was an unlikely mechanism, given that fine-root biomass declined greatly with depth, as did extractable cations (Appendix S1: Tables S2 and S14). Moreover, primary minerals are essentially absent at depth at our site (Kleber et al. 2007).

Simple cation budgets (Table 3) indicated that cation inputs from precipitation plus extractable soil cations were lower than cation accumulation rates in biomass and surface litter for Ca in all species except *Pentaclethra* and for Mg in *Pentaclethra* and *Virola*. These budgets are conservative because leaching losses were not included. Together, these findings indicate that a heretofore unknown source of cations contributed to accrual of Ca in biomass for three of the species, Mg in one species, and K for all species. This further supports our hypothesis that tree species differentially influenced the release of occluded cations by differentially altering soil pH.

Species traits and cation accrual in biomass

The species in this experiment altered soil pH differentially from an initial surface-soil value of 4.5 (Fig. 2, Appendix S1: Table S2). Two species traits, nodulation with N₂-fixing microbes and Al accumulation in biomass were associated with the largest pH changes, consistent with the concept that plant-driven release and consumption of H⁺ can alter soil pH. The range across

all plots, 4.08–4.85, corresponds to a difference in H⁺ concentrations that is greater than five-fold. Soil pH declined to 4.14 ± 0.02 in *Pentaclethra macroloba*, a nodulated with N-fixing microbes. In contrast, soil pH increased to 4.71 ± 0.08 under *Vochysia*, which accumulated Al stocks 17-fold greater than the other species. This increase in soil pH occurred despite the fact that soil respiration, usually a soil acidifying process, was highest in *Vochysia* (Fig. 3). Future experiments that involve controlled laboratory testing of the effects soil pH per se on soil colloid dispersion and cation liberation will advance the testing of this mechanism.

For traits that could potentially influence cation uptake and retention in biomass, no single trait explained the variability for all cations (Table 5). This analysis included the traits of leaf C:cation, fine-root growth, litterfall fluxes of cations, and leaf turnover time. This variation among species in multiple traits and their impacts on cation biomass stocks likely reflects the multiplicity of plant strategies with respect to mineral nutrition in a nutrient-depleted soil.

Consequences of species traits

Given that Ca, Fe, K, Mg, and Mn are essential nutrients for plants, their availability in and uptake from soil can limit plant growth, and hence aspects of tropical forest productivity (Cuevas and Medina 1988, Wright et al. 2011). While geological processes play an important role in cation bioavailability across landscapes and through time, our results suggest that species composition can also alter cation dynamics on decadal time frames, and may thus influence forest productivity in cation-limited soils.

To place our results from a single site into a broader context for tropical forests, we compared aboveground biomass stocks of Ca, Mg, and K with global ranges for mature moist tropical forests (Appendix S1: Table S21). On a global basis in lowland sites, stocks of Mg varied nearly eightfold. Among only four tree species in our study site, Mg stocks varied 3.6-fold, encompassing one-half the global range, with values highest in *Vochysia* (Appendix S7). For K, stocks varied sevenfold globally, whereas in our study, K stocks varied nearly threefold, covering 36% of the global range across parent material types (Appendix S8). Globally, Ca stocks in aboveground biomass vary 16-fold. Among our plots, Ca stocks varied nearly twofold (Appendix S6), corresponding to the lower 8% of the global range in Ca stocks in the moist tropical forest biome.

The focus on effects of individual species on ecosystems has become especially relevant, given the magnitude of changes in vegetation composition that are occurring now within the wet tropical biome, in particular, reduced tree species diversity following deforestation (Wright 2005). Although many trait-based predictions of species effects on ecosystems focus on a single trait, or even a suite of traits, a multiple-trait approach has

been shown to improve the predictive capacity (Eviner 2004). Given the recent development of global plant-trait databases (Kattge et al. 2011), the opportunities for developing multiple-trait-based vegetation and biogeochemical models are increasing. Our results indicated that inclusion of the less-studied traits of leaf C:cation ratios improved model predictions of cations accrued in biomass for some, but not all, cations. Across the set of seven cations studied, the three other more commonly modeled traits had a similar predictive capacity (Table 5). This supports the idea that a multiple-trait approach will be required for modeling the effects of individual species, at least when the traits relate to physiological responses of individual species within a given set of climate and soil conditions.

In contrast, our results also suggested that a single species trait could have a high predictive capacity if the trait strongly influenced the geochemical environment. The traits of nodulation to support N fixation and Al^{+3} accumulation were associated with straightforward trends in alteration of soil pH, a master soil variable that has clear relevance for cation availability and ecosystem function. Moreover, these two pH-altering traits will serve in a generalizable framework for the humid tropics because the traits are not rare. Tree species associated with N_2 -fixing microbes are common throughout many tropical forests (Vitousek et al. 2013, Bauters et al. 2016b). Accumulation of Al is also a fairly common trait in tropical trees, occurring in 52 families (APG 1998). This trait results in Al uptake from soil into plants, a process that consumes soil H^+ , thereby decreasing soil acidity and increasing pH. We are not aware of another study that has proposed a biogeochemical connection, i.e., liberation of occluded soil cations, for this trait of Al accumulation.

Together, the elements of our proposed framework that explicitly integrates these species traits with biogeochemical processes provide a context for understanding how biotic and abiotic factors interact. The framework also provides insight into how species might influence variability in cation supply that supports productivity in one of the powerhouse biomes of the world, the tropical rainforest.

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SUPPORTING INFORMATION

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DATA AVAILABILITY

Data available from the Dryad Digital Repository: <https://doi.org/10.5061/dryad.07k4p>