

Parent Material and Topography Determine Soil Phosphorus Status in the Luquillo Mountains of Puerto Rico

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ABSTRACT

Phosphorus (P) availability in terrestrial ecosystems depends on soil age, climate, parent material, topographic position, and biota, but the relative importance of these drivers has not been assessed. To ask which factor has the strongest influence on long- and short-timescale metrics of P availability, we sampled soils across a full-factorial combination of two parent materials [quartz diorite (QD) and volcanoclastic (VC)], three topographic positions (ridge, slope, and valley), and across 550 m in elevation in 17 sub-watersheds of the Luquillo Mountains, Puerto Rico. VC rocks had double the P content of QD (600 vs. 300 ppm; $P < 0.0001$), and soil P was similarly approximately 2× higher in VC-derived soils ($P < 0.0001$). Parent material also explained the most variance in our two other long-timescale metrics of P status: the fraction of recalcitrant P (56% variance explained) and the

loss of P relative to parent material (35% variance explained), both of which were higher on VC-derived soils ($P < 0.0001$ for both). Topographic position explained an additional 10–15% of the variance in these metrics. In contrast, there was no parent material effect on the more labile NaHCO₃- and NaOH-extractable P soil pools, which were approximately 2.5× greater in valleys than on ridges ($P < 0.0001$). Taken together, these data suggest that the relative importance of different state factors varies depending on the ecosystem property of interest and that parent material and topography can play sub-equal roles in driving differences in ecosystem P status across landscapes.

Key words: phosphorus; parent material; topography; Puerto Rico; state factors.

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INTRODUCTION

Phosphorus (P) may limit net primary production (NPP) and decomposition in many tropical ecosystems (Vitousek 1984; Vitousek and Farrington 1997; Davidson and others 2007; Elser and others 2007; Cleveland and others 2011). Although P availability (or nutrient availability in general) can be attributed to some combination of soil parent material, soil age, topography, climate and biological activity (Jenny 1941; Amundson and Jenny 1997), our understanding

of the relative importance of these factors for soil P status remains limited. The effects of soil age and climate are typically invoked to explain the apparent P poverty of the tropics relative to the temperate zone (Vitousek and Sanford Jr. 1986; Reich and Oleksyn 2004; McGroddy and others 2004; Brookshire and others 2011). However, soil age and climate can vary considerably within a given tropical landscape (Porder and Chadwick 2009). Denudation can create differences in P availability along a catena that is similar to those seen across sites varying by millions of years in soil age (Porder and others 2005). Elevation differences can result in differences in soil redox status and thus P availability (Silver and others 1994, 1999), and parent material can influence soil P through differences in P concentration (Kitayama and others 2000; Takyu and others 2002; Dieter and others 2010) and texture (Raich and others 1996). Given that many tropical landscapes show variation in all these factors (Townsend and others 2008), robust predictions of ecosystem P status in the tropics have remained elusive.

We suggest that any attempt to describe the biogeochemistry of a tropical landscape will be most useful when simultaneously incorporating variation in multiple state factors (sensu Jenny 1941) with the goal of assessing the relative importance of each factor in determining the biogeochemical property of interest. Yet the vast majority of studies exploring the effects of state factors seek to isolate a single factor by minimizing variation in others. Thus, chronosequence sites are located on minimally eroded surfaces that share common parent material, climate, and vegetation (Walker and Syers 1976; Vitousek 2004; Wardle and others 2004; Selmants and Hart 2008), and climosequences minimize variation in everything but rainfall (Schuur and Matson 2001), and so on. Although this approach is well suited to documenting whether a state factor has an effect, it is not as useful in estimating the relative importance of these factors across a landscape where several state factors may vary from one area to another. This in turn precludes prediction of how the P status (or other ecosystem properties of interest) of one system differs from another, even if the state factors for both systems have been well quantified.

In addition to gaging their relative importance, the interaction between state factors can only be elucidated through such multi-factor studies. For example, work in the Hawaiian Islands suggests that large climate gradients ($0.2\text{--}2.5\text{ m y}^{-1}$ rainfall) drive only minor differences in soil weathering after 10 ky of soil development, but similar climatic differences produce dramatically different soils

after 170 ky (Porder and others 2007). Vegetation and climate can also interact, in the same Hawaiian system the effects of vegetation on soil P status persist in mesic climates for at least 350 ky, whereas in wet climates they last fewer than 170 ky (Porder and Chadwick 2009). These examples suggest that a predictive model of ecosystem properties based on a state factor approach cannot depend solely on experiments that isolate the effects of individual state factors. However, the paucity of data with a well-defined matrix of variation in multiple state factors precludes extrapolation of the few results we have to other systems. Without the ability to make such extrapolations, it is difficult to develop a reliable characterization of tropical biogeochemistry that may help us predict how tropical ecosystems will respond to global changes in temperature, precipitation, and nitrogen (N) deposition (Townsend and others 2011).

In this context, we explored the relative importance of two state factors, parent material and topographic position, and elevation (which influences two additional state factors: climate and biological community, Barone and others 2008) on the P status of a matrix of sites in the Luquillo Mountains of Puerto Rico. We sampled soils to 80 cm across a full-factorial combination of two parent materials [quartz diorite (QD) and volcanoclastic (VC)] and three topographic positions (ridge, slope, and valley) spanning an elevation gradient from 350 to 800 m to elucidate the effect of these factors on soil P status. We considered three metrics of P status: (1) total soil P concentration, (2) soil P forms as operationally defined by a modified Hedley Fractionation (Tiessen and Moir 1993), and (3) the loss of soil P relative to parent material, as determined by indexing to an immobile element (in this case niobium; Kurtz and others 2000).

Total soil P concentration is relatively infrequently measured in ecological studies, but is often strongly correlated with soil organic P (P_o) concentration, and thus may be an important metric of ecosystem P status (Harrison 1987; Turner and Engelbrecht 2011). Total P explains a significant, if small, fraction of the variance in aboveground NPP (ANPP) across a wide range of tropical sites (Cleveland and others 2011). Total P alone, however, is not adequate to describe soil P status, because not all P in soil becomes biologically available over the same timescale (Richter and others 2006; Syers and Johnston 2008). Our second metric of P status is based on a modified Hedley Sequential Fractionation (Hedley and others 1982; Tiessen and Moir 1993), and seeks to chemically approximate immediately biologically available, organic, primary

mineral, and recalcitrant P pools (Cross and Schlessinger 1995; Johnson and others 2003). Although these chemical approximations are, at best, a coarse representation of the conceptually defined P pools that matter in ecosystems (Walker and Syers 1976), they do capture some of the changes in P form observed during long-term soil development (Crews and others 1995) and across climatic gradients (Miller and others 2001). Our final metric of P status, the loss of P relative to parent material, can be used to understand the progression of weathering and depletion that soil has undergone since its inception (Porder and Chadwick 2009). This window into the history of pedogenesis allows us to assess whether P depletion was occurring at different rates in different portions of the Luquillo landscape.

The watersheds in this study receive high rainfall (3–4 m y⁻¹), and high rates of chemical weathering on ridgetops produce 8–10-m deep weathering profiles on most ridges (White and others 1998; Buss and others 2010; Buss, unpublished data). This, coupled with previous work that suggested relatively high atmospheric dust inputs of P (Pett-Ridge 2009), led us to expect little influence of parent material on the P status of ridges. We also expected that lower landscape positions would be rejuvenated by frequent landslides that strip weathered soils from slopes and increase more labile forms of P in the soil (Porder and others 2005). Finally, we expected a rock-type by P loss interaction, and predicted that iron (Fe) and clay-rich VC-derived soils would lose P more slowly than those derived from the sandy Fe-poor QDs, because Fe binding to P is a primary mechanism of P occlusion in tropical soils (Sanchez 1976; Chacon and others 2006). We did not expect elevation to influence P status in this landscape because all our sites have a highly positive water balance and thus are likely to experience relatively similar rates of soil P depletion despite differences in temperature, rainfall, and biological community (Chadwick and others 2003; Porder and Chadwick 2009).

METHODS

Study Site

We worked in 17 sub-watersheds in the steeply dissected Luquillo Mountains in northeastern Puerto Rico (18°30'N, 65°80'W; Figure 1). The Luquillo Mountains are composed of the QD Rio Blanco stock and surrounding intermediate-mafic VCs (Scatena 1989; Frizano and others 2002), which underlie Dystrudepts and Hapludoxes,

respectively (United States Department of Agriculture 2002). The mean annual temperature decreases from around 24 °C at 300 m to around 21 °C at 800 m and precipitation increases with elevation from 3 m y⁻¹ at the lowest sites to 4 m y⁻¹ at 800 m (www.sas.upenn.edu/lczo accessed 9/7/2012). The lower elevations (<600 m) are dominated by mixed Tabonuco Forest (*Dacryodes excelsa* Vahl), at higher elevation Palo Colorado (*Cyrilla racemiflora* L.) trees become more abundant and Tabonuco less so (Weaver 1991; United States Department of Agriculture 2002), but there is overlap between these forest types between 500 and 700 m elevation. The steep slopes in the region (up to 50°) are subject to landslides that reset soil development every few thousand years on VC parent material (Zarin and Johnson 1995) and more frequently on QD (F. N. Scatena, personal communication; Larsen and Torres-Sanchez 1998). However, chemical weathering is sufficiently rapid such that QD ridgetops are underlain by an 8–10-m saprolite (White and others 1998; Buss and others 2010), and given landscape denudation rates of 0.1 mm y⁻¹ (at least for some QD watersheds; Riebe and others 2003), the weathering zone residence time on ridgetops may thus exceed 100 ky. Denudation rates for VCs have not been determined, but weathering zones are comparable and may be even deeper (H. Buss, unpublished data).

Sub-watershed Selection

To span biologically meaningful gradients in elevation, we initially selected a full-factorial combination of parent material and forest type with four replicates in each sub-watershed type (and five in the Tabonuco forest underlain by VCs) based on local lithologic and vegetation maps (Bawiec 1999; Huffaker 2002; Figure 1). These sub-watersheds spanned 350–800 m in elevation, and within each we sought out pronounced local ridges (slope <10°) that do not receive significant deposition from above. From each ridge, we sampled along catenas that descended into local ephemeral stream valleys without crossing into a different lithology. At each sub-watershed, we confirmed the mapped lithologic classification (QD vs. VC) by collecting rocks from channels on either side of the ridge, and by examination of rocks in landslides or present as surface float along the slopes. Although our preliminary sub-watershed selection was based on mapped forest type, forest community composition changes with elevation in this landscape (Barone and others 2008), and detailed analyses of community composition in each sub-watershed were

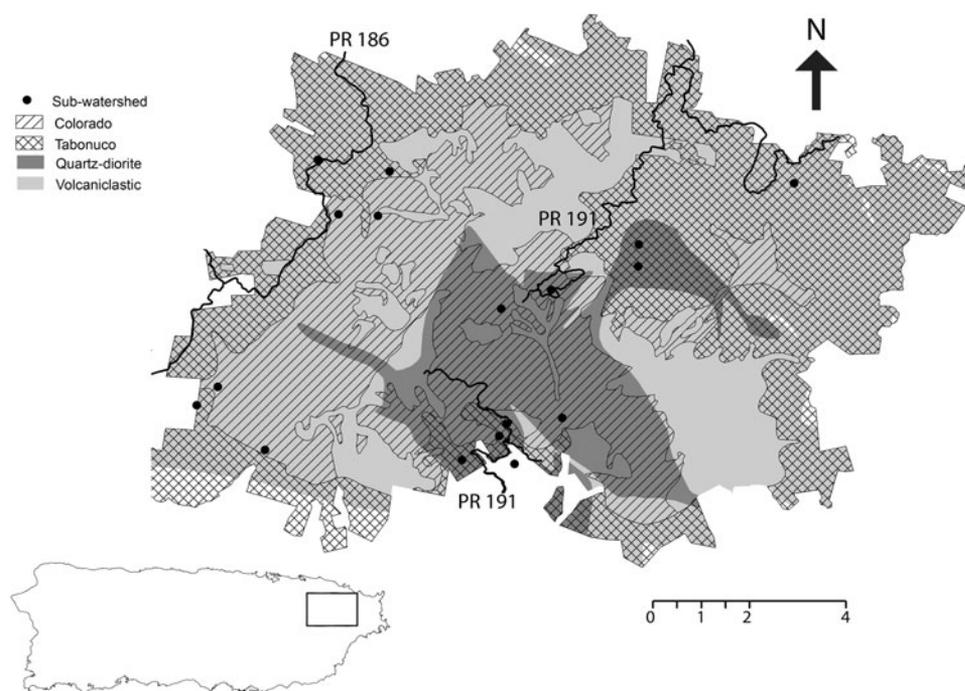


Figure 1. Location of the sub-watersheds within the Luquillo Forest. *Light gray* indicates VC and *dark gray* indicates QD, *crosshatched pattern* indicates Colorado forest and *striped pattern* indicates Tabonuco forest.

not available. Thus, for the analyses we present here, we use mean sub-watershed elevation as an independent variable rather than forest type. Elevation, rainfall, and temperature also co-vary in this landscape, but similar to forest type we did not have long-term climate data from each sub-watershed, and thus used sub-watershed elevation as the most readily quantifiable of these interrelated variables.

Soil Sampling

We collected soils from 144 soil pits in July 2010 and from nine additional pits in August 2011. Within each sub-watershed, we sampled soils along three ridge–slope–valley transects. Ridges were defined as flat ($<10^\circ$) local topographic highs such that we were confident no deposition was occurring. We dug three soil pits to a depth of 80 cm in each topographical position, for a total of nine pits per sub-watershed. Within a given sub-watershed, the ridge pits were located on a single ridge, but in some (but not all) sub-watersheds we selected transects on both sides of the ridge and in those slope and valley samples came from separate downslope areas. Typical valley sites were located 20–60 m in elevation below the ridge. After removing the litter layer, we excavated a 25×25 cm quantitative pit to a depth of 20 cm (for bulk density calculations), and used a 10-cm diameter soil corer to sample from 20 to 50 and 50 to 80 cm. We handpicked large roots from the 0- to

20-cm sample in the field, weighed and removed them, and collected a soil subsample for analysis and a second subsample that was dried at 105°C for bulk density analyses. We composited soils by depth for a given location in a watershed (for example, all three 0–20-cm ridgetop soils from a given site were combined prior to analysis) for the analyses described here, thus we had a total of 159 soil samples—one from each of three depths from a full-factorial combination of parent material, “forest type,” and topographic position.

Soil Analyses

Soils were stored at room temperature in Puerto Rico before shipment to the University of Pennsylvania, where they were air-dried and sieved (<2 mm) within 2 weeks of collection. After drying, the samples were shipped to Brown University, where we performed a modified Hedley sequential fractionation of soil P following Tiessen and Moir (1993) on all the composited soils. Although air-drying can influence the more labile P fractions (Turner and Haygarth 2003) it was not possible to analyze this number of field moist soils in a timely manner. First, we extracted 0.5 g of soil with 30-ml 0.5 M NaHCO_3 . We then digested an aliquot of the extractant with 0.5-g potassium persulfate in an autoclave at a temperature of 121°C and determined total P in that extractant. We calculated P_o as the difference between total and inorganic P (P_i). We carefully transferred the NaHCO_3 -extracted soil

for extraction with 30-ml 0.1 M NaOH and analysis of NaOH-extractable inorganic P, and assessed NaOH-P_o similarly. We then extracted the NaOH-extracted soil with 1 M HCl. All P concentrations in the extractions described above were measured colorimetrically on a Westco SmartChem 200 (Westco Instruments, Brookfield, Connecticut). In addition to the Hedley sequential fractionation, a 10 g subsample of each soil was analyzed by lithium borate flux fusion for major elemental composition, including Al and Fe, using X-ray fluorescence (XRF) and trace element concentration by ICP-MS at ALS Chemex (Sparks, Nevada, USA). We calculated the residual P pool as the difference between total P and the sum of the aforementioned fractions. We report depth-weighted concentration results from 0 to 50 cm in the text below, and note if trends differ for other depth intervals. We also report P data on a mass per area basis for 0–20 cm, for which we measured bulk density from quantitative pits.

We measured soil P loss relative to its parent material by indexing total soil P concentrations to parent material concentrations using a putatively immobile element, niobium (Nb; Brimhall and Dietrich 1987; Chadwick and others 1999). This calculation requires an accurate determination of P and Nb for both parent material and soil. Thus, during the summer of 2011, we collected 31 unweathered bedrock samples (exposed in stream channels or landslide scars) from the VC sites, and 20 samples from the less-variable QD sites for analysis using XRF and ICP-MS as described above (Supplemental Material Table 1).

We calculated soil P loss relative to parent material (τ_p) as

$$\tau_p = \left(\frac{C_{j,w}}{C_{j,p}} * \frac{C_{Nb,p}}{C_{Nb,w}} \right) - 1, \quad (1)$$

where C is concentration, p and w indicate parent material or weathered soil, respectively, *j* is the element of interest (in this case P) and Nb is niobium. τ values of –1 indicate 100% loss relative to parent material, whereas values of zero indicate no loss. Positive τ_p indicates gain relative to parent material, which can occur as a result of P uptake and retention by plants (Porder and Chadwick 2009) or by exogenous inputs to the system. Note that τ_p is independent of bulk density.

Statistical Analysis

We used multi-variate regression trees (De'ath and Fabricius 2000) with our P metrics as response variables, and parent material (QD, VC), topographic

position [ridge (R), slope (S), valley (V)], and mean watershed elevation as independent variables. This non-parametric analysis identifies the combinations of independent variables that produce groups with the most different dependent variable values. Increasing the number of branches in these trees almost always explains some additional variance, thus we selected the tree with the lowest Akaike's Information Criterion (AIC) value. We then tested for differences between leaf groups as defined by these regression trees using ANOVA and correcting for multiple comparisons among groups of unequal sample size using Tukey's HSD. As parent material and topography, but not elevation, were often important in explaining variation, we also present means and standard errors for the six groups (QD-R, QD-S, QD-V, VC-R, VC-S, VC-V) to help guide our discussion. We used JMP (SAS Institute, North Carolina) v10.0 for all statistical analyses.

RESULTS

Variation in our first metric of P status, total soil P concentration, was driven by differences in both parent material and topographic position, whereas elevation had no significant effect. VC parent material had double the total P (~600 ppm) of QD parent material (~300 ppm; $P < 0.0001$). Similarly, total soil P varied by a factor of two between the VC-derived Hapludoxes and the QD-derived Dystrudepts ($P < 0.0001$; Table 1). Parent material alone explained 49% of the variance in total P, whereas increases in total P downslope explained an additional 12% for VC-derived soils (Figure 2).

Our second metric, the different forms of soil P as defined by Hedley Sequential Fractionation, were also dependent on parent material and topography (and not elevation), but for the putatively more labile P pools (those extracted by NaHCO₃ and NaOH-P_o; Johnson and others 2003) topographic position explained more variance than parent material (Table 1; Figure 3). Sodium bicarbonate-extractable inorganic P (NaHCO₃-P_i) was undetectable in most of these soils, so we report NaHCO₃-P_t here, which is equivalent to NaHCO₃-P_o in almost every pit. Both VC- and QD-derived soils had higher NaHCO₃-P_t in the valleys than on ridges/slopes derived from the same parent material, but this difference was only significant for VC-derived soils (Table 1, $P < 0.001$). Across the entire dataset, topography explained about 32% of the variance in these data. Similarly, the concentration of NaOH-P_o increased from ridges to valleys; although, this increase was only significant for VC-derived soils ($P < 0.0001$). Topographic posi-

Table 1. Phosphorus Fractions (ppm) from 0–50-cm Depths Across a Matrix of Topographic and Lithologic Conditions

	Quartz diorite	Volcaniclastic
Total P	$R^2 = 0.62$	
Ridge	140 ± 23a	290 ± 15c
Slope	170 ± 31ab	280 ± 20bc
Valley	170 ± 25ab	410 ± 43d
NaHCO ₃ -P _t	$R^2 = 0.38$	
Ridge	4.1 ± 0.59a	6.3 ± 0.86a
Slope	8.2 ± 1.9a	6.4 ± 0.76a
Valley	11 ± 0.85ab	15 ± 2.4b
NaOH-P _o	$R^2 = 33$	
Ridge	61 ± 9.2a	67 ± 3.5a
Slope	79 ± 17a	75 ± 4.4a
Valley	120 ± 16ab	140 ± 11b
NaOH-P _i	$R^2 = 27$	
Ridge	17 ± 3.6a	34 ± 9.8ab
Slope	36 ± 10.0ab	38 ± 11ab
Valley	34 ± 7.0ab	59 ± 20ab
Residual:total	$R^2 = 67$	
Ridge	0.27 ± 0.02a	0.59 ± 0.05c
Slope	0.28 ± 0.02ab	0.56 ± 0.03c
Valley	0.10 ± 0.03a	0.47 ± 0.03bc
τ_P	$R^2 = 51$	
Ridge	-0.69 ± 0.01ac	-0.82 ± 0.01c
Slope	-0.55 ± 0.05ab	-0.83 ± 0.01c
Valley	-0.46 ± 0.07b	-0.71 ± 0.07ac

R^2 gives the total variance in the dataset explained by multivariate regression trees splitting the data into these groups. $N = 8$ for each quartz diorite group and $N = 9$ for each volcaniclastic group. Contrasting letters indicate significant differences at $P < 0.05$ using Tukey's HSD.

tion explained 33% of the variance in NaOH-P_o (Table 1). Parent material explained an additional 8% of the variance in the 0–20-cm soils but had no statistically significant influence on NaOH-P_o for the 0–50- or 0–80-cm intervals.

In contrast to the organic P fractions, both parent material and topographic position explained roughly equal amounts of variance in NaOH-P_i. For the 0–20 cm and 0–50 cm depths, parent material explained the most variance (8 and 10%, respectively). Topographic position had no significant effects in the 0–20-cm interval, but in the 0–50-cm interval it explained an additional 11% of the variance for VC-derived soils and 6% for QD-derived soils. Integrating across 0–80 cm, topographic position explained 22% of the variance, and parent material explained an additional 3% for the ridge and slope positions and 14% for in the valley position. None of the independent variables were useful predictors of primary mineral P (HCl-P), which was less than 5% of total P in any of our sites.

VC-derived soils had a significantly higher ($P < 0.0001$) fraction of P in residual form (Table 1), and parent material explained 56% of the variance in this dataset, whereas topography had no significant explanatory power. Given the role that Fe and aluminum (Al) play in binding residual P, it is worth noting that VC-derived soils had double the Al (23 ± 0.6 vs. 12 ± 0.5 wt% Al₂O₃) and triple the Fe (12 ± 0.4 vs. 4.7 ± 0.4 wt% Fe₂O₃) concentration of QD-derived soils ($P < 0.0001$ in both cases). The fraction of residual P was tightly correlated with both the Fe and the Al contents of the soil ($R^2 = 0.56$ and 0.54 for Fe and Al, respectively, $P < 0.001$ for both). Parent material also explained 35% of the variance in our final P status metric, the loss of P relative to parent material (τ_P), which was lower (less loss, τ_P closer to zero) on QD than VC-derived soils. τ_P also decreased downslope (Table 1), although this decrease was only significant ($P < 0.05$) for QD-derived soils.

Similar to the results based on concentration, the more labile P fractions (NaHCO₃-P_t, NaOH-P_o) as expressed on a mass per area basis were most influenced by topographic position, which explained 38 and 20% of the variance in these data, respectively, at least in the upper 20 cm of soil (for which we have bulk density measurements from quantitative pits, Table 2). Variation in total P (on a mass per area basis) was explained by topographic position (16%) and lithology (14%), because the low bulk density of the VC-derived soils (0.65 vs. 0.91 g cm⁻³ on QD-derived soils) offsets their higher P concentrations.

DISCUSSION

Our results point to both a strong lithologic and topographic control over the concentration of most of the measured soil P pools in this region. This result belies our initial hypothesis that soils would show little influence of parent material, especially on highly weathered ridges. The influence of parent material persists despite rapid weathering rates (White and others 1998), putatively high dust inputs of P (Pett-Ridge 2009), and a 50% reduction of P at the rock-saprolite boundary at about 8 m depth (at least on the QDs; White and others 1998; Frizano and others 2002). On slopes, we expected the higher landslide frequency on QD-derived soils (F. N. Scatena, personal communication; Larsen and Torres-Sanchez 1998) to result in more substantial downslope rejuvenation of total P on this lithology. In contrast to this expectation, there was significant downslope rejuvenation of total P on VC

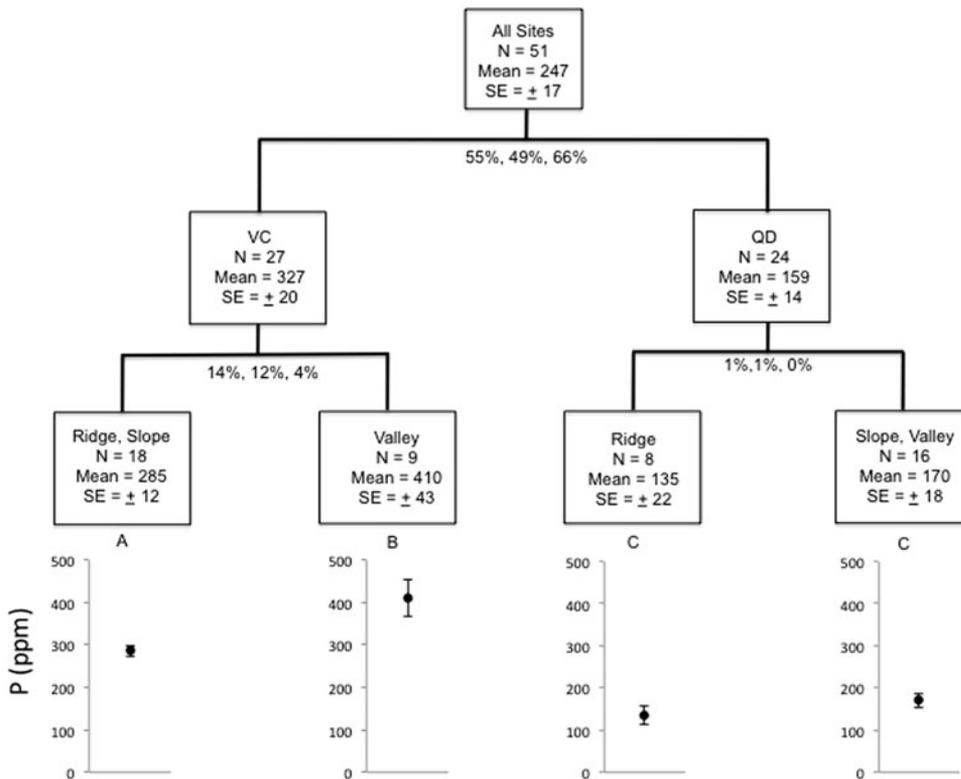


Figure 2. Multivariate regression tree showing the variance in the 0–50-cm soil total P concentration (ppm) explained by differences in parent material and topographic position. Values shown at each split are the percent variance explained for the 0–20-, 0–50-, and 0–80-cm soils data, respectively. *Graphs* show the means and standard errors of the groups as defined by the regression tree. *Contrasting letters* indicate significant differences at $P < 0.05$ following Tukey's HSD.

but not on QD-derived soils (Figure 3), and this effect was small relative to the differences in total P in soils derived from different parent materials.

The importance of parent material on soil P under intense weathering has also been noted across a 2,000-m elevation gradient on Mount Kinabalu, Borneo. There, soils derived from sedimentary rocks had 2–4 times higher total P concentrations than those derived from serpentinite (Kitayama and others 2000). The P content of the parent materials was not analyzed, but a recent analysis suggests that the median P content of serpentinite is less than half that of fine-grained siliclastic rocks (260 vs. 600 ppm, respectively; Porder and Ramachandran 2012). These data indicate that the influence of parent material on total P concentration persists even under high (3–4 m) annual rainfall, and highlights the role of parent material as a driver of spatial variation in tropical soil P concentration.

In contrast to our “long-timescale” metrics of P availability, we found that topography explained most of the variance in the concentrations of more readily-extractable P fractions (for example, $\text{NaHCO}_3\text{-P}_i$ and NaOH-P_o). The importance of topography has also been noted in Hawaii, where labile P (resin and NaHCO_3 extractable) increased downslope (Vitousek and others 2003). This increase

occurs because fresh rock is exposed to weathering on slopes and provides a new source of rock-derived nutrients (Porder and others 2005). Along slopes on Mount Kinabalu, Takyu and others (2002) found that the stocks of “soluble P” (hydrochloric acid/ammonium fluoride extractable) increased 8–12-fold from ridge to valley on sedimentary rocks, but the change resulted from downslope changes in bulk density rather than P concentration, and did not occur on serpentinite. In contrast, our sub-watersheds showed similar increases in the concentration of $\text{NaHCO}_3\text{-P}_i$ and NaOH-P_o downslope (indicating no parent material by P fraction influence for these fractions; Table 1). Exploring the interaction between geomorphic setting, parent material, and the effects of topographic position on P status is a potentially important area for additional research if we hope to make spatially explicit predictions of P status in tropical systems.

Incorporating these interactions may improve our predictive capabilities, but even controlling for three independent factors (parent material, topographic position, and elevation) and two other potentially important variables that change with elevation (forest type and rainfall) we can only explain approximately 30% of the variance in labile P pools. We hypothesize that air drying may have masked differences that were greater under

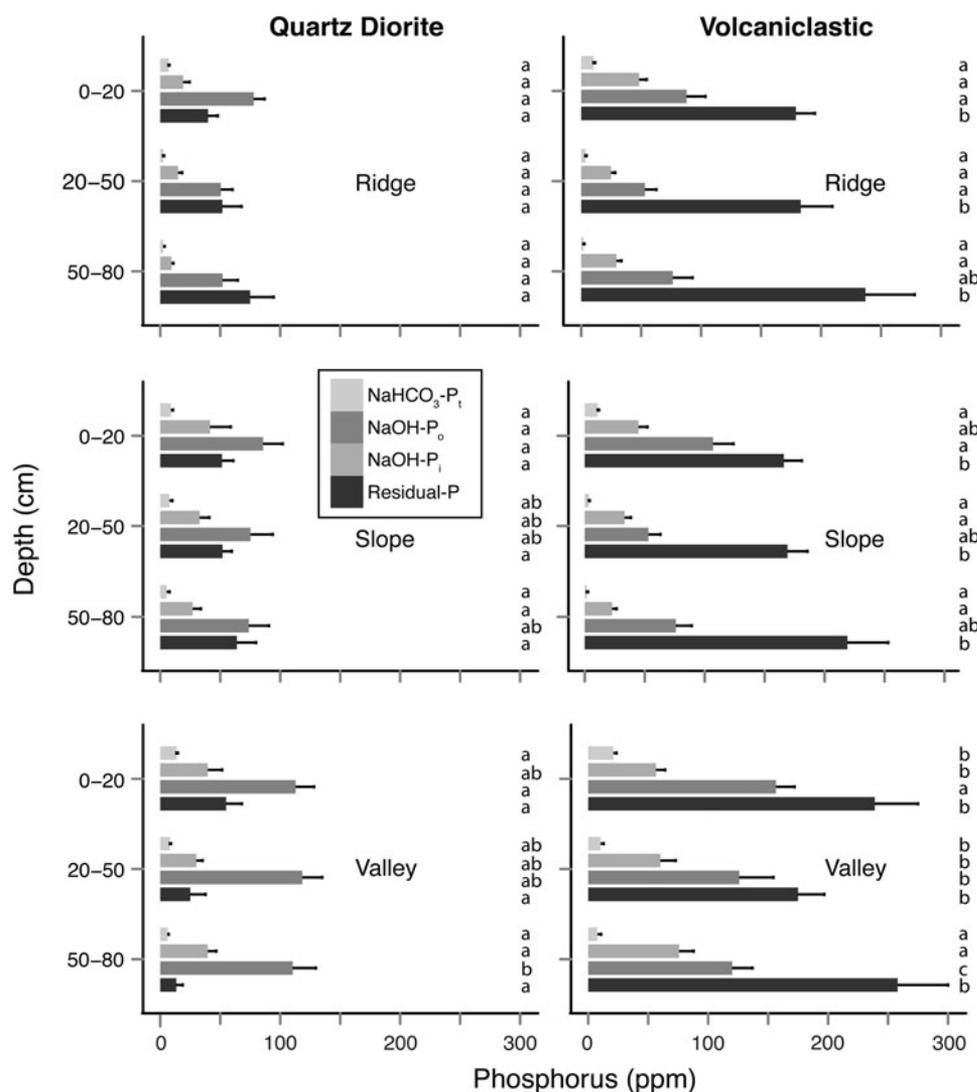


Figure 3. Variation in soil P fractions with depth across parent material and topography. Error bars show 1 SE. Significant differences ($P < 0.05$ using Tukey's HSD) across a particular fraction and depth (for example, comparing 0–20-cm $\text{NaHCO}_3\text{-P}_t$) among the six different types of sub-watersheds are shown with different letters.

Table 2. Bulk Density (g cm^{-3}) of 0–20 cm Soils Across a Matrix of Topographic and Lithologic Conditions

	Quartz diorite B.D. (g cm^{-3})	Volcaniclastic B.D. (g cm^{-3})
Ridge	$0.92 \pm 0.09a$	$0.67 \pm 0.27b$
Slope	$0.93 \pm 0.06a$	$0.63 \pm 0.04b$
Valley	$0.97 \pm 0.08a$	$0.64 \pm 0.05b$

$N = 8$ for each group, as we do not have bulk density for one of the subwatersheds in the VC. Contrasting letters indicate significant differences at $P < 0.05$ using Tukey's HSD.

field conditions (Turner and Haygarth 2003). In addition, we note that our method of sampling by depth (0–20, 20–50, 50–80 cm) rather than by horizon may have introduced additional heterogeneity to the datasets. For example, a relatively

recent tree throw that exposes deeper soil would be identified when sampling by horizon, the A horizon would be thinner than usual, but not when sampling by depth. Although sampling by depth allows more rapid soil pit excavation, and thus allows large soil collections such as this one, such an approach may have led us to miss some small-scale spatial heterogeneity in soil P status. This problem seems less pronounced for our “long-term” metrics—total P, fraction residual P, and τ_p . Variation in these parameters, largely explained by differences in parent material, are not likely affected by air-drying.

Phosphorus poverty and limitation in tropical ecosystems is commonly ascribed to P sorption to Fe and Al secondary minerals rather than solely to low initial total P concentrations (Sanchez 1976; Vitousek 1984). Along some (but not all) chronosequences, shifts toward residual P forms are

accompanied by a decline in total P (Walker and Syers 1976; but see Crews and others 1995). Our data suggest that the fraction of residual P varies as much across rock types in these mountains as it does across hundreds of thousands of years of ecosystem development on a single parent material (Walker and Syers 1976; Crews and others 1995). Soils atop VC parent material have a significantly higher fraction of total P in residual form than QD-derived soils ($P < 0.0001$); VC soils also have almost twice the amount of Fe and Al. We cannot rule out the possibility that soils derived from VC have longer residence times than those on QDs (denudation rates have not been measured in VC sub-watersheds), but suspect that differences in parent material chemistry are more important than those of residence time for explaining variation in soil Fe and Al. VC ridges are not much broader than those on QD, and fresh rock is often exposed on slopes underlain by both lithologies, indicating that denudation is relatively rapid in both settings. The effect of parent material on residual P forms has not been systematically assessed across the tropics. However, in a seasonal lowland tropical rainforest system on Barro Colorado Island, Panama, soils formed from predominantly VC parent material not unlike those in this study had the majority of the P (70–80%) in this pool (Dieter and others 2010). In contrast, soils from Terra Firme forest in Venezuela, derived from metamorphosed granites not unlike the QD in Luquillo had only 30% of P in residual form despite orders of magnitude longer soil residence time (Porder, unpublished data). Similarly, forest sites in central Rondônia atop granite-derived soil (Germer and others 2010) had approximately 20% P in residual form as defined here (Garcia-Montiel and others 2000). Although soil Fe and Al binding to P increases as a given pedon weathers over time, these data suggest the difference in Fe content between parent materials may result in a strong parent material influence on P forms as well.

The influence of parent material on total P reported here is difficult to reconcile with the hypothesis, supported by strontium (Sr) isotope analysis, that approximately 50% of the P in Luquillo watersheds is derived from Saharan dust deposition (Pett-Ridge 2009). Such inputs would tend to homogenize P content across lithologic boundaries, and yield the expectation of similar soil P content across the landscape (as well as more similar soil mineralogy). It may be that the more Fe- and Al-rich VC-derived soils are more efficient at retaining P added as dust, but this hypothesis remains to be tested. It is also possible that P budgets derived from Sr-isotopes are subject to an

overestimation of inputs in this system (Sr differs dramatically from P in its biological cycling and loss pathways).

Finally, the importance of parent material in driving $\text{NaHCO}_3\text{-P}_i$ and NaOH-P_o is diminished when considering stocks rather than concentrations. These results highlight a question that remains largely unanswered, whether P concentrations or stocks are the more ecologically relevant parameter? Recent evidence from a 4.1 ma chronosequence in Hawaii suggests that the concentration of acid fluoride-extractable P explains differences in microbial limitation (Reed and others 2011). However, neither P concentrations nor stocks alone explain the transition from N, to NP, to P limitation of ANPP with soil age (Crews and others 1995; Vitousek and Farrington 1997). Across the tropics, total soil P concentration explains a significant, if small, portion of variation in ANPP (Cleveland and others 2011), but whether total P stocks would have more explanatory value remains unknown. Given that P is transferred to roots via diffusion through the soil solution, and that most forests have soil solution P stocks well in excess of biological demand (Johnson and others 2003), an argument can certainly be made that concentration is the more relevant parameter, but that hypothesis remains to be tested.

CONCLUSION

Nutrient limitation in tropical forests will play a critical role in driving their response to changes in climate, nutrient inputs, and land use over the coming decades, yet our ability to understand the spatial distribution of nutrient limitation in the tropics is quite limited (Cleveland and others 2011). Although the state factor framework has been instrumental in demonstrating that a particular driving variable can influence nutrient availability and limitation, the relative influence of these quasi-independent variables remains largely unexplored. Here, we show that soil P status is strongly influenced by both topography and parent material. The former is not unexpected, and is relatively easy to quantify across the tropics using ever-higher resolution remotely sensed data as it becomes available. But the latter is quite difficult to quantify in the tropics, where deep soils often obscure the bedrock. However, if even on ridges with 10-m thick saprolite, the influence of parent material on some parameters (total P concentration, residual P, τ_P) was stronger than that of topography, it may be that a more exhaustive mapping of lithologic contrasts across tropical forests would result in a more nuanced view of their nutrient status.

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REFERENCES

- Amundson R, Jenny H. 1997. Thinking of biology: on a state factor model of ecosystems. *Bioscience* 47(8):536–43.
- Barone JA, Thomlinson J, Anglada-Cordero P, Zimmerman JK. 2008. Metacommunity structure of tropical forests along an elevational gradient in Puerto Rico. *J Trop Ecol* 24:1–10.
- Bawiec WJ, Ed. 1999. Geology, geochemistry, geophysics, mineral occurrences and mineral resource assessment for the Commonwealth of Puerto Rico. US Geological Survey Open-File Report 98-038 (available online only).
- Brimhall GH, Dietrich WE. 1987. Constitutive mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemical systems: results on weathering and pedogenesis. *Geochim Cosmochim Acta* 51:567–87.
- Brookshire ENJ, Gerber S, Webster JR, Vose JM, Swank WT. 2011. Direct effects of temperature on forest nitrogen cycling revealed through analysis of long-term watershed records. *Glob Change Biol* 17:297–308.
- Buss HL, Mathur R, White AF, Brantley SL. 2010. Phosphorus and iron cycling in deep saprolite, Luquillo Mountains, Puerto Rico. *Chem Geol* 269:52–636.
- Chacon N, Silver WL, Dubinsky EA, Cusack DF. 2006. Iron reduction and soil phosphorus solubilization in humid tropical forests soils: the roles of labile carbon pools and an electron shuttle compound. *Biogeochemistry* 78:67–84.
- Chadwick OA, Derry LA, Vitousek PM, Huebert BJ, Hedin LO. 1999. Changing sources of nutrients during four million years of ecosystem development. *Nature* 397:491–7.
- Chadwick OA, Gavenda, RT, Kelly EF, Ziegler K. 2003. The impact of climate on the biogeochemical functioning of volcanic soils. *Chemical Geol* 202:195–223.
- Cleveland CC, Townsend AR, Taylor P, Alvarez-Clare S, Bustamante MMC, Chuyong G, Dobrowski SZ, Solomon Z, Grierson P, Harms KE, Houlton BZ, Marklein A, Partion W, Porder S, Reed SC, Sierra CA, Silver WL, Tanner EVJ, Edmund VJ, Wieder WR. 2011. Relationships among net primary productivity, nutrients climate in tropical rain forest: a pan-tropical analysis. *Ecol Lett* 14(9):939–47.
- Crews TE, Kitayama K, Fownes JH, Riley RH, Herbert DA, Mueller-Dombois D, Vitousek PM. 1995. Changes in soil phosphorus ecosystem dynamics across a long chronosequence in Hawaii. *Ecology* 76(5):1407–24.
- Cross AF, Schlesinger WH. 1995. A literature review and evaluation of the Hedley fractionation: applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma* 64:197–214.
- Davidson EA, Reis de Carvalho CJ, Figueira AM, Ishida FY, Ometto JPHB, Nardoto GB, Saba RT, Hayashi SN, Leal EC, Vieira ICG, Martinelli L. 2007. Recuperation of nitrogen cycling in Amazonian forests following agricultural abandonment. *Nature* 449:995–8.
- De'ath G, Fabricius KE. 2000. Classification and regression trees: a powerful yet simple technique for ecological data analysis. *Ecology* 81:3178–92.
- Dieter D, Elsenbeer H, Turner BL. 2010. Phosphorus fractionation in lowland tropical rainforest soils in central Panama. *Catena* 82(2):118–25.
- Elser JJ, Bracken MES, Cleland EE, Gruner DS, Harpole WS, Hillebrand H, Ngai JT, Seabloom EW, Shurin JB, Smith JE. 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in fresh-water, marine, and terrestrial ecosystems. *Ecol Lett* 10:1135–42.
- Frizano J, Johnson AH, Van DR, Scatena FN. 2002. Soil phosphorus fractionation during forest development on landslide scars in the Luquillo Mountains, Puerto Rico. *Biotropica* 34(1):17–26.
- Garcia-Montiel DC, Neill C, Melillo J, Suzanne T, Steudler PA, Cerri CC. 2000. Soil phosphorus transformations following forest clearing for pasture in the Brazilian Amazon. *Soil Sci Soc Am J* 64:1792–804.
- Germer S, Neill C, Krusche AV, Elsenbeer H. 2010. Influence of land-use change on near-surface hydrological processes: undisturbed forest to pasture. *J Hydrol* 380(3–4):473–80.
- Harrison AF. 1987. Soil organic phosphorus: a review of world literature. Wallingford: CAB International.
- Hedley MJ, Stewart JWB, Chauhan BS. 1982. Changes in inorganic and organic soil phosphorus fractions by cultivation practices and by laboratory incubations. *Soil Sci Soc Am J* 46:970–6.
- Huffaker, L. 2002. In: Brannon GR, Ragus GF, Eds. Soil survey of Caribbean National Forest and Luquillo Experimental Forest, Commonwealth of Puerto Rico. United States Department of Agriculture and Natural Resource Conservation Service. 181 pp.
- Jenny H. 1941. Factors of soil formation: a system of quantitative pedology. New York (NY): McGraw Hill.
- Johnson AH, Frizano J, Vann DR. 2003. Biogeochemical implications of labile phosphorus in forest soils determine by the Hedley fractionation procedure. *Oecologia* 135(4):487–99.
- Kitayama K, Majalap-Lee N, Aiba S. 2000. Soil phosphorus fractionation and phosphorus-use efficiencies of tropical rainforests along altitudinal gradients of Mount Kinabalu, Borneo. *Oecologia* 123(3):342–9.
- Kurtz AC, Derry LA, Chadwick OA, Alfano MJ. 2000. Refractory element mobility in volcanic soils. *Geology* 28:683–6.
- Larsen MC, Torres-Sanchez AJ. 1998. The frequency and distribution of recent landslides in three montane tropical regions of Puerto Rico. *Geomorphology* 24:309–31.
- McGroddy ME, Daufresne T, Hedin LO. 2004. Scaling of C:N:P stoichiometry in forests worldwide: implications of terrestrial redfield-type ratios. *Ecology* 85(9):2390–401.
- Miller AJ, Schuur EAG, Chadwick OA. 2001. Redox control of phosphorus pools in Hawaiian montane forest. *Geoderma* 102:219–37.
- Pett-Ridge JC. 2009. Contributions of dust to phosphorus cycling in tropical forests of the Luquillo Mountains, Puerto Rico. *Biogeochemistry* 94:63–80.

- Porder S, Payton A, Vitousek PM. 2005. Erosion landscape development affect plant nutrient status in the Hawaiian Islands. *Oecologia* 142:440–9.
- Porder S, Hilley GE, Chadwick OA. 2007. Chemical weathering, mass loss, dust inputs across a climate by time matrix in the Hawaiian Islands. *Earth Planet Sci Lett* 258(3–4):414–27.
- Porder S, Chadwick OA. 2009. Climate and soil-age constraints on nutrient uplift and retention by plants. *Ecology* 90(3):623–36.
- Porder S, Ramachandran S. 2012. The phosphorus content of common rocks—a potential driver of ecosystem P status. *Plant and Soil*. doi:10.1007/s11104-012-1490-2.
- Raich JW, Russell AE, Crews TE, Farrington H, Vitousek PM. 1996. Both nitrogen and phosphorus limit plant production on young Hawaiian lava flows. *Biogeochemistry* 32:1–14.
- Reed SC, Vitousek PM, Cleveland CC. 2011. Are patterns in nutrient limitation belowground consistent with those aboveground: results from a 4 million year chronosequence. *Biogeochemistry* 106(3):323–36.
- Reich PB, Oleksyn J. 2004. Global patterns of plant leaf N and P in relation to temperature and latitude. *PNAS* 101(30):11001–6.
- Riebe CS, Kirchner JW, Finkel RC. 2003. Long-term rates of chemical weathering and physical erosion from cosmogenic nuclides and geochemical mass balance. *Geochim Cosmochim Acta* 67(22):4411–27.
- Richter DD, Allen HL, Li J, Markewitz D, Raikes J. 2006. Bio-availability of slowly cycling soil phosphorus: major restructuring of soil P fractions over four decades in an aggrading forest. *Oecologia* 150:259–71.
- Sanchez PA. 1976. Properties and management of soils in the tropics. New York: Wiley.
- Scatena FN. 1989. An introduction to the physiography and history of the Bisley experimental watersheds in the Luquillo Mountains of Puerto Rico. US Forest Service General Technical Report.
- Schuur EAG, Matson PA. 2001. Net primary productivity and nutrient cycling across a mesic to wet precipitation gradient in Hawaiian montane forest. *Oecologia* 128(3):431–42.
- Selmants PC, Hart SC. 2008. Substrate age and tree islands influence carbon and nitrogen dynamics across a retrogressive semiarid chronosequence. *Global Biogeochem Cycles* 22:1–13.
- Silver WL, Scatena FN, Johnson AH, Siccama TG, Sanchez MJ. 1994. Nutrient availability in a montane wet tropical forest: spatial patterns methodological considerations. *Plant Soil* 164(1):129–45.
- Silver WL, Lugo AE, Keller M. 1999. Soil oxygen availability and biogeochemistry along rainfall and topographic gradients in upland wet tropical forest soils. *Biogeochemistry* 44:301–28.
- Syers JK, Johnston AE, Curtin D. 2008. Reconciling changing concepts of soil phosphorus behaviour with agronomic information: efficiency of soil and fertilizer phosphorus use. Rome: FAO.
- Takyu M, Aiba S, Kitayama K. 2002. Effects of topography on tropical lower montane forests under different geological conditions on Mount Kinabalu, Borneo. *Plant Ecol* 159:35–49.
- Tiessen H, Moir JO. 1993. Characterization of available P by sequential extraction. *Soil sampling methods of analysis*. Canadian Society of Soil Science. Boca Raton: Lewis Publishers. pp. 75–86.
- Townsend AR, Asner GP, Cleveland CC. 2008. The biogeochemical heterogeneity of tropical forests. *Trends Ecol Evol* 23(8):424–31.
- Townsend AR, Cleveland CC, Houlton BZ, Alden CB, White JWC. 2011. Multi-element regulation of the tropical forest carbon cycle. *Front Ecol Environ* 9(1):9–17.
- Turner BL, Haygarth PM. 2003. Changes in bicarbonate-extractable inorganic and organic phosphorus by drying pasture soils. *Soil Sci Soc Am J* 67:344–50.
- Turner BL, Engelbrecht BMJ. 2011. Soil organic phosphorus in lowland tropical rain forests. *Biogeochemistry* 103:297–315.
- United States Department of Agriculture. 2002. Soil Survey of Caribbean National Forest and Luquillo Experimental Forest, Commonwealth of Puerto Rico.
- Vitousek PM. 1984. Litterfall, nutrient cycling, and nutrient limitation in tropical forests. *Ecology* 65:285–98.
- Vitousek PM, Sanford RL Jr. 1986. Nutrient cycling in moist tropical forest. *Annu Rev Ecol Syst* 17:137–67.
- Vitousek PM, Farrington H. 1997. Nutrient limitation and soil development: Experimental test of a biogeochemical theory. *Biogeochemistry* 37:63–75.
- Vitousek PM, Chadwick O, Matson P, Allison S, Derry L, Kettley L, Luers A, Mecking E, Monastra V, Porder S. 2003. Erosion and the rejuvenation of weathering-derived nutrient supply in an old tropical landscape. *Ecosystems* 6:762–72.
- Vitousek PM. 2004. Nutrient cycling and limitation: Hawai'i as a model system. Princeton (NJ): Princeton University Press.
- Walker TW, Syers JK. 1976. The fate of phosphorus during pedogenesis. *Geoderma* 15:1–19.
- Wardle DA, Walker LR, Bardgett RD. 2004. Ecosystem properties and forest decline in contrasting long-term chronosequences. *Science* 305:509–13.
- Weaver PL. 1991. Environmental gradients affect forest composition in the Luquillo Mountains of Puerto Rico. *Interciencia* 16:142–51.
- White AF, Blum AE, Schulz MS, Vivit DV, Stonestrom DA, Larsen M, Murphy SF, Eberl D. 1998. Chemical weathering in a tropical watershed, Luquillo mountains, Puerto Rico: I. Long-term versus short-term weathering fluxes. *Geochim Cosmochim Acta* 62(2):209–26 (table headings).
- Zarin DJ, Johnson AH. 1995. Nutrient accumulation during primary succession in a montane tropical forest, Puerto Rico. *Soil Sci Soc Am J* 59:1444–52.