

Pedogenic Thresholds and Soil Process Domains in Basalt-Derived Soils

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ABSTRACT

Pedogenic thresholds occur where soil properties change abruptly and/or nonlinearly with a small increment in environmental forcing; soil process domains are the regions between thresholds where soils change much more gradually across a large range of environmental forcing. We evaluated thresholds and domains in basalt-derived soils on two rainfall gradients in Hawaii—one from 260 to 3,540 mm/y precipitation on 150,000-year-old substrate, the other from 600 to 3,760 mm/y on 4,100,000-year-old substrate. We identified thresholds associated with the initiation of biological uplift of nutrients at about 700 mm/y on the younger substrate, the depletion of primary minerals at about 2,100 mm/y on the younger and about 900 mm/y on the older substrate, and the initiation of anoxic conditions and associated Fe mobility at about 2,500 mm/y on the older substrate. These thresholds delineated process domains characterized by pedogenic carbonate accumulation

and wind erosion (dry young substrate); by weathering and biological uplift of nutrients (intermediate rainfall young substrate and dry old substrate); by surface Fe enrichment and nutrient depletion (wet young substrate and intermediate rainfall old substrate); and by Fe mobilization and loss (wet old substrate). Soils on the older substrate were more highly weathered, lower in total and available P, and characterized by more crystalline clays than otherwise comparable soils on the younger substrate. Prior to European contact, Hawaiian cultivators developed an intensive rain-fed agricultural system in the weathering/biological uplift domain on the younger substrate; we suggest that only this domain could support indigenous agricultural intensification in upland soils.

Key words: basalt-derived soil; biological uplift; gradient; Hawaii; indigenous agriculture; pedogenic threshold; process domain; weathering.

Received 1 April 2013; accepted 28 May 2013

Electronic supplementary material: The online version of this article (doi:10.1007/s10021-013-9690-z) contains supplementary material, which is available to authorized users.

Author Contributions: PMV and OAC designed the research, carried out the research and performed the analyses, and wrote the paper.

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INTRODUCTION

Soil properties and processes may not change linearly in response to extrinsic differences in environmental forcing such as rainfall; rather their response may be characterized by “pedogenic thresholds” that represent abrupt and/or nonlinear (but predictable) changes in soil properties and processes (Muhs 1984; Chadwick and Chorover 2001). For example, along a rainfall gradient from 180 to 3,000 mm/y in Kohala, Hawaii, Chadwick

and others (2003) demonstrated that base (non-hydrolyzing) cation saturation of soil exchange sites dropped from about 80 to 5% between 1,300 and 1,500 mm of rainfall. This threshold in base cation saturation was associated with a precipitous decline in pH and effective cation retention capacity; acid neutralizing capacity (ANC) also decreased, signaling the irreversibility of this change. These changes were caused by depletion of primary minerals in higher rainfall sites, so that mineral weathering could not buffer atmospheric and biological acidity there. In support of this explanation, Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) also changed abruptly at this threshold, from values characteristic of Hawaiian basalt in drier sites to those characteristic of marine aerosol in wetter sites (Stewart and others 2001; Chadwick and others 2003).

Chadwick and Chorover (2001) identified a second threshold in higher rainfall Hawaiian soils on a separate gradient; this threshold was associated with anaerobiosis and consequent iron reduction and mobility in high-rainfall sites. Subsequent research there elucidated interactions among iron reduction, phosphorus retention, and organic matter dynamics that changed across this threshold (Miller and others 2001; Thompson and others 2011). Chadwick and Chorover (2001) suggested that these and other pedogenic thresholds could be expressed in substantial changes in bulk soil parameters such as mineral crystallinity, nutrient availability, organic matter retention and release, and colloidal dynamics.

A strong case for the importance of pedogenic thresholds has been made in the Hawaiian Islands—in part because the Islands support a climate-time matrix imposed on very similar parent material that make thresholds easier to detect, and in part because rapid weathering of basalt-derived primary minerals and the persistence of metastable and chemically reactive secondary aluminosilicates and metal oxyhydroxides there makes pedogenic thresholds sharper and more distinct. However, pedogenic thresholds have been identified in continental systems, and on lithologies other than basalt (Muhs 1984). For example, Dahlgren and others (1997) analyzed soil properties along a climate gradient in the Sierra Nevada Range and identified a relatively narrow zone where primary mineral weathering and clay mineral formation were enhanced greatly by a favorable combination of temperature and rainfall. Similarly, Ewing and others (2006) demonstrated a strong shift from accumulation of atmospheric salts in the hyperarid core of the Atacama Desert to in situ mineral weathering and pedogenic carbonate formation on

the wetter, arid fringes of the desert. Additional thresholds exist along regional scale ecotones such as transitions from tundra to boreal forest (Ugolini and Spaltenstein 1992).

Where pedogenic thresholds are important, we suggest that it would be rewarding to evaluate soil properties and processes in the regions between thresholds, which we term “soil process domains.” Although pedogenic thresholds represent locations where soil properties or processes change markedly and/or nonlinearly in response to a small increment in forcing, soil process domains conversely represent regions in which soil properties or processes change much more slowly across a wide range of forcing. In this paper, we use a large set of surface soils, in addition to information from well-characterized soil profiles, to evaluate the prevalence of pedogenic thresholds along two broad and continuous gradients of rainfall in basalt-derived soils of the Hawaiian Archipelago—one developed in parent material around 150 kyears old, the other in older than 4,000 kyear parent material. Where pedogenic thresholds occur, we evaluate whether consistent thresholds can be detected on the two substrate ages—and if so, whether the position of these thresholds changes with substrate age. Additionally, we summarize the dominant soil properties and processes within the soil process domains that occupy the regions between thresholds. Finally, we explore the significance of these thresholds and domains for human use of these lands.

METHODS

Sites

The Hawaiian Islands can be used to determine the patterns and controls of soil properties and processes because many of the factors that influence soils can be held constant there to a much greater extent than is possible in most continental settings (Chadwick and others 2003; Vitousek 2004). The parent material in which soils form is basalt, varying from tholeiitic basalt erupted during the shield-building stage of a volcano's evolution to alkalic basalt produced later in its life (MacDonald and others 1983). The constructional surface of shield volcanoes supports little topographic variation, and remnants of constructional surfaces can be identified on the oldest high islands. Even the dominant organisms are (relatively) consistent; the few plant species that dispersed naturally to Hawaii have radiated to occupy a very wide range of environments. On the other hand, substrate age and

climate vary widely, but generally in well-defined and continuous ways. Lava flow and other surface ages are well constrained, and vary nearly continuously from recent deposits to nearly 5 million years from southeast to northwest across the archipelago. Temperature varies with elevation, and current precipitation varies predictably from less than 250 to greater than 10,000 mm/y. These features are well suited to the detection of abrupt, nonlinear transitions in soil properties along continuous gradients of substrate age or precipitation.

Although climate has varied through the history of the archipelago (Hotchkiss and others 2000) and Hawaiian soils carry the imprint of past as well as present climate (they are polygenetic, in the sense of Richter and Yaalon 2012), the enduring characteristics determining rainfall patterns in Hawaii are the interaction of the Northeast trade winds with island topography. The direction of the trade winds has been consistent for several million years (Porter 1979), and consequently dry sites on modern rainfall gradients have long received less rainfall than wet sites, and older sites have accumulated more rainfall (and leaching) than younger sites (Hotchkiss and others 2000).

In this analysis, we evaluate soils sampled along precipitation gradients on the Islands of Hawaii (the youngest island in the archipelago) and Kauai (the oldest high island). Two distinct types of soil samples were included in our analysis—numerous depth-integrated surface samples to 30 cm depth, and whole soil-profile samples. Initially, the surface samples were collected on the Island of Hawaii as part of an analysis of the distribution and limits of indigenous Hawaiian agriculture prior to European contact (Vitousek and others 2004; Palmer and others 2009); equivalent samples later were collected on the Island of Kauai for comparison. These samples were collected along transects using a tiling shovel, normally at around 200-m intervals within or near ancient agricultural systems and 500-m intervals away from them; GPS coordinates were obtained for each sample, and rainfall at that point was obtained from the online Hawaii Rainfall Atlas (Giambelluca and others 2012). For this analysis, we use only sites in upland slope positions in sites without clear evidence of erosion or deposition.

Soils were collected as a continuous sample from the surface to 30 cm on multiple transects across the rainfall gradient on Kohala Volcano, the oldest volcano on the Island of Hawaii. Here, we include 160 samples from across a rainfall range from 260 to 3,540 mm/y on the Hawi Volcanic Formation (substrate age \sim 150,000 y) (Spengler and Garcia 1988). In addition, we collected 33 integrated 30 cm samples

in upland slope positions across a rainfall gradient on the Island of Kauai (substrate age \sim 4,100,000 y), with a rainfall range from 600 to 3,760 mm/y. Five of the samples in the center of this gradient were near a canyon rim, and had evidence of erosion; we based our analysis on the other 28.

These 30 cm samples allow extensive spatial analyses, but exclude deeper soil properties and feedbacks between surface and subsurface processes. Accordingly, we drew upon information from complete soil profiles that had been characterized, sampled by horizon, and analyzed in 13 sites along the rainfall gradient on Hawi substrate (Chadwick and others 2003); soil pits were excavated to the depth of unweathered bedrock (about 1 m in low to moderate rainfall areas, but increasing to nearly 5 m at 2,500 mm rainfall), either by hand or using a backhoe in several sites (Porder and others 2007; Porder and Chadwick 2009). On Kauai, we sampled and characterized deep soil profiles in 6 sites along the rainfall gradient; soils were sampled from hand-excavated pits, supplemented by deeper sampling (to 4 m depth) with an auger, and in one case sampling to 17 m from a cliff face exposed by recent erosion. Soils on the dry extreme of the Hawi gradient classified as either Typic Haplotorrands or Sodic Haplocambids; soils of intermediate rainfall sites were Andic Haplustands, Humic Haplustands, and Pachic Haplustands, giving way to Hydric Fulvudands and ultimately Hydric Pachic Placudands and Alic Epiaquands in the wettest sites (Sato and others 1973, Chadwick and others 2003). Kauai soils ranged from Haplotorrox, Typic Eutrotorrox, and Tropeptic Haplustox in the driest sites through Haplustox and Plinthic Acrorthox to Typic Gibbsihumox and ultimately a Humic Epiaquept in the highest rainfall site (Foote 1972).

Soil Analyses

Soils were air-dried, passed through a 2 mm sieve, and divided into three homogenous subsamples. All of the 30 cm samples were analyzed as described in the supplemental material to Vitousek and others (2004). Briefly, one subsample was analyzed for resin-extractable phosphorus (P) and for total carbon (C) and nitrogen (N) at Stanford University; P was determined using the anion-exchange resin method of Kuo (1996) and analyzed on an Alpkem RFA/2 AutoAnalyzer, whereas total C and N were analyzed using a Carlo Erba NA 1500 elemental analyzer. A second subsample was analyzed for pH and cation exchange capacity (CEC) and exchangeable Ca, Mg, Na, and K at the

University of California, Santa Barbara, using the NH_4OAc method at pH 7.0 (Lavkulich 1981). We measured CEC buffered at pH 7 and used it in the calculation of base saturation as a way to standardize our measurements among mineralogically diverse soils. When CEC and effective cation exchange capacity (unbuffered ECEC) are compared along the Hawi climate gradient, CEC increases linearly with increasing rainfall whereas ECEC increases up to a point where soluble Al begins to outcompete the base cations for exchange sites (Chadwick and others 2003). By calculating base saturation using CEC, we assume that the inverse of % base saturation is % acid saturation, which is composed of Al^{3+} (and its divalent and monovalent counterparts) and H^+ (Ross and others 2008). The third subsample was shipped to ALS Chemex (Sparks, Nevada, USA) and analyzed for total concentrations of 11 elements (Si, Al, Fe, Ca, Mg, Na, K, Ti, P, Nb, Zr) using lithium borate fusion followed by X-ray fluorescence spectrometry. The depth profile samples were analyzed similarly, except that total N and resin P measurements were not made on all samples.

Calculations

We summarized results of horizon-based soil profile sampling on the Hawi substrate by calculating integrated element concentrations and other soil properties on a depth- and bulk density-weighted basis for the entire profile from the surface to the top of C horizon (generally hard rock or saprolite). No Kauai profiles (even the 17 m deep one) reached to the C horizon, accordingly we calculated integrated soil element concentrations and other properties on a depth-weighted basis to a consistent depth of 1.3 m—the shallowest profile sampled on Kauai.

Element concentrations alone can give a misleading picture of element mobility and loss, in that hydration and added organic matter in effect inflate the denominator of any concentration, whereas loss of more mobile elements reduces the denominator for concentrations of less-mobile elements. (The volume of soil can be altered similarly.) To correct for these changes, we used Nb as an index element to calculate the accumulation or loss of elements in soils. Although Zr is commonly used for this purpose elsewhere, earlier research demonstrated that Nb (with Ta) is the least mobile element in Hawaiian soils (Kurtz and others 2000). Accordingly, we calculated element gain or loss following Chadwick and others (1990) and Brimhall and others (1992), using

$$\text{ER}_x = 100 * (X_s/\text{Nb}_s)/(X_{\text{pm}}/\text{Nb}_{\text{pm}}),$$

where ER_x is the percentage of element X remaining in the soil, relative to its abundance in parent material; X_s and X_{pm} are the concentrations of element X in the soil and parent material, respectively, and Nb_s and Nb_{pm} are the concentrations of Nb in soil and parent material. We used the average of 12 rock samples to characterize parent material on Kohala (Chadwick and others 2003), and an average value for Hawaiian alkalic basalt for Kauai (Chadwick and others 1999).

One challenge with this approach is that it can be difficult to define the composition of the parent material, because soil material can be derived from a mixture of sources in addition to the underlying rock substrate. In Hawaii, this additional material can include volcanic tephra from younger eruptions in the archipelago, the deposition of material that was eroded nearby by water or especially wind, and the long-distance transport of dust from continental sources (Kurtz and others 2001). Tephra from other volcanoes or eruptive phases is likely to be most important as a source of variation in parent material on a volcanic archipelago, while the eolian deposition of material from very different sources is much greater in most continental situations than it is in Hawaii (Simonson 1995). The relative contribution of these sources can vary at different positions on a single rainfall gradient. We estimated the contribution of two distinct eruptive phases and continental dust to surface soils on the Hawi gradient to illustrate the challenges involved (Electronic supplementary material); the strong and well-characterized distinction between the widespread alkalic Hawi Formation and tholeiitic Pololu Formation substrates on Kohala Volcano (Spengler and Garcia 1988; Wolfe and Morris 1996) makes this calculation feasible. A similar calculation for the parent material underlying the Kauai gradient would be less easy to justify. Accordingly, we focus on soil properties rather than provenance here, although we make use of calculations of elements remaining from parent material where they are useful, and we discuss the likely significance of mixed parent materials as appropriate.

RESULTS

We consider multiple soil properties in this analysis, including: (1) concentrations of the abundant elements Al, Fe, and Si, which together make up nearly 80% of the initial parent material (when

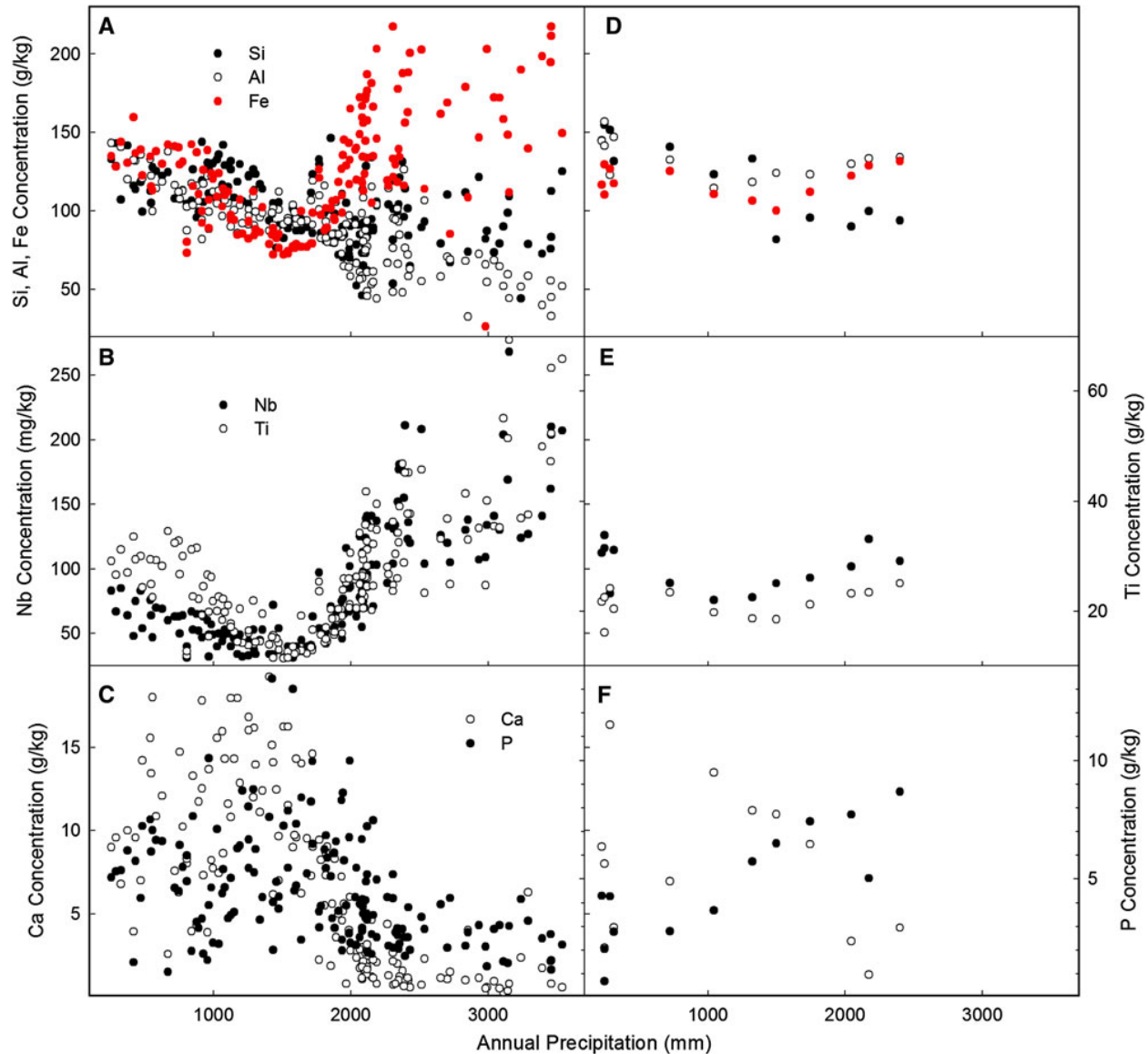


Figure 1. Concentrations of rock-derived elements in soils on 150,000-year-old Hawi substrate. **A** Concentrations of the abundant elements Si, Al, and Fe in the surface 30 cm of soil. **B** Concentrations of the relatively immobile elements Nb and Ti in surface soil. **C** Concentrations of the biological nutrients Ca and P in surface soil. **D** Concentrations of Si, Al, and Fe calculated on a depth- and bulk density-integrated basis from the surface to the top of the C horizon. **E** Nb and Ti from surface to C. **F** Ca and P concentrations from surface to C.

calculated as oxides); (2) concentrations of the immobile elements Nb and Ti; (3) concentrations of the biological nutrients Ca and P, to illustrate the dynamics of relatively mobile and relatively immobile biologically essential elements, respectively; and (4) a set of more dynamic measures of soil properties relating to soil fertility and nutrient availability, including pH, base saturation, resin-extractable P, the ratio of exchangeable Ca to exchangeable Na, soil C, and C:N ratio. We report

soil properties from the surface 30 cm, and compare these surface properties with integrated values from the surface to the top of the C horizon for the Hawi gradient, or to 1.3 m depth for Kauai.

Kohala-Hawi Rainfall Gradient

Concentrations of the rock-derived elements Si, Al, Fe, Ti, Nb, Ca, and P across the Hawi rainfall gradient are summarized in Figure 1; the panels to the

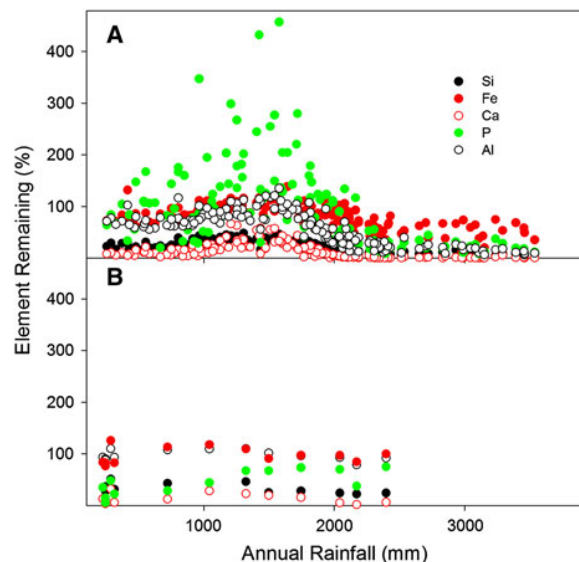


Figure 2. Elements in the upper 30 cm of soil (**A**) and integrated from the surface to top of the C horizon (**B**) as a percentage of the quantity of each element in parent material, for sites on the Hawi rainfall gradient. Calculated as described in the text, using Nb as an immobile index element and the mixture of parent material described in the electronic supplementary material.

left show results for the upper 30 cm of soil from 160 sites (Palmer and others 2009; Kagawa and Vitousek 2012), whereas the panels to the right show results integrated from the surface to the top of the C horizon from 13 deep soil pits along the gradient (Chadwick and others 2003; Porder and Chadwick 2009). Concentrations of Si, Al, and Fe in surface soils decrease with increasing rainfall from the driest sites to approximately 1,700 mm/y; thereafter, Fe concentrations increase whereas Si and Al concentrations continue to decline, sharply so for Al in the interval from 1,700 to 2,100 mm (Figure 1A). Correcting for changes in soil mass and volume using Nb as an index element, there is net loss of Fe as well as Si and Al from surface soils above 1,700 mm annual rainfall (Figure 2A); the increased Fe concentration there (Figure 1A) reflects loss of Al (and other mobile elements) rather than any absolute gain in Fe. Concentrations of the immobile elements Nb and Ti initially decline from dry sites to around 1,500 mm/y, reflecting dilution by hydration of soil minerals and increasing soil organic matter concentrations. Above 1,500 mm/y, Nb and Ti concentrations increase substantially, reflecting the loss of more mobile elements in these sites (Figure 1B). The relatively greater concentrations of Ti compared to Nb in drier sites (Figure 1B) reflect an admixture of tholeiitic Pololu substrate

there, as illustrated in Figure S1 in Electronic supplementary material.

Concentrations of the biologically important elements Ca and P follow a different pattern. Both are intermediate in concentration in the driest sites, higher (and more variable) in concentration in intermediate rainfall sites, and low in concentration in the wettest sites (Figure 1C). This pattern is not an artifact of the accumulation or mobility of other elements; the overall pattern of enrichment at intermediate rainfall is similar when Ca and P are expressed in terms of the percentage of element remaining from parent material (Figure 2A). In fact, there is an absolute increase in P (relative to Nb, and so relative to parent material) in many surface soils in this intermediate rainfall zone.

The patterns of variation in multiple element concentrations in surface soils (to 30 cm depth) generally are not reflected in element concentrations integrated through soil profiles (Figure 1D–F), though there is a progressive decrease in Si and particularly Ca concentrations in profiles from wetter sites. Correcting for the gain or loss of other material using Nb as an index element, there has been little gain or loss of Al or Fe along the rainfall gradient from the profiles as a whole (Figure 2B); the differences observed in surface soils reflect within profile translocation of these elements rather than absolute loss. The more mobile elements Si and Ca—and surprisingly P—have been lost from the profiles, especially (for Si and Ca) in the wettest sites.

Enriched P in surface soils (Figures 1C, 2A) does not carry over to the profiles as a whole (Figures 1F, 2B), and observations of the depth distribution of P in soils show that it is depleted at intermediate depth as well as enriched at the surface soil in sites with intermediate rainfall (Figure 3), as Vitousek and others (2004) and Porder and Chadwick (2009) observed. This pattern of surface enrichment reflects biological uplift from deeper in the soil to the surface (Jobbagy and Jackson 2001), over the tens of thousands of years that these sites have been vegetated. Drier sites are either too unproductive to lift up much P, or any enriched layer has been removed by wind erosion; in wetter sites, intense leaching prevents the maintenance of an enriched surface layer.

More dynamic soil properties (pH, base saturation, exchangeable Ca, resin-extractable P, soil C and C:N ratios) also vary substantially in surface soils across the Hawi gradient (Figure 4). Base saturation and pH are variable but relatively high at low rainfall, decline (remarkably consistently in the case of base saturation) to about 2,100 mm/y, and then remain low to the wettest sites sampled (Figure 4A).

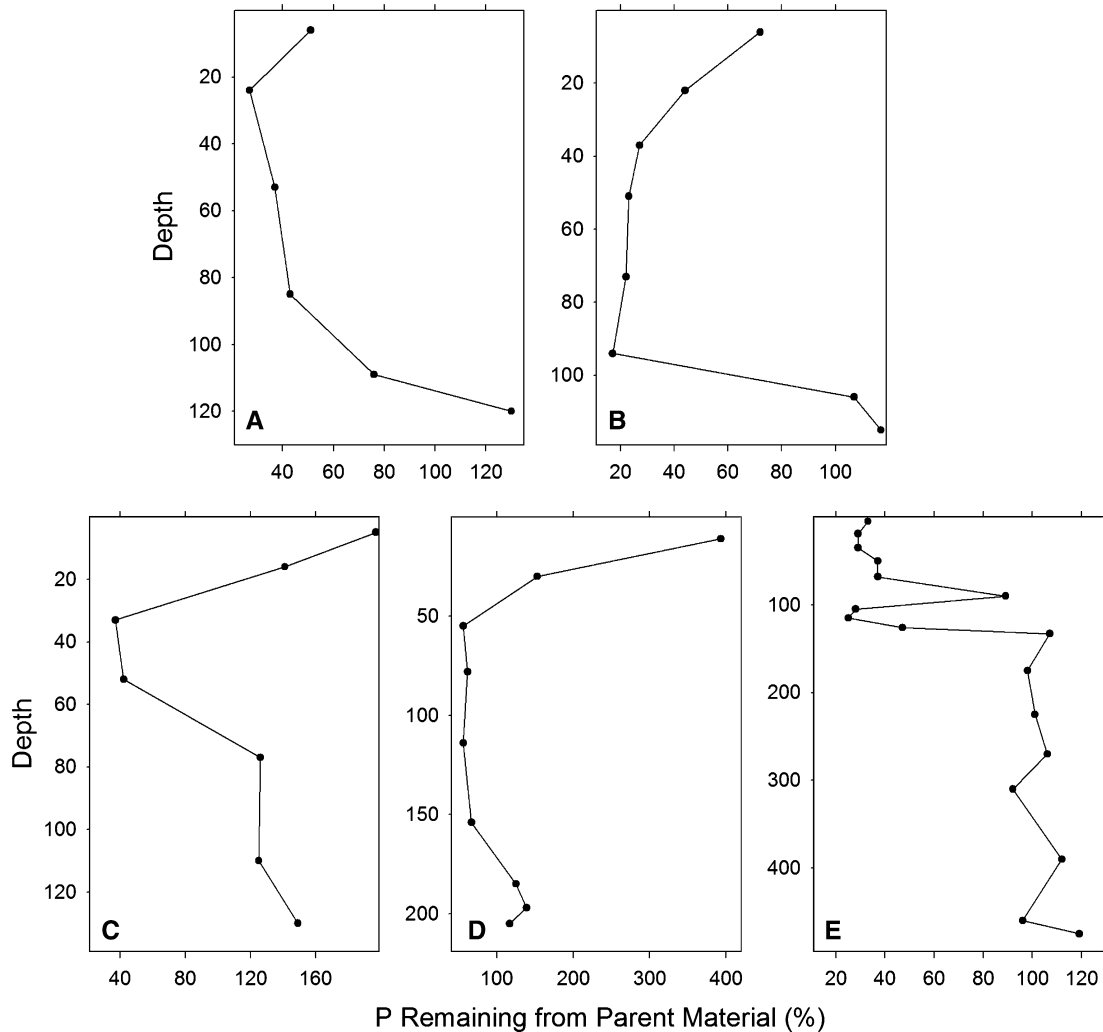


Figure 3. Depth profiles of the percentage of P remaining from parent material (calculated using Nb as an immobile index element) for 5 sites arrayed along the rainfall gradient on Hawi substrate. **A** 227 mm/y. **B** 722 mm/y. **C** 1,323 mm/y. **D** 1,745 mm/y. **E** 2,397 mm/y.

Resin-extractable P (an index of biologically available P) has a distinct hump-shaped pattern, with intermediate concentrations in surface soils in dry sites, variable but often extremely high concentrations in intermediate rainfall sites (with a peak near 1,200 mm/y), and very low concentrations in wetter sites (Figure 4B). The ratio of exchangeable Ca (which is strongly accumulated biologically) to exchangeable Na (which is not) also has a hump-shaped pattern along the rainfall gradient. Although Ca and Na are present in Hawi basalt at a ratio of 1.05 (by mass), and in marine aerosol at a ratio of less than 0.04, the ratio exchangeable Ca to exchangeable Na in the top 30 cm of soil is elevated substantially between 750 and 2,100 mm/y precipitation, peaking at an average >40 (by mass) near

1,200 mm/y precipitation (Figure 4B). These results reinforce the suggestion derived from overall Ca and P concentrations that there is a very strong signal of biological uplift—probably as a legacy of the seasonally dry forests that occupied these sites before humans arrived (Chadwick and others 2007)—that shapes P and Ca pools and biological availability in surface soils in this intermediate rainfall zone. Concentrations of C in surface soil increase consistently from 10 to over 100 g/kg up to about 1,700 mm/y precipitation; at higher rainfall and higher elevation, they average over 100 g/kg (but are highly variable) (Figure 4C). Soil C:N ratios are strikingly variable at low rainfall (from 4 to 16), and consistently around 12–13 in surface soils in wetter sites (Figure 4C).

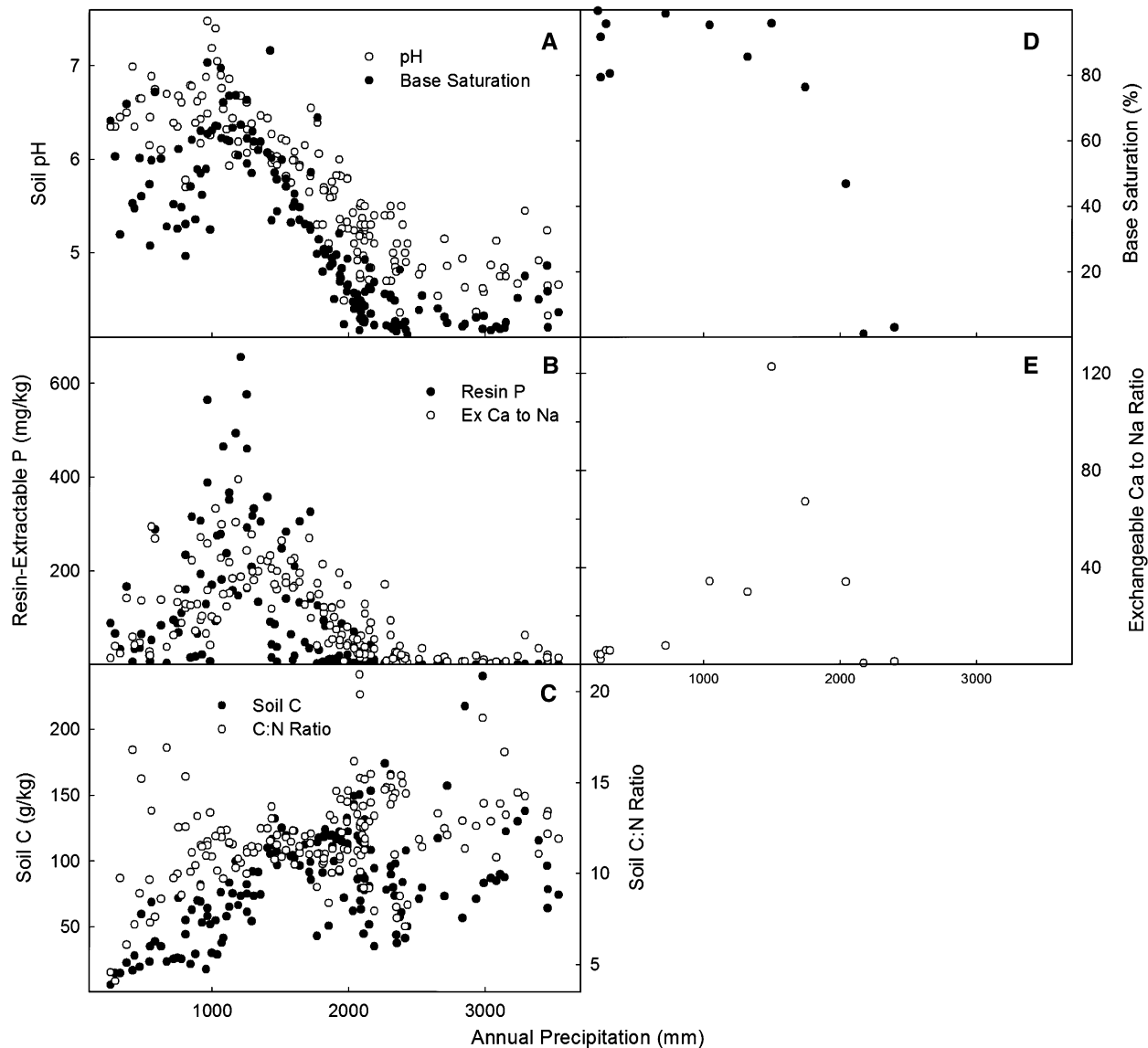


Figure 4. Selected soil properties on a rainfall gradient on 150,000-year-old Hawi substrate. **A** pH and base saturation in the surface 30 cm of soil. **B** Resin-extractable P and the ratio of exchangeable Ca to exchangeable Na in surface soil. **C** Soil C and C:N ratio in surface soils. **D** Base saturation integrated from the surface to the top of the C horizon. **E** Exchangeable Ca to Na, integrated from the surface to the top of the C horizon.

Base saturation and exchangeable Ca:Na ratios vary similarly along the rainfall gradient in whole soil profiles (integrated from the surface to the top of the C horizon) as they do in the top 30 cm of soil. The transition for base saturation in whole profiles is sharper than that in surface soils; base saturation decreases from close to 100% to near zero by 2,100 mm/y, whereas exchangeable Ca:Na ratios are elevated to similar levels in the intermediate rainfall zone in both surface and profile samples (Figure 4D, E). The transition in base saturation represents the threshold described for this rainfall

gradient by Chadwick and others (2003), now shifted to a higher rainfall value because the new rainfall atlas for Hawaii (Giambelluca and others 2012) reports higher rainfall in this transition region than did the previous atlas (Giambelluca and others 1986) used by Chadwick and others (2003).

Kauai Rainfall Gradient

Concentrations of the rock-derived elements Si, Al, Fe, Ti, Nb, Ca, and P across the Kauai rainfall gradient are summarized in Figure 5; the panels to the

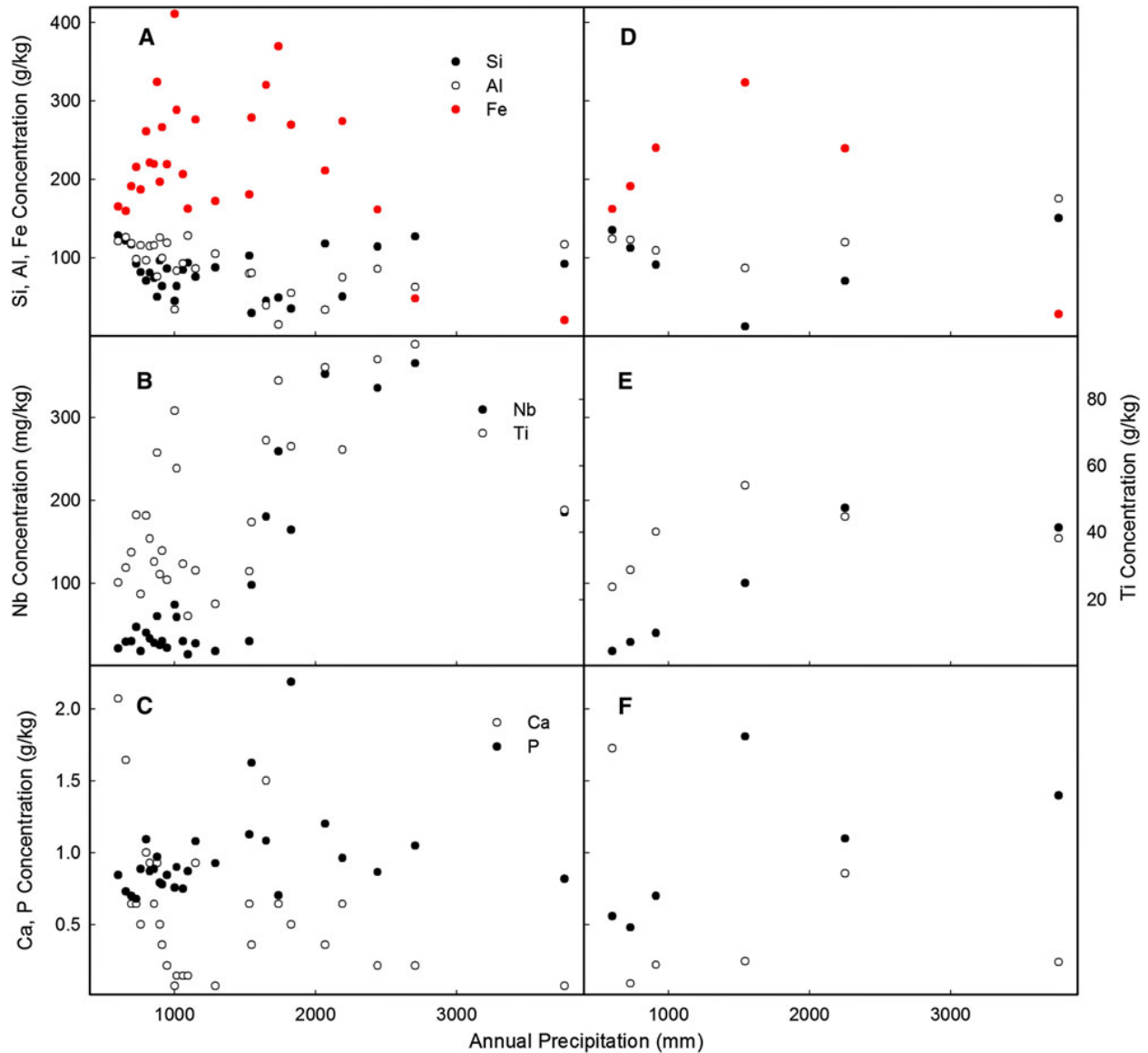


Figure 5. Concentrations of rock-derived elements in soils on approximately 4,100,000-year-old substrate on the Island of Kauai. **A** Concentrations of the abundant elements Si, Al, and Fe in the surface 30 cm of soil. **B** Concentrations of the relatively immobile elements Nb and Ti in surface soil. **C** Concentrations of the biological nutrients Ca and P in surface soil. **D** Concentrations of Si, Al, and Fe, integrated from the surface to around 1.3 m depth. **E** Concentrations of Nb and Ti, integrated from surface to 1.3 m. **F** Concentrations of Ca and P, integrated from surface to 1.3 m.

left show results from 28 samples of the top 30 cm of soil, whereas the panels to the right show results integrated from the surface to a depth of 1.3 m from 6 soil profiles along the gradient. Concentrations of Si in surface soil are relatively constant across the gradient, and substantially lower in the drier Kauai sites than the drier Hawi sites (Figures 5A, 1A). Concentrations of Al decline with increasing rainfall to around 2,500 mm/y, then increase slightly; concentrations of Fe are high in

most Kauai sites, higher than those along the Hawi gradient (Figures 5A, 1A). However, Fe drops to very low concentrations in the wettest Kauai site. The increase in Al concentration in wetter sites occurs because the loss of Fe leads to residual enrichment of Al. Concentrations of the relatively immobile elements Nb and Ti increase markedly in higher rainfall surface soils (Figure 5B), reflecting residual enrichment associated with the loss of most other elements.

Concentrations of Ca are highest in the two driest Kauai sites, and then decline to very low concentrations—but even the highest Ca concentrations on Kauai are little more than a tenth of those on the younger Hawi substrates (Figures 5C, 1C). Concentrations of P are relatively constant across the Kauai gradient and again substantially lower on the Kauai than the Hawi gradient (Figures 5C, 1C). The fraction of Ca and P remaining from parent material (Figure 6A) also is substantially less on Kauai than on Hawi substrates, at all rainfall levels along the gradient.

The concentrations of most elements integrated from the soil surface to 1.3 m depth vary substantially (if often not linearly) across the Kauai gradient (Figure 5D–F); in contrast to the Hawi gradient (Figure 1D–F), many of the changes along the Kauai gradient represent loss from the soil profile rather than translocation within it. In particular, concentrations of Fe are enriched in intermediate rainfall sites, reflecting residual enrichment from the whole-profile loss of Al and Si; in the wettest site, Fe is mobilized and lost from the profile as a whole, causing a relative enrichment in Al and Si (compared to intermediate rainfall sites) (Figure 5D). In both cases, there is an absolute loss of elements (in comparison to their abundance in parent material, calculated using Nb as an index element) moving from drier to wetter sites (Figure 6B).

The element remaining calculation (Figure 6) yields the expected pattern of decreasing retention of multiple elements with increasing rainfall along the gradient—but the absolute values are too high for the less-mobile elements in some of the whole profiles from drier sites (Figure 6B), with values reaching over 200% for Al, Fe, and Ti. One possible explanation for the high values for less-mobile elements in the drier profiles is that the Kauai parent material represents a mixture of sources, as described for the Hawi gradient in the Electronic supplementary material. The initial parent material Nb concentration we use for Kauai—24 ppm—is appropriate for alkalic basalt, which certainly was produced in later phases of Kauai's eruptive history, and it appears to be about the right value for surface soils (Figure 6A), where later eruptions could have deposited alkalic tephra on older surfaces. However, the bulk of the profiles (at least in the dry sites) may represent tholeiitic basalt from an earlier eruptive phase. Tholeiitic basalt typically has Nb concentrations near 10 ppm; using this value for parent material Nb would yield near the expected value of 100% retention of less-mobile elements in the driest Kauai sites.

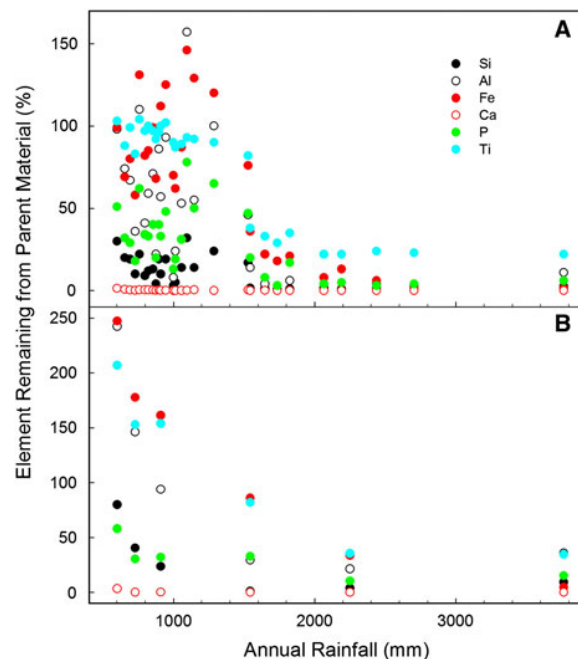


Figure 6. The percentage of elements remaining from parent material across the Kauai rainfall gradient, calculated using Nb as an immobile index element. **A** Elements remaining in the top 30 cm of the soil profile. **B** Elements remaining to a depth of 1.3 m.

More dynamic soil properties (pH, base saturation, exchangeable Ca, resin-extractable P, soil C, and C:N ratios) across the Kauai gradient are summarized in Figure 7. All of these properties vary substantially in surface soils. Base saturation and pH are relatively high in the driest sites; base saturation declines rapidly to around 10% around 900 mm/y precipitation and pH declines below 4.5 by around 1,500 mm/y (Figure 7A). These declines occur at lower rainfall than do comparable declines on Hawi substrate (Figure 4A). The ratio of exchangeable Ca to exchangeable Na varies similarly to base saturation, reaching very low levels at rainfall greater than 900 mm (Figure 7B). Resin P concentrations are much lower everywhere on the Kauai gradient than on the Hawi gradient (peak concentrations < 2 mg/kg on Kauai versus > 500 mg/kg on Hawi substrate—Figure 7B, 4B). Soil C concentrations vary across a similar range and in a similar pattern on the Kauai and Hawi gradients, although the wettest Kauai site has a higher soil C concentration than any Kohala site (Figures 7C, 4C). However, soil C:N ratios are higher in surface soils on Kauai, especially in the wetter sites—reaching a surprisingly high ratio of 55 in the wettest site (Figures 7C, 4C). Neither base saturation nor the exchangeable Ca:Na ratio varies

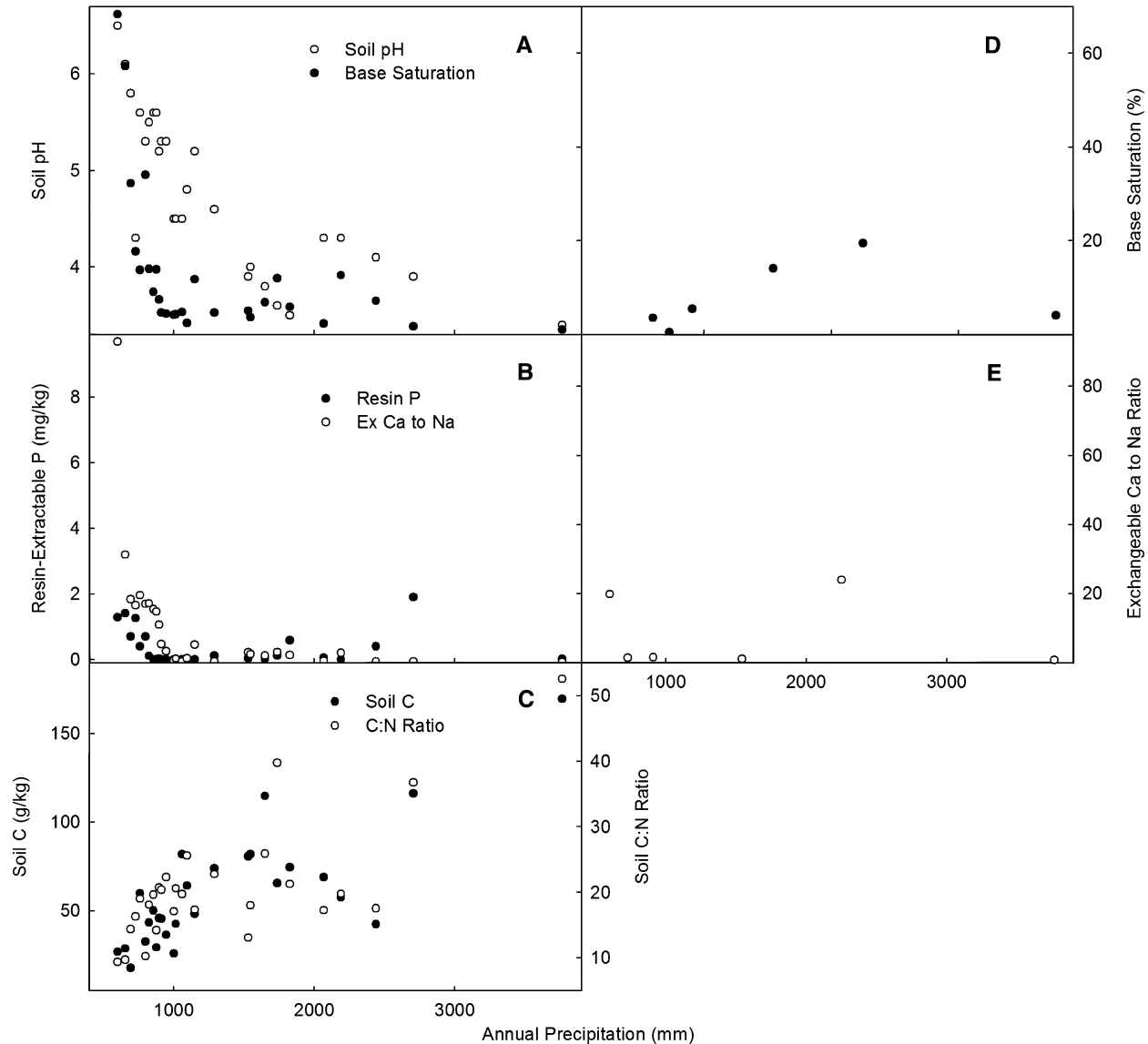


Figure 7. Selected soil properties on a rainfall gradient on 4,100,000-year-old substrate on the Island of Kauai. **A** pH and base saturation in the surface 30 cm of soil. **B** Resin-extractable P and the ratio of exchangeable Ca to exchangeable Na in surface soil. **C** Soil C and C:N ratio in surface soils. **D** pH and base saturation integrated to around 1.3 m depth. **E** Ratio of exchangeable Ca:Na integrated to 1.3 m depth.

substantially across the Kauai gradient, when integrated through full soil profiles (Figure 7D, E).

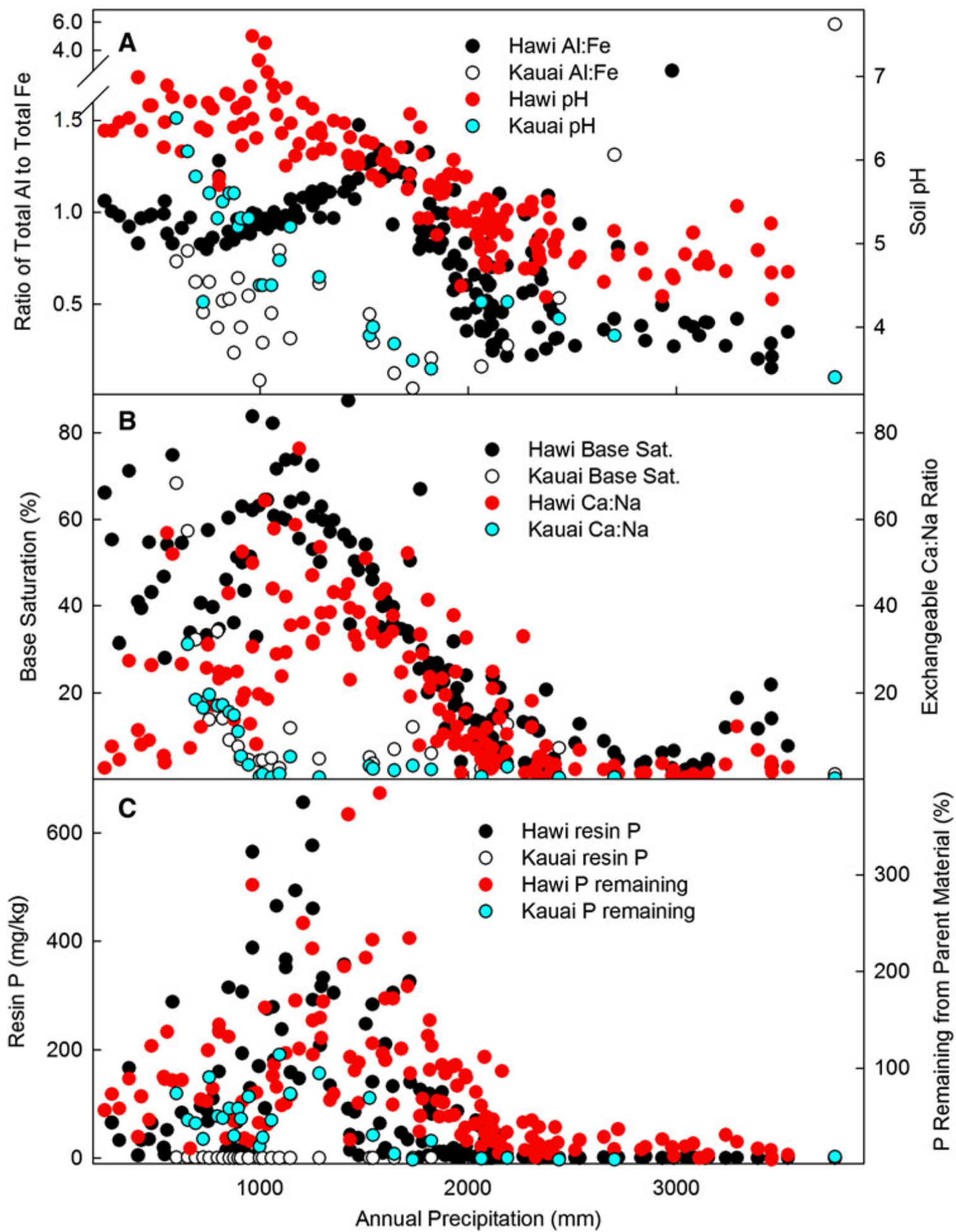
DISCUSSION

In Figure 8, we compare several characteristics of surface soils that change informatively along both rainfall gradients, including: (i) the ratio of total Al to total Fe; (ii) pH; (iii) base saturation; (iv) the ratio of exchangeable Ca to exchangeable Na; (v) resin-extractable P; and (vi) the proportion of P

remaining from parent material. These characteristics are useful in determining the distribution and importance of pedogenic thresholds along these gradients, in evaluating the properties of any soil process domains between thresholds, and in discussing the implications of pedogenic thresholds and soil process domains.

Pedogenic Thresholds

The ratio of total Al to total Fe in soils changes abruptly at multiple points along both gradients.



around 1,700 mm/y represents the beginning of this transition; above 1,700 mm/y Al mobility increases rapidly as the pH falls below 6. Another consistent threshold occurs around 700 mm/y, where the imprint of biological uplift becomes evident.

A pedogenic threshold comparable to the one at 2,100 mm/y on Hawi substrate occurs near 900 mm/y rainfall on the much older Kauai substrate. Base saturation and the ratios of total Al to total Fe and exchangeable Ca to exchangeable Na all are elevated in the driest sites but reach low levels by 900 mm/y (Figure 8A, B). Because the minimum rainfall across the Kauai gradient is fairly high (600 mm/y), we cannot detect any thresholds below 900 mm/y. However, a new pedogenic threshold emerges at higher rainfall (~2,500 mm/y) on Kauai, where the Al:Fe ratio increases substantially—ultimately reaching a very high value around 6 at the wettest extreme of the Kauai gradient (versus <0.5 between 900 and 2,200 mm/y on Kauai, and between 2,100 and 3,500 mm/y on Hawi substrate) (Figure 8A). This threshold also occurred along a rainfall gradient on 420,000-year-old substrate on the Island of Maui, Hawaii (Chadwick and Chorover 2001; Miller and others 2001), where the Al:Fe ratio began to increase detectably at around 3,500 mm/y, and reached greater than 4 near 5,000 mm/y. This threshold reflects the onset of anaerobiosis leading to iron reduction and the loss of ferrous iron from soil profiles in wet, poorly drained soils (Thompson and others 2006a, b, 2007).

Soil Process Domains

The pedogenic thresholds we recognize on the Hawi and Kauai rainfall gradients, and the soil process domains that they bound, are summarized in Figure 9. Mineral weathering and (on shorter time scales) cation exchange buffer atmospheric and biological acidity in the domain between 700 and 2,100 mm/y rainfall on the Hawi gradient, and biological uplift of elements from deeper in the soil profile enriches the quantity and availability of nutrients in surface soils (Figure 8). Soil properties are not constant within this domain—pH and base saturation decline in the higher rainfall portion, and biological uplift has its greatest influence in the middle—but the same processes are important across it. Near the upper-rainfall edge of this domain, above 1,700 mm/y, Al mobilization and translocation becomes important (Figure 8A); we could recognize the region from 1,700 to 2,100 mm/y as a narrow domain of its own, or as

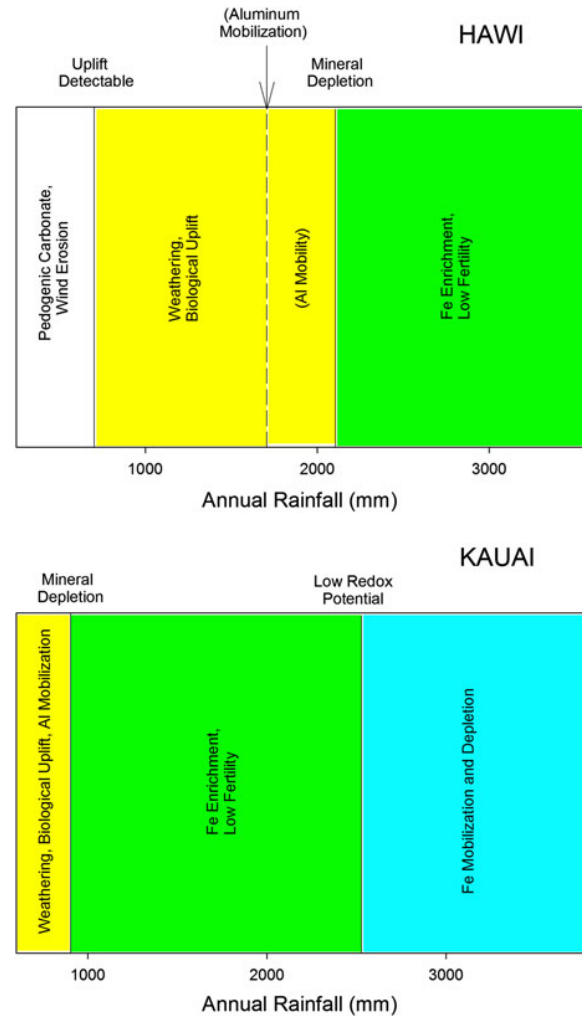


Figure 9. Distribution of pedogenic thresholds (labeled above each figure) and soil process domains (color coded and labeled within each figure) along the Hawi (*top*) and Kauai rainfall gradients.

we prefer a fairly narrow threshold region separating two domains.

In the domain above 2,100 mm/y, we see little systematic change in surface soils to the highest rainfall sampled (~3,500 mm/y). Most major element concentrations are low, and Fe and organic matter dominate the upper 30 cm of soil. Although concentrations of refractory elements are relatively constant in this domain, weathering is ongoing at depth and weathering profiles represent the residuum of a greater quantity of parent material in the wetter sites (Figure 1B). Primary minerals have been depleted; neither mineral weathering nor base saturation can buffer atmospheric and biological acidity in the surface soil (or indeed in the top meter of the profile—Chadwick and others

2003). Although substantial Al has been lost from surface soils, the remaining Al is reactive and Al chemistry provides the major buffer system (Chadwick and Chorover 2001).

Soils in the domain below 700 mm/y on Hawi substrate contain pedogenic carbonate (caliche) (Chadwick and others 2003), and carbonate chemistry represents the major buffering system for atmospheric and biological acidity there. However, these soils are variable in multiple properties compared to wetter sites (Figure 1A–C). Low rainfall leads to lower plant productivity and sparser vegetation cover in this area, and historic grazing (and possibly frequent burning of this zone by Polynesians—Handy and others 1972) has produced large areas of bare soil. Although biological uplift should be less important in low productivity sites—and its imprint is not detectable in this domain—it is striking that in many places the upper 30 cm of soil is depleted in biological nutrients (including relatively immobile P) compared to parent material, and compared to slightly wetter soils. A consistent explanation for both variability and depletion in this domain is wind erosion of surface soils that once held an imprint of biological uplift. Wind erosion is inherently variable both spatially and temporally, depending on fine scale topography and residual plant cover. Low rates of uplift in these unproductive sites could have produced a thin surface zone of enriched soil—and when that soil blew away, the exposed subsoil was depleted in biological nutrients. Those dynamics are consistent with analyses of silicon isotopes in these soils (Bern and others 2010) and the depth profiles for P in Figure 3.

The two pedogenic thresholds we observed on the Kauai gradient also delineate three soil process domains (Figure 9). The domain from 900 to 2,500 mm/y on Kauai is analogous to the domain from 2,100 to 3,500 mm/y on the Hawi gradient, in that surface soils are rich in Fe, atmospheric and biological acidity is buffered by reactive Al, base saturation is low, and biological nutrients are in short supply. Kauai soils in this domain are not identical to those on the Hawi gradient; they are richer in Fe, and the much greater age of the Kauai substrate has allowed clay minerals to “ripen” to halloysite and goethite rather than nanocrystalline allophane and ferrihydrite (Chorover and others 1999, 2004). As a consequence, the Kauai soils in this domain classify as Oxisols (Foote 1972), rather than the much more chemically reactive Andisols found on the Hawi substrate. Nevertheless, the Kauai and Hawi soils are comparable in their low nutrient availability and in the minimal influence

of ongoing primary mineral weathering and biological uplift.

The Kauai domain with rainfall above 2,500 mm/y is sparsely represented in our sample—just one site at 3,760 mm/y expresses it fully, though the next-wettest sites at 2,700 and even 2,430 mm/y have some similar features (Figure 8). However, soils in this domain were characterized reasonably well in an earlier study on the Island of Maui (Miller and others 2001; Chadwick and Chorover 2001; Thompson and others 2006a, 2007, 2011). Soils on both Maui and Kauai are frequently water-saturated and have low redox potentials; Fe is reduced and mobilized from at least the surface 1.3 m of soil (Figures 5, 8), and soils are rich in organic matter that has a remarkably high C:N ratio (55 in the wet site on Kauai) (Figure 7C). The high C:N ratios could reflect inefficient decomposition in these saturated soils (Schuur and others 2001), along with rapid denitrification of any nitrate produced (Houlton and others 2006)—together leading to low biological N availability. At the same time, Fe reduction mobilizes P from complexation with ferric iron, leading to increased P availability but also increased losses of P (Miller and others 2001; Chacon and others 2006). No analogous domain exists in our sample of the Hawi rainfall gradient, although we believe that similar processes occur in wetter sites beyond the range of our sampling (Sato and others 1973).

Kauai soils that receive less than 900 mm/y are analogous to those between 1,700 and 2,100 mm/y on the Hawi rainfall gradient (Figure 9); pH, base saturation, and the ratio of exchangeable Ca to Na decline rapidly with increasing rainfall to low values at about 900 mm/y, and Al is being mobilized from the surface 30 cm of soil. These soils are nutrient-rich relative to the wetter Kauai sites, and they display some influence of primary mineral weathering and biological uplift; however, they differ from those on the Hawi gradient in that resin-extractable P remains relatively low throughout the Kauai gradient (Figure 8C). In part, low P availability reflects a progressive occlusion and loss of P with increasing age (Crews and others 1995; Vitousek 2004); also P is elevated in Hawi parent material compared with most Hawaiian basalts (Spengler and Garcia 1988; Porder and Chadwick 2009).

We raise two cautions about soil process domains as we have interpreted them here. First, we describe domains along rainfall gradients, in situations where pedogenic thresholds and the soil process domains that they bound can be identified relatively straightforwardly. However, soils that fit into these domains can develop by other pathways.

For example, erosion and deposition on slopes can bring little-weathered primary minerals into surface soil on old substrates (Vitousek and others 2003); on Hawi substrate, that process yields patches of fertile soil well supplied with rock-derived nutrients (Porder and others 2005) within what would otherwise (on the basis of rainfall alone) represent a domain of infertile, iron-enriched soils. Biological processes also influence soil process domains; we have observed Fe mobilization in sites receiving about 3,500 mm/y on Hawi substrate where *Sphagnum* moss dominates the understory. The very high water-holding capacity of *Sphagnum* and the peat it produces can drive positive feedbacks toward water-saturated, low redox conditions that may move soils into a different domain (van Breemen 1995).

Second, soils reflect past as well as present environmental conditions. Here, we show that analogous pedogenic thresholds and soil process domains are shifted to lower rainfall on the much older Kauai substrate. This shift could represent a gradual accumulation of the influences of weathering and leaching leading to changing process domain boundaries over the long history of these sites. However, this shift also could be a consequence of past conditions when rainfall was greater in the low-rainfall Kauai sites. The interaction between northeast trade winds and mountain topography has kept the leeward southwest end of the gradients relatively dry for a very long time, and Hotchkiss and others (2000) concluded that for most of the Pleistocene, rainfall has been lower than at present across both rainfall gradients. However, the history of Kauai reaches back before the Pleistocene, and we can only guess its climate during its first million years of soil development, more than 3 million years ago. It is possible that the distribution of pedogenic thresholds and soil process domains on Kauai reflects in part a legacy of a very different Pliocene climate, as well as a varying Pleistocene climate and the modern climate.

Implications

We focus here on one implication of soil process domains—their connection with indigenous agriculture. Initially, surface 30 cm soils on the Hawi gradient were analyzed to provide context and potential constraints for an intensive rainfed Hawaiian agricultural system that occupied part of the area prior to European contact (Ladefoged and Graves 2000; Vitousek and others 2004; Palmer and others 2009). We now see that this indigenous

system occupied the whole of the domain of weathering and biological uplift (Figure 9) on the Hawi substrate, with its low-rainfall boundary around 700 mm/y and its high-rainfall boundary around 2,100 mm/y (using the new rainfall values in Giambelluca and others 2012). No such system occurred on Kauai (Ladefoged and others 2009), because over time the entire weathering/uplift domain has shifted to much drier conditions and to lower nutrient availability on the much older Kauai substrate. We suggest that the potential for development of large, intensive rainfed agricultural systems—and the social and cultural features that accompanied them (Kirch 1994, 2012; Ladefoged and others 2009)—was tied to the distribution of the weathering/biological uplift domain. As described above, it is also possible for erosion and deposition to move soils into the weathering/uplift domain (Porder and others 2005), and Vitousek and others (2010) showed that strips of valley-side colluvial soils on old substrates that were intensively farmed by Polynesian cultivators had properties that place them within this domain, although nearby upland soils fall into the domain of low fertility and Fe enrichment (and did not support intensive Polynesian agriculture). We suggest that this association of soil fertility (in the sense of relative feasibility of rainfed agricultural intensification) with the domain of weathering and biological uplift probably extends to volcanic soils beyond the Hawaiian Archipelago; we speculate that it could extend to parent materials beyond basalt-derived soils.

In addition to indigenous agriculture, soils in this domain likely also supplied high levels of nutrients to the mesic and seasonally dry tropical forests that occupied these sites before Hawaiian cultivation (Chadwick and others 2007), as they do to the intensively managed ranches that utilize the area now. All of these communities and land uses were influenced by the soils of this domain, and all influenced those soils. Other soil process domains likely have their own broader implications for and interactions with human and ecological systems.

ACKNOWLEDGMENTS

We thank Emmanuel Frossard and Dan Richter for insightful comments on an earlier draft of this manuscript, and the Kauai Division of Forestry and Wildlife and Kohala landowners for access to field sites. This research was supported by NSF Grants ETBC-1020791 and ETBC-1019640.

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