Changes in Soil Phosphorus Fractions and Ecosystem Dynamics across a Long Chronosequence in Hawaii

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CHANGES IN SOIL PHOSPHORUS FRACTIONS AND ECOSYSTEM DYNAMICS ACROSS A LONG CHRONOSEQUENCE IN HAWAII[1]

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Abstract. We tested the Walker and Syers (1976) conceptual model of soil development and its ecological implications by analyzing changes in soil P, vegetation, and other ecosystem properties on a soil chronosequence with six sites ranging in age from 300 yr to 4.1×10^6 yr. Climate, dominant vegetation, slope, and parent material of all of the sites were similar. As fractions of total P, the various pools of soil phosphorus behaved very much as predicted by Walker and Syers. HCl-extractable P (presumably primary mineral phosphates) comprised 82% of total P at the 300-yr-old site, and then decreased to 1% at the 20,000-yr-old site. Organic phosphorus increased from the youngest site to a maximum at the 150 000 yr site, and then declined to the 4.1 $\times 10^6$ yr site. Occluded (residual) P increased steadily with soil age. In contrast to the Walker and Syers model, we found the highest total P at the 150 000-yr-old site, rather than at the onset of soil development, and we found that the non-occluded, inorganic P fraction persisted through to the oldest chronosequence site. Total soil N and C increased substantially from early to middle soil development in parallel with organic P, and then declined through to the oldest site.

Readily available soil P, NH_4^+, and NO_3^- were measured using anion and cation exchange resin bags. P availability increased and decreased unimodally across the chronosequence. NH_4^+ and NO_3^- pools increased through early soil development, but did not systematically decline late in soil development.

In situ decomposition rates of *Metrosideros polymorpha* litter were highest at two intermediate-aged sites with high soil fertility (20 000 yr and 150 000 yr), and lowest at the less-fertile beginning (300 yr) and endpoint (4.1×10^6 yr) of the chronosequence. *M. polymorpha* leaves collected from these same four sites, and decomposed in a common site, suggested that leaves from intermediate-aged sites were inherently more decomposable than those from the youngest and oldest sites. Both litter tissue quality and the soil environment appeared to influence rates of decomposition directly.

The highest mean soil N_2O emissions (809 $\mu g \cdot m^{-2} \cdot d^{-1}$) were measured at the 20 000-yr-old site, which also had the highest soil nitrogen fertility status.

Plant communities at all six chronosequence sites were dominated primarily by *M. polymorpha,* and to a lesser extent by several other genera of trees and shrubs. There were, however, differences in overall vegetation community composition among the sites. Using a detrended correspondence analysis (DECORANA), we found that a high proportion of species variance among the sites (eigenvalue = 0.71) can be explained by site age and thus soil developmental stage.

Overall, long-term soil development across the chronosequence largely coincides with the conceptual model of Walker and Syers (1976). How P is distributed among different organic and inorganic fractions at a given stage of soil development provides a useful context for evaluating contemporary cycling of P and other nutrients, and for determining how changes in P availability might affect diverse ecosystem processes.

Key words: decomposition; Hawaii; Metrosideros polymorpha; *nitrogen; nitrous oxide; phosphorus; soil development; vegetation.*
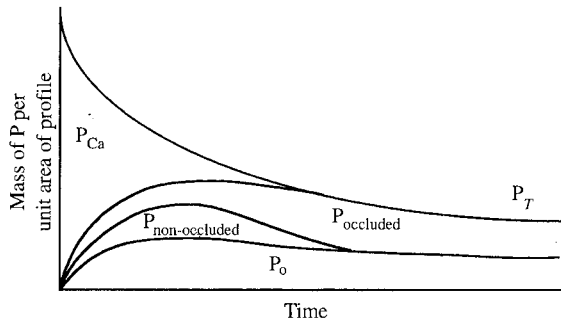
FIG. 1. Walker and Syers' (1976) diagram of P transformations with time. P_{Ca} = calcium phosphates, P_T = total phosphorus, P_o = P bound to organic matter.

INTRODUCTION

Walker and Syers (1976) put forth a model of soil phosphorus transformations during soil development that provides a useful starting point for investigating P dynamics and C–N–P interactions at different stages in soil development (Fig. 1). The model suggests that all soil P is in the primary mineral form (mainly as calcium apatite minerals) at the beginning of soil development, which also coincides with the onset of primary succession. With time, the primary mineral-P slowly dissolves and is either taken up by organisms, thus entering the organic-phosphorus (P_o) pool, or is sorbed onto secondary mineral surfaces (Tiessen and Stewart 1985). This sorbed inorganic P (termed "non-occluded P" by Walker and Syers) remains labile for a period of time and can be desorbed in response to a diffusion gradient around a plant root or microbe (Mattingly 1975). Sorbed P that is not taken up by organisms eventually can become surrounded or occluded by Fe or Al hydrous oxides, or allophane (an amorphous alumino-silicate) in the case of certain young volcanic ash soils, rendering the P largely unavailable to the biota (Uehara and Gillman 1981, Nanzyo et al. 1993). The opportunities for occlusion of inorganic P increase greatly later in soil development as secondary silicate minerals dissolve, giving way to Fe and Al oxides that have a strong affinity for P (Fox et al. 1991). Phosphorus taken up by organisms (P_o) may be cycled back to the inorganic soil pool, or may become incorporated into chemically recalcitrant decomposition products (also P_o) that remove P from biotic cycling for long periods.

The Walker and Syers model of P transformations through time has provided a powerful theoretical context for evaluating the dominant soil processes controlling P cycling during particular stages of pedogenesis (Singleton and Lavkulich 1987, Lajtha and Schlesinger 1988, Birkeland et al. 1989, Walker 1989, Chapin et al. 1994). The model has also contributed to ecosystem theory regarding C, N, P, and S interactions during ecosystem development (McGill and Cole 1981,

Tate and Salcedo 1988). However, testing the model itself, and its ecosystem-level implications, has not been straightforward due to the difficulty of finding sites that form an unambiguous chronosequence that includes very distinct stages of pedogenesis (Yaalon 1975).

The Hawaiian islands provide an exceptional chronosequence for evaluating soil P transformations with time, and relationships between soil P and contemporary ecosystem processes. In this study we addressed the following questions: Do changes in soil P fractions as well as total N and C across a broad chronosequence agree with predictions made by the Walker and Syers model? Is phosphorus availability to the biota at its lowest early in soil development, when the majority of soil P is held in apatite minerals, and late in soil development, when most phosphorus is irreversibly bound to sesquioxides (sensu Walker and Syers 1976)? Does biologically available N roughly track available P dynamics as would be expected if biologically available P regulates N accumulation and transformation rates (Cole and Heil 1981, Vitousek and Howarth 1991)? Do decomposition rates respond to variation in site fertility across the chronosequence, resulting in feedbacks that could intensify or relax nutrient limitation (Vitousek 1982)? Does soil nitrous oxide flux correspond to N availability at different stages of soil development (Robertson and Tiedje 1984)? Does variation in forest stature and plant species composition from site to site correspond to changes in soil properties associated with pedogenesis (Mueller-Dombois 1986)?

THE CHRONOSEQUENCE

The Hawaiian archipelago is well suited for chronosequence studies because of how it was formed (Sherman and Ikawa 1968). Basaltic magma has erupted from a stationary convective plume or "hotspot" in the mantle for millions of years, creating large volcanic islands. With the northwest movement of the Pacific Plate, volcanoes are carried away from the hotspot and become inactive, while new volcanoes are formed in their place (Moore and Clague 1992). While the ages of the Hawaiian volcanoes vary continuously from presently active (the island of Hawaii), to $>4 \times 10^6$ yr (the island of Kauai), parent material composition has remained relatively constant reflecting the convective plume of mantle material (Clague and Dalrymple 1987). By matching elevation, precipitation, slope position, and disturbance history it is possible to put together a sequence of sites that varies mainly in soil age.

The chronosequence we used consisted of a total of six sites, all located in montane rainforest on the islands of Hawaii, Molokai, and Kauai (Fig. 2, Table 1). The six sites were Thurston (300 yr old), Olaa (2100 yr), Laupahoehoe (20 000 yr), Kohala (150 000 yr), Kolekole (1.4×10^6 yr), and Kokee (4.1×10^6 yr). It was
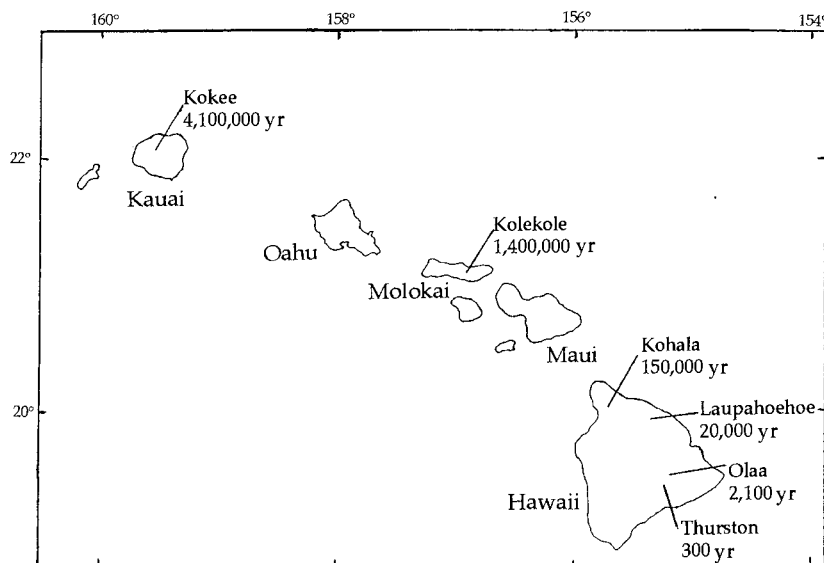
FIG. 2. Locations and ages of the six chronosequence field sites in Hawaii.

not always possible to conduct all measurements at each of the six sites, so some components of our study involve four or five of the sites. Below we describe the soil chronosequence using Jenny's (1941) five state factors of soil formation: parent material, time, climate, organisms, and topography.

Parent material and time

Soils of the Hawaiian archipelago encompass an extremely broad range of developmental stages, but all were formed from basaltic tephra or lava flows. Although they are quite similar when compared with other parent materials, the Hawaiian lavas do vary chemically as a function of residence time in subsurface magma reservoirs (Wright and Helz 1987), cooling rates, and, most importantly, stage of volcanism. Shield-building lavas, which flow from young to middle-aged volcanoes, are generally uniform, tholeiitic basalts, rel-

atively high in silica (Macdonald et al. 1983, Clague and Dalrymple 1987). In older active volcanoes, shield building ceases and subsequent eruptions of post-shield lavas and tephra form caps over the younger tholeiitic basalt shields (Moore and Clague 1992). Post-shield lavas are generally enriched in K-, Na-, and P-bearing minerals such as hawaiite, mugearite, and trachyte (Macdonald et al. 1983).

Soils of the chronosequence sites were derived mostly from volcanic tephra as opposed to lava flows—with the possible exception of the oldest site, Kokee, where it is difficult to tell at such a late weathering stage. The two youngest chronosequence sites, Thurston and Olaa, have soils that were formed from tephra associated with the shield-building phase of the volcano Kilauea. Soils of the four older chronosequence sites were developed on parent material from post-shield volcanic activity (Clague and Dalrymple 1987).

TABLE 1. Hawaiian chronosequence: site descriptions.

Site	Parent material age (10^3 yr)	Elevation (m)	Approx. mean annual temp. (°C)	Approx. mean annual precip. (mm)	Soil classification	Location
Thurston	0.3	1176.	16	2500	Hydric Dystrandept	Hawaii Volcanoes National Park
Olaa	2.1	1200	16	2500	Typic Hydrandept	Hawaii Volcanoes National Park
Laupahoehoe	20	1170	16	2500	Typic Hydrandept	Laupahoehoe Forest Reserve
Kohala	150	1122	16	2500	Typic Placandept	Kohala Forest Reserve
Kolekole	1,400	1210	16	2500	Petroferric Acrohumox	Nature Conservancy Kamakou Preserve
Kokee	4,100	1134	16	2500	Plinthic Acrudox	Napali-Kona Forest Reserve

The youngest of our sites is near Thurston Lava Tube on Kilauea Volcano, within Hawaii Volcanoes National Park (Fig. 2). The Thurston soil is a Hydric Dystrandept (Soil Survey Staff 1973) developed on several tephra depositions ranging in age from 200 to 400 yr (J. Lockwood, *personal communnication*), totaling ≈38 cm in depth. We therefore consider this site to be ≈300 yr old from the standpoint of ecosystem development.

The next site on the soil chronosequence is located in the southwest corner of the Olaa Forest, which is also associated with Kilauea volcano within the boundaries of Hawaii Volcanoes National Park. This soil is a Typic Hydrandept (Soil Survey Staff 1973), developed in numerous tephra deposits that date back at least 2100 yr. A major tephra deposit 2100 yr BP (Dzurisin et al., *in press*) most likely marked the initiation of ecosystem development at the Olaa site.

The Laupahoehoe soil is also a Typic Hydrandept (Soil Survey Staff 1973) that developed in 10–30 000-yr-old tephra deposits from the Laupahoehoe Volcanics of Mauna Kea (D. Clague, *personal communication*). The tephra at this site is the youngest parent material on the chronosequence from a post-shield building stage. We consider ecosystem development to have begun at this site ≈20 000 yr BP.

The Kohala site soils are Typic Placandepts (Soil Survey Staff 1973) that were developed on tephra from Hawi Volcanics. Dates of four cinder cones in the vicinity of our site are 141, 152, 196, and 204 × 10³ yr BP (D. Clague, *unpublished data*). Assuming the last eruptions covered the surface with tephra, we estimate the age of the Kohala site to be ≈150 000 yr.

Soils of the Kolekole site on the island of Molokai are classified as Petroferric Acrohumoxes (Soil Survey Staff 1972); they developed in tephra from Pu'u Kolekole and possibly other vents of the Upper East Molokai Volcanics, roughly 1.35–1.49 × 10⁶ yr BP (Clague and Dalrymple 1987). We place the age of the Kolekole site parent material at ≈1.4 × 10⁶ yr.

Soils of the Kokee site are Plinthic Acrudoxes (Soil Survey Staff 1992) that developed on tephra and/or lava from the Olokele formation of the Waimea Canyon Volcanics roughly 3.9–4.2 × 10⁶ yr BP (D. Clague, *personal communication*). We place the age of the Kokee parent material at ≈4.1 × 10⁶ yr.

A potentially important source of exogenous secondary minerals to the older soils of the chronosequence is dust from Asia. The dust is transported in the atmosphere from Asia, particularly the desert and loess plateau regions of Central China, and deposited primarily in rainfall across the North Pacific (Merrill 1989). Jackson et al. (1971) reported accumulations of quartz and mica of continental provenance ranging from 0.2 to 45% in A horizons of older Hawaiian soils. Eolian dust inputs into highly weathered Hawaiian soils may constitute an important source of base cations and possibly P to ecosystems (Jackson et al. 1971, Fox et al. 1991).

Climate

We selected sites that have mean annual rainfall near 2500 mm (Giambelluca et al. 1986). The majority of this precipitation is well distributed throughout the year, as it is associated with the relatively constant northeast Trade Winds (Carlquist 1980). All sites were established near 1200 m in elevation, which corresponds to a mean annual air temperature of 16°C (Department of Geography, University of Hawaii 1983).

Although the modern climate appears to be comparable at all sites, climate has varied due to global and perhaps local processes during the full course of soil development, especially at the four older sites (Gavenda 1992). Porter (1979) described evidence of numerous glacial episodes on Mauna Kea ranging from ≈300 000 yr ago to the most recent, late-Pleistocene ice cap that disappeared ≈10 000 yr BP. Assuming lapse rates were equal to those of today, Porter (1979) estimated that the July temperature in the vicinity of Mauna Kea during the last glacial period was roughly 5°C less than that of today. Porter's estimate is supported by recent evidence from Sr/Ca as well as oxygen isotope thermometry of submerged coral reefs off of Barbados, which suggest that tropical sea surface temperatures during the last glacial period were ≈5°C lower than today (Guilderson et al. 1994). There is evidence that precipitation patterns in Hawaii also differed during glacial times (S. C. Hotchkiss and J. O. Juvik, *personal communication*).

Gradual subsidence of the Hawaiian Islands has also been a source of climatic variation over pedogenic time. The mass of islands causes considerable isostatic subsidence, especially in their post-shield-forming phase (Moore 1987). The Island of Hawaii is currently estimated to be sinking at ≈2.6 mm/yr (Moore and Clague 1992). At this rate of subsidence, a modern site at 1200-m elevation would have been at ≈1460 m 100 000 yr ago. At a lapse rate of 5.7°C/1000 m, the 1460-m site would have been 1.5°C cooler in mean annual temperature than the modern 1200-m site.

Organisms

The organism factor as described by Jenny (1941, 1980) is the entire flora and fauna that could potentially occupy a site. Because of its extreme isolation from continental habitats, the Hawaiian archipelago has a flora and fauna that is relatively species poor with a high degree of endemism, and many of the species and genera occupy an extraordinarily broad range of environments in comparison to continental taxa (Carlquist 1980). Individual islands also support considerable endemism, but many species specific to single islands evolved from common ancestors (Carr 1987).

We selected sites within montane rainforest that had never been cleared by humans. Consistent with the overall Hawaiian flora, the montane rainforest has an unusually low level of species richness, and is domi-

nated by the tree *Metrosideros polymorpha* at all of our sites. As the species name implies, *M. polymorpha* takes on a number of forms, including the pubescent-leaved varieties *incana* and *polymorpha*, and the glabrous-leaved variety, *glaberrima*. The pubescent varieties make up ≈95% of the *Metrosideros* at the Thurston site, 30% at Olaa, 40% at Kohala (hairs caducous), and 5% at Kolekole. *M. polymorpha* v. *glaberrima* makes up the balance at these sites, and is the sole variety of *Metrosideros* at Laupahoehoe and Kokee. The pubescent and glabrous varieties of *Metrosideros* differ slightly but significantly in leaf tissue chemistry; where they co-occur, the glabrous variety generally has higher concentrations of N, P, and base cations (see Vitousek et al. 1995) than the pubescent varieties. In addition to *Metrosideros*, the trees *Cheirodendron trigynum* and *Ilex anomala* are frequent in upper canopies but are less important than *Metrosideros* in their contribution to total system biomass. Sub-canopy plants that are common at most chronosequence sites include *Coprosma* spp., *Myrsine* spp., *Vaccinium calycinum*, and *Cibotium* spp.

With one exception, the Hawaiian montane rainforest lacks nitrogen-fixing vascular plant–microbe symbioses (Vitousek and Walker 1989). The exception is *Acacia koa*, which at 1200 m typically grows in areas that receive <2500 mm of rainfall per year. A few *A. koa* were observed near the Laupahoehoe and Kokee sites (within 100 m).

Although the native flora of the montane rainforest sites are largely intact, people have been responsible for the introduction of numerous sub-canopy species. The most prominent exotic plant species that have established at one or more chronosequence sites are *Hedychium gardenrianum*, *Polygonum glabrum*, and *Rubus* spp.

Jenny's (1941, 1988) organism state factor also includes the soil macro- and microfauna, which we have not yet evaluated. All chronosequence sites support populations of native macroinvertebrates (i.e., millipedes), as well as earthworms, which were post-European introductions (Howarth 1985). The arrival of earthworms may have significantly altered ecosystem processes at these sites.

Humans have been responsible for the introduction of numerous other alien animal species to montane rainforest communities. Feral pigs (*Sus scrofa*) are among the alien animal species that have had the greatest impact on the montane rainforest (Cuddihy and Stone 1990).

Topography

In selecting sites we located soils on minimal slopes (<6%) that would have undergone relatively little erosion. Volcanoes in the shield-building stage have gentle slopes, but once volcanoes become less active, erosion begins to dissect the landscape with stream gullies and canyons. The two youngest sites, Thurston and Olaa,

are situated on the gentle-sloping, undissected shield of Kilauea. The landscapes of the four older sites are dissected with stream gullies at Laupahoehoe and Kohala, and river canyons at Kolekole and Kokee. At these older four sites, minimally sloping surfaces exist on ridge tops and in valley bottoms. We established sites on broad ridge tops where the soils are relatively well drained and not of depositional origin, and the vegetation receives similar exposure to sunlight.

While the Thurston and Olaa soils were clearly developed on recently formed landscapes, the four older soils of the chronosequence developed partially or entirely on erosional surfaces; the implication is that although the parent material of the Kokee site may be 4.1×10^6 yr old, development of at least part of the present soil was initiated more recently. The ridge-top locations of the Laupahoehoe, Kohala, and Kolekole sites are all situated on recognizable constructional landscapes. The Kokee site is the only one that appears to be entirely on an erosional surface.

METHODS

Study plots

We established 2–4 study plots within a 1-ha area at each of the field sites except for Olaa; several of the measurements took place in these study plots, while others were carried out in the 1-ha area surrounding them. Two 10-m-radius plots were established at Thurston, Kohala and Kolekole; two 15-m-radius plots were used at Laupahoehoe (because of the larger trees at that site). At Kokee we used four 10 × 10 m plots that were already defined for controls in a fertilization study (Herbert and Fownes, *in press*). All sampling at Olaa took place in a 1-ha area.

P fractionation

We sampled 5–7 horizons from each of 10 soil pits at all sites on the chronosequence. Pits were randomly distributed over ≈0.5 ha at each site, encompassing the study plots. We combined analogous horizons from the 10 pits at each site and refrigerated the samples for up to 2 mo before undertaking the P fractionations.

We used a version of the phosphorus fractionation described by Hedley et al. (1982) with modifications by Tiessen and Moir (1993). Duplicate samples of 0.5–0.6 g of soil (triplicates for Olaa) were weighed out at field moisture into 50 mL polypropylene centrifuge tubes. We determined oven dry masses on separate soil samples. Before weighing out organic horizons, we separated finer particulate organic matter from undecomposed structural material by suspending ≈30 g of soil organic matter in a 600-mL beaker filled to 250 mL with deionized H_2O (H. Tiessen, *personal communication*). We then sonicated the suspension at 175 W for 2 min, and poured off suspended fine organic matter into 250-mL centrifuge bottles. After repeated rinsings and decantation of fine organic matter from

root, leaf, and other structural material, we centrifuged the suspension at 1.6×10^4 m/s² for 20 min, decanted the water, and sampled the fine organic matter for analysis.

We sequentially extracted soil samples using the following extraction agents: anion exchange resin (0.4 g Biorad 1-X8, 20–50 mesh resin beads, Cl^- form in 86 mesh [≈190-μm openings] polyester bags), 0.5 mol/L $NaHCO_3$ adjusted to pH 8.5 with 5 mol/L NaOH, 0.1 mol/L NaOH, a second round of 0.1 mol/L NaOH after sample sonication at 175 W for 2 min, 1 mol/L HCl, concentrated HCl (hot) (see Tiessen and Moir 1993), and a final digestion of remaining soil materials in concentrated H_2SO_4 (boiling) with repeated additions of a 30% H_2O_2 solution. The Olaa soil fractionations, which were carried out at a later time than for the other soils, involved the same procedure except that we excluded the sonicated NaOH and hot HCl steps. Extractions took 16 h in a home-built, end-over-end soil rotisserie. We collected supernatant by centrifuging samples at 1.7×10^4 m/s² (3200 rpm) for 5 min in a clinical centrifuge, followed by filtering samples through a 0.45-μm micropore filter. After filtration, we recovered as much of the soil from the filter as possible by gently scraping with a clean spatula, and then rinsing the soil from the spatula back into the centrifuge tube with the subsequent extract. We determined total P(organic + inorganic) in the $NaHCO_3$, NaOH, sonicated NaOH, and hot, concentrated HCl extracts by potassium persulfate digestion. Organic phosphorus fractions were estimated by subtracting inorganic P from the total P measured in each of these extracts. We adjusted the pH of final solutions to ≈4.5 using p-nitrophenol or a pH meter, and added standard acid molybdate reagents (Olsen and Sommers 1982) to develop color in the samples, and measured P at 712 nm on a spectrophotometer.

The P fractionation scheme was designed to extract the most labile P first, with subsequent extracts removing P that is decreasingly available to the biota. In brief, labile, inorganic P (P_i) was extracted by the anion exchange resin and $NaHCO_3$. Labile, organic phosphorus (P_o) was extracted by $NaHCO_3$ and NaOH. Conventionally, the bicarbonate fraction is considered to be the most labile P_o; however this assumption is now being questioned as it has been shown not to extract relatively labile P_o associated with cellulose (H. Tiessen, *personal communication*). Non-occluded P_i was extracted from surfaces of Fe and Al minerals with NaOH. Calcium phosphates (presumably apatites) were removed with 1 mol/L HCl. Occluded P_i was extracted with NaOH after sonication with hot concentrated HCl, and the final H_2SO_4/H_2O_2 digest. Protected and recalcitrant P_o was extracted in the sonicated NaOH and hot concentrated HCl extracts. For thorough reviews of the P pools believed to be extracted with each step, as well as background references for the different fractions, see Stewart and McKercher (1982), Sharpley et al. (1987), Tiessen (1991), and Tiessen and Moir (1993).

We realize that the chemical extractions and digests of this and other phosphorus fractionations represent approximations of theoretical pools, but they have proved useful in practice (Tiessen et al. 1984, 1992, Lajtha and Schlesinger 1988, Frossard et al. 1989, Schoenau et al. 1989).

We transformed the P fractionation data to units comparable with the Walker and Syers (1976) model (Fig. 1) by first multiplying P mass per fraction by the bulk density and depth of the corresponding horizon. Next we summed all horizons to 50 cm to estimate the P associated with a given fraction per profile. We then combined fractions to approximate the phosphorus pools depicted in the Walker and Syers (1976) model as follows: resin P_i + $NaHCO_3$-P_i + NaOH-P_i = non-occluded P_i; $NaHCO_3$-P_o + NaOH-P_o + sonic NaOH-P_o + hot HCl P_o = P_o; HCl-P_i = calcium phosphates (P_{Ca}); sonic NaOH-P_i + hot HCl P_i + residual (H_2SO_4/H_2O_2) P_i = occluded P. Since the Olaa fractionation did not include sonic NaOH or hot HCl fractions, all residual P_o and P_i was measured in the final H_2SO_4/H_2O_2 digest. We interpolated the percentage of P_o in the Olaa residual P to be 30% using the ratios of residual P_o to total residual P at Thurston and Laupahoehoe.

The profile depth we compared between sites was 50 cm, whereas the soil of the 300-yr-old Thurston site was only ≈38 cm deep. To allow a meaningful comparison between Thurston and other sites, we estimated the P content of 12 cm of the underlying pahoehoe parent material at Thurston, and added it to the primary P_{Ca} fraction (HCl-extractable P) of the overlying soil. In making this estimate we assumed the pahoehoe to have a bulk density of 1.3 g/cm³ (J. Lockwood, *personal communication*), and a P_2O_5 content of 0.25% (Wright 1971). Before this adjustment, the 0–38 cm Thurston profile was 70% P_{Ca}, while after adding the pahoehoe P, the profile P_{Ca} increased to 82%.

Other soil analyses

We determined total nitrogen and carbon on all horizons sampled at each site using a Carlo Erba C:H:N analyzer. To convert the data to a mass per volume form, we multiplied the N and C mass values of each horizon by the corresponding bulk densities and horizon depths. The total C and N in each horizon was then summed to a depth of 50 cm.

We used the clod method (Blake and Hartge 1986) with paraffin as a coating to estimate bulk densities of the different soil horizons. We analyzed three well-preserved clods selected from each composite soil sample for bulk density analysis. We used the mean bulk density of each horizon in our calculations of P fractions and total profile C and N.

Soil pH was determined in a 2:1 ratio of deionized H_2O : soil. The soil water was allowed to equilibrate for 1 h, and pH values were measured using an Orion Sure-flow combination pH probe.

We used resin bags buried in the field (Lajtha 1988) to provide a relative measure of soil nutrient availability in these sites. Three grams of anion exchange resin (Biorad, AG 1-X8, 20–50 mesh, Cl⁻ form) and cation exchange resin (Biorad, AG 50W-X8, 20–50 mesh, H⁺ form) were weighed into separate 30-cm² bags of 86 mesh ($\approx$190-μm openings) polyester. In the field an anion and a cation resin bag were tethered to a polyvinyl chloride (PVC) pipe with heavy-duty cotton–polyester button thread, and buried in a horizontal orientation at 4–7 cm depth. In burying the resin bags, care was taken to maintain the structure of the topsoil that overlaid the bags. Except at Kokee, five resin bag locations were evenly distributed on the forest floor under the *Metrosideros* canopy at each plot within the site. At Kokee, the resin bags were distributed at three locations in two plots, and four locations in one plot. Resin bags were collected monthly, and fresh bags were tethered to the same PVC pole, but not buried in the same place as the previous month's bags. We used regenerated resin bags until they were irreversibly discolored by organic acids (up to 3 times). In standard recovery trials we found regenerated bags to have P recovery rates comparable to new bags.

Upon collection we rinsed the resin bags with DI water to remove any soil adhered to the polyester, and extracted the resin bags in 20 mL, 0.5 mol/L HCl for 6 h in a 5 rpm, home-built, end-over-end rotisserie. HCl extract from the anion bags was analyzed for phosphate and nitrate (after neutralizing extract with NaOH), and extract from the cation bags was analyzed for ammonium on a Scientific Instruments autoanalyzer.

Decomposition

As part of a broader study of the effects of substrate quality vs. site characteristics in controlling decomposition, we measured rates of decomposition of *Metrosideros* litter in three sites along the chronosequence—Thurston, Kohala, and Kokee. Measurements were also carried out at a location near our Laupahoehoe site, on the same substrate but at 300-m-lower elevation. We followed the experimental design of Vitousek et al. (1994), except in the present study leaf litter was collected in each site using litter traps rather than by hand, and we used litter bags rather than a tethered-leaf approach. Nylon bags containing 1 g air-dried litter were distributed among sites as follows: 30 bags were placed in the site where they were collected (hereafter referred to as "in situ litter"); 20 bags from each site were placed in the Thurston site (hereafter "common site"); and 30 bags of leaf litter from the 1855 flow were placed in each of the sites (hereafter "common leaves"). We collected 3–5 litter bags of each type at 1, 3, 6, 12, 18, and 24 mo following the start of the measurements. Decomposition measurements were initiated in January 1992.

Subsamples of the initial material, and all subsequent collections from the field, were oven-dried at 70°C, weighed, and ground. Samples were acid-digested for N and P analyses in a block digester using a persulfate procedure with a mercuric oxide catalyst; samples for cation analyses were dry-ashed at 550°C, and the residue was taken up in hot nitric acid. The initial material was also analyzed for lignin and cellulose using the procedure of Van Soest and Wine (1968). Exponential decay constants were calculated by regressing the natural log of fraction mass remaining against time (Olson 1963), and rates of net immobilization or mineralization of nutrients were determined by dividing the mass of an element at any collection (concentration times volume) by the initial content of that element.

In order to compare decay constants (k) of the low-elevation (915 m) Laupahoehoe site and the other three sites, we derived a correction factor for the Laupahoehoe site. We interpolated between k values calculated for *Metrosideros* decomposition rates at 915-m and 1550-m sites on a 5000-yr-old a'a lava flow in the Laupahoehoe Forest Reserve (P. M. Vitousek and P. Scowcroft, *unpublished data*). The correction was $k_{1200} = 0.78k_{915}$. Significant differences in mean decay constants were determined based on 95% confidence limits of the regressions.

N_2O flux measurements

Soil N_2O fluxes for the Thurston, Kohala, and Kokee sites were measured by Riley and Vitousek (1995); the measurements for the Laupahoehoe site were added for this study. A similar static-chamber technique was used for all measurements. Depending on the sampling date, between 8 and 50 rings (25 cm diameter) were set 1–2 cm in the soil of a site, at least 10 min before sampling. ABS (acrylonitrile-butadiene-styrene) chambers were placed over each ring and chambers were sampled 5 times over the course of a 30-min incubation using 10-mL nylon syringes fitted with nylon stopcocks. Samples were taken to the lab where they were analyzed for N_2O on a Shimadzu model 8a gas chromatograph (Columbia, Maryland, USA) fitted with a Porapak-Q column. Analyses were usually completed within 8 h, with a maximum of 24 h. Measured N_2O concentrations were regressed against sampling times, and fluxes were estimated as the slope of the best-fitting line through the sample data points from each chamber.

Vegetation analyses

We placed five contiguous 20 × 20 m relevés adjacent to and into the study plots on the chronosequence. At Olaa we placed the five relevés in the area where soil and leaves were sampled. The vegetation was stratified into structural layers, all vascular plant species present in each layer were identified, and finally the cover values of each species were estimated using Braun-Blanquet's cover-abundance scales (Mueller-Dombois and Ellenberg 1974). In addition, we mea-
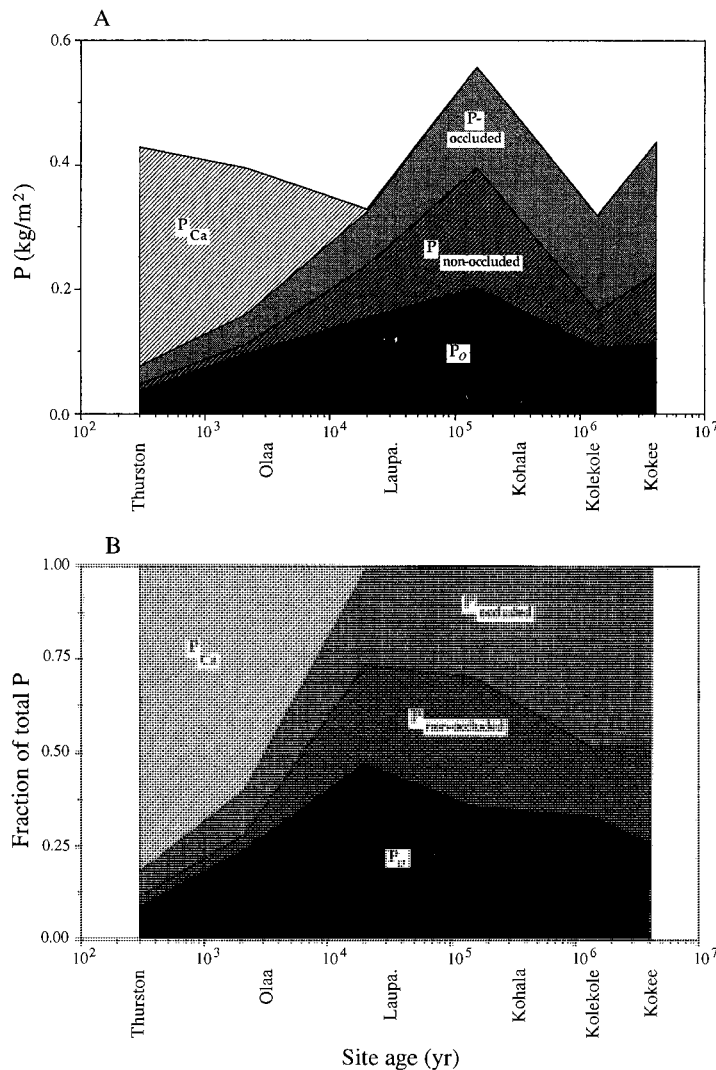
FIG. 3. Changes in P fractions with time at six chronosequence sites. (A) P fractions presented on a mass per volume basis; (B) P fractions presented as fractions of total P. Fractions are sums of individual horizon-fractions to a depth of 50 cm. P_{Ca} = calcium phosphates; P_o = organic phosphorus. Note the x-axis logarithmic scales.

sured the five tallest *Metrosideros polymorpha* trees in each relevé.

In all sites other than Olaa we measured the diameter at breast height (dbh) of all stems >30 mm of all species in each study plot. Stem basal area was estimated from dbh measurements.

Species cover-abundance scales were converted to mid-point values (Mueller-Dombois and Ellenberg 1974), composited by site, and used for computing mean species values for each site. This procedure resulted in a data matrix of 6 samples (sites) and 135 taxa. We applied a detrended correspondence analysis (an indirect ordination) to the matrix using the computer program DECORANA (Hill 1979). We also applied an unweighted pair group cluster analysis to the 6 samples based on the same matrix (MVSP Plus 2.0; Kovach 1990). These two analyses were performed to investigate relationships among the samples, which were defined by quantitative species composition.

Nomenclature followed Wagner et al. (1990) for flowering plants, and the 1987 checklist by Wagner and Wagner (*unpublished data*) for pteridophytes. Leaf pubescence is an important character to differentiate *Metrosideros polymorpha* varieties. We observed some intermediate leaf forms with caducous hairs, and these were identified as the glabrous variety in vegetation analyses.

RESULTS

Soil P transformations

Changes in P pools with time are presented in the same format as the original Walker and Syers (1976) diagram (mass of each fraction per unit area) in Fig. 3A, and as the percentage of total P that was present in each fraction in Fig. 3B. The P_{Ca} (calcium phosphates) fraction declined during early soil formation and is exhausted by 20 000 yr (Fig. 3A and B). The rate at which the primary calcium phosphates are transformed may be faster than the straight line between

TABLE 2. Sums and ratios of total carbon, nitrogen, and organic phosphorus (P_o) in 50-cm soil profiles from the six Hawaiian chronosequence sites.

	Thurston	Olaa	Laupahoehoe	Kohala	Kolekole	Kokee
			Pool sizes (kg/m²)			
C	15.3	14.6	32.4	33.6	28.0	24.1
N .	0.98	0.98	1.56	1.46	1.38	1.13
P_o	0.036	0.095	0.155	0.202	0.106	0.112
			Element ratios			
C/P_o	425	152	209	166	264	215
C/N	16	15	21	23	20	21
N/P_o	27	10	10	7	13	10

Olaa (60% P_{Ca}) and Laupahoehoe (1% P_{Ca}) implies. The occluded-P fraction increases from only 7% of total-P after 300 yr, to 48% of total P at the two oldest sites. The P_o (organic phosphorus) fraction increased to an absolute maximum at Kohala and a proportionate maximum at Laupahoehoe, and then declined later in soil development. Similarly the non-occluded P_i (labile inorganic pool) grew to a maximum in mid-soil development, and then declined. Levels of total P varied from site to site and showed no clear relationship with soil age (Fig. 3A). The lowest total-P values were from the Laupahoehoe and Kolekole sites, while the highest total P was at the Kohala site.

Total C, N, and P_o of soil profiles

Pools of total soil nitrogen and carbon were relatively small at the two youngest sites, while P_o was low at Thurston and increased to Olaa. Pool sizes of C, N, and P_o increased to a maximum during mid-soil development (Laupahoehoe and Kohala), after which time they declined through to the oldest site (Table 2).

C to N ratios of soil organic matter were narrowest at the two youngest sites, after which they broadened to between 20:1 and 23:1 at the four older sites (Table 2). The C to P_o and N to P_o ratios at Thurston were quite wide at 425:1 and 27:1, respectively, whereas at

all older sites the ratios narrowed to 152:1–264:1 for C:P_o and 7:1 to 13:1 for N:P_o. In almost all cases the C to N, C to P_o and N to P_o ratios of soil organic matter across the chronosequence were wider than the global averages of 14:1, 108:1, and 8:1, respectively, reported by Stevenson and Elliott (1989).

Soil nutrient availability

Available soil phosphorus as measured by buried anion-exchange resin bags was quite low at the youngest and oldest sites on the gradient, while the intermediate-aged Kohala soil had more than an order of magnitude greater available P than the youngest site (Table 3).

Thurston, the youngest site, had low resin-available ammonium and nitrate while the 20 000-yr-old Laupahoehoe and 1.4×10^6-yr-old Kolekole sites had the highest NH_4^+-N and NO_3^--N values, respectively (Table 3). Kohala had intermediate resin-available NH_4^+-N values, but very low NO_3^--N levels.

Decomposition

Leaves grown and decomposed at the same site (in situ leaves) exhibited a very broad range in decomposition rates, from 62% of the initial leaf mass remaining after 2 yr at the oldest site on the gradient

TABLE 3. P and N availability, nitrous oxide flux, gross N-mineralization and nitrification, and pH of Hawaiian chronosequence sites. Data are means ± 1 SE; n = the number of months buried resin bags (see *Materials: Other soil analyses*) were sampled at each site.

Site	In situ resin P (μg·bag⁻¹·d⁻¹) $\bar{X}$	SE	n	In situ resin NH_4-N (μg·bag⁻¹·d⁻¹) $\bar{X}$	SE	n	In situ resin NO_3-N (μg·bag⁻¹·d⁻¹) $\bar{X}$	SE	n	N_2O-N* (μg·m⁻²·day⁻¹) $\bar{X}$	SE	Gross N* mineralization (mg·m⁻²·d⁻¹) $\bar{X}$	SE	Gross* nitrification (mg·m⁻²·d⁻¹) $\bar{X}$	SE	pH† in H_2O	Soil‡ dry mass (kg/m²)
Thurston	0.20	0.08	5	3.09	1.44	5	0.22	0.12	5	2	2	195	70	33	9	5.02	347
Olaa	§			§			§			§		§		§		5.39	303
Laupahoehoe	1.21	0.28	8	8.12	2.05	8	4.25	1.27	8	809	60	§		§		3.57	187
Kohala	2.19	0.30	7	4.90	1.24	7	0.31	0.12	7	110	27	432	69	52	13	4.09	249
Kolekole	0.51	0.16	5	4.02	1.72	5	10.53	5.42	5	§		§		§		3.79	272
Kokee	0.41	0.17	6	4.12	2.29	6	10.29	4.91	6	71	25	647	114	112	52	3.99	400

* From Riley and Vitousek (1995) except for the Laupahoehoe N_2O, which is reported here.
† Measured on the uppermost mineral horizon.
‡ To 50 cm depth except for Thurston, which was to 38 cm depth.
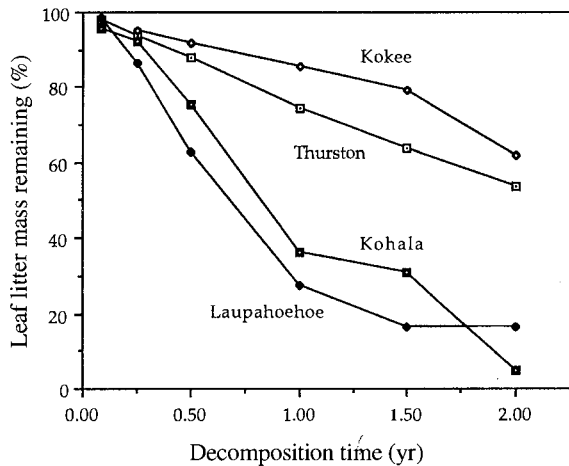§ No data available.

FIG. 4. Percentage of original mass of *Metrosideros polymorpha* leaf litter remaining during 2 yr of decomposition at four chronosequence sites. Leaf litter was collected and decomposed at the same site (in situ treatment). The Kokee, Thurston, and Kohala sites were at 1200 m elevation, whereas the Laupahoehoe site was at 915 m.

(Kokee), to <10% of initial leaf mass remaining after the same period of time at Kohala (Fig. 4). There was a clear bifurcation of decomposition rates, with high rates occurring on intermediate-age soils of the chronosequence and low rates occurring at the beginning and end points of soil development. This pattern was further illustrated when first-order, exponential, decomposition constants (k) were plotted as a function of substrate age (Fig. 5). Rates of in situ decomposition at Laupahoehoe and Kohala were significantly greater than those at Thurston and Kokee (P < 0.05).

Results from the common-site experiment, in which leaves from all four sites were decomposed at Thurston, suggest that leaves from intermediate-aged sites are inherently more decomposable than leaves from early or late stages of soil development. Leaves from Thurston decomposed at significantly lower rates than leaves from Laupahoehoe and Kohala (P < 0.05) (Fig. 5).

Results from the common-leaf experiment suggest a similar pattern of decomposition dynamics occurred for the common leaves as the in situ leaves (Fig. 5), although the overall rates of decomposition of the common leaves were reduced because of their low initial tissue quality (Table 4). Common leaves at Kokee decomposed at significantly lower rates than common leaves at Laupahoehoe and Kohala (P < 0.05).

Substantial fractions (36–57%) of the initial N and P in the litter at intermediate-aged sites were mineralized within 1 yr, at a time when litter in the youngest and oldest sites was still immobilizing N and P (Table 5). Net immobilization of P in the Thurston leaves, and N and P in the Kokee leaves continued even after 1.5 yr.

Soil N_2O fluxes

The mean N_2O-N flux we measured at the 20 000 yr Laupahoehoe site was 809 $ug \cdot m^{-2} \cdot d^{-1}$ (Table 3). This mean flux represents only sixteen chambers at one sampling date, but it is similar to other measurements made at different times at 900 m and 1500 m in elevation on the same tephra deposit (A.R. Townsend, *personal communication*).

Vegetation

Total basal area of trees >30 mm dbh ranged between 34 and 38 m^2/ha, and *Metrosideros polymorpha* comprised between 81% and 88% of the total community basal area at the five sites measured (Table 6). Several other genera, including *Cibotium, Cheirodendron, Ilex, Coprosma*, and *Vaccinium*, accounted for most of the remaining cover (Fig. 6). The maximum height of the *Metrosideros* canopy increased from Thurston to Laupahoehoe, and then declined to Kolekole, followed by a final increase at Kokee (Table 6).

Growing amidst the *M. polymorpha* and other common shrub and tree species were less common plants that appeared at anywhere from one to all six sites. The total number of species of native, vascular plants per 0.2 ha was lowest at the youngest site, with 28 species, and highest at the oldest site, with 64 species (Table 7). The four middle sites range from 37 to 45 species per 0.2 ha.

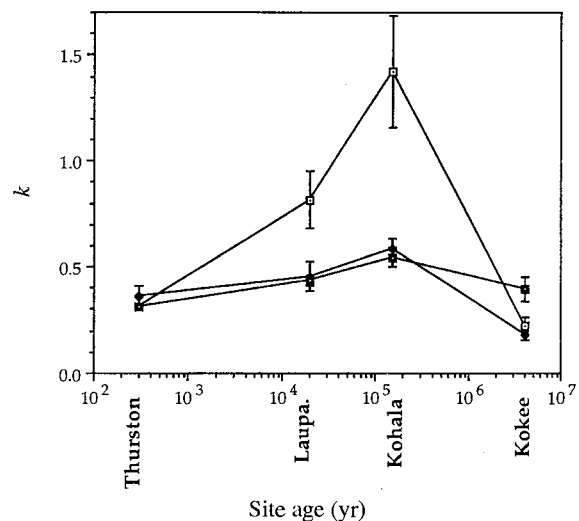In addition to quantifying changes in species rich-

FIG. 5. Exponential decomposition constants (k) for *Metrosideros polymorpha* litter decomposed over 2 yr in three treatments: in situ decomposition (□) where leaves were decomposed in the same site where they were collected; common leaf decomposition (♦) where leaves from one site were decomposed at the four chronosequence sites; and common site decomposition (■) where leaves from each of the four chronosequence sites were decomposed at one site. For comparison, k values of the 915-m elevation Laupahoehoe site were corrected to approximate decomposition at 1200 m. Bars = ±1 SE. Note the x-axis logarithmic scale.

TABLE 4. Initial litter quality of senescent leaves of *Metrosideros polymorpha* from the two extreme and two middle-aged sites on the chronosequence. Also listed are values of the senescent common leaves that were collected from *M. polymorpha* on the 1855 pahoehoe flow of Mauna Loa. Values are means ± 1 SE; where no SE is reported, senescent leaf samples were batched.

Site	N (%)	P (%)	Ca (%)	Mg (%)	K (%)	Lignin (%)	Lig-nin: N	Cellulose (%)
Thurston	0.40 ± 0.01	0.026 ± 0.001	1.75 ± 0.14	0.22 ± 0.01	0.13 ± 0.02	25.8 ± 2.2	65	32.2 ± 1.0
Laupa.	0.80 ± 0.04	0.053 ± 0.003	1.22 ± 0.02	0.24 ± 0.002	0.20 ± 0.02	36.0 ± 0.7	45	27.4 ± 0.3
Kohala	0.74 ± 0.02	0.054 ± 0.001	0.73 ± 0.04	0.26 ± 0.004	0.20 ± 0.007	24.9 ± 2.1	34	28.7 ± 0.4
Kokee	0.37 ± 0.015	0.022 ± 0.001	0.82 ± 0.08	0.13 ± 0.004	0.04 ± 0.005	36.7	99	32.3
1855	0.36 ± 0.01	0.026 ± 0.001	1.71 ± 0.04	0.25 ± 0.02	0.28 ± 0.01	31.7 ± 3.1	88	27.0 ± 0.4

ness, we measured shifts in community composition along the chronosequence using a detrended correspondence analysis (DECORANA; Hill 1979) to ordinate the samples (sites) (Fig. 7). The axis with the highest eigenvalue (0.71) arrayed the sites exactly in their chronological order, suggesting that a high proportion of species variance among the sites is explained by properties associated with age and/or pedogenesis along the chronosequence. This finding was reinforced by results from an unweighted pair-group cluster analysis (Fig. 8) in which we found site clusters to correspond with the soil developmental sequence.

DISCUSSION

Soil development

Several predictions made by the Walker and Syers (1976) model (see Fig. 1) are supported by our results. The decrease and exhaustion of P_{Ca} (calcium phosphates) early in soil development, and the increase and eventual dominance of the occluded-P fraction later in soil development were both essential characteristics of the model that our findings upheld (Fig. 3A and B). Further, Walker and Syers (1976) suggested that P_o (organic P) should increase until P_{Ca} is exhausted, at which time the P_o should begin a decline; this pattern is evident in our results as well (Fig. 3B).

In contrast to the Walker and Syers model, we found the non-occluded P_i (inorganic P) pool to persist throughout the chronosequence as a significant fraction of total P (cf. Figs. 1 and 3B). One possible cause for the substantial quantity of non-occluded P at the Kolekole and Kokee sites could be the accumulated effect of Asian dust deposition (Jackson et al. 1971, Duce and Tindale 1991). Although this P would likely be-

come occluded with time (Fox et al. 1991), Asian dust inputs could have the effect of preventing the oldest Hawaiian soils from reaching a terminal steady state, largely devoid of non-occluded P. Similarly, Swap et al. (1992) suggested that dust inputs from the Sahara and Sahel comprise an important nutrient source to ecosystems of the Central Amazon Basin. Indeed, it seems possible that deposition of exogenous dust may prevent soils planet-wide from reaching a terminal steady state, characterized by an overwhelming dominance of iron oxides.

The persistence of the non-occluded P_i pool may also suggest that occlusion of P by secondary Fe and Al minerals is not entirely permanent. Some plant and mycorrhizal symbioses, especially those well adapted to P-impoverished conditions, might have the capacity to dissolve certain P-occluding minerals, thus re-introducing P to the actively cycling pool. The likelihood of P cycling out of the occluded pool is supported by Tiessen et al. (1994), who found mycorrhizal hyphae growing in lateritic nodules in an Amazonian Oxisol.

A notable difference between our results (Fig. 3A) and the Walker and Syers (1976) model (Fig. 1) is the shape of the total phosphorus curve through time. Where Walker and Syers' model and chronosequence results show the greatest total-P per unit area profile occurring at the onset of soil development and gradually decreasing over time, our results show a sizable increase in total P at the middle-aged Kohala site, well above the level measured at our youngest site, Thurston.

Differences in total P between sites may in part be related to the variation in soil bulk densities (Table 3). Bulk densities decline substantially from the 300-yr

TABLE 5. Percentage of initial N and P remaining in *Metrosideros polymorpha* leaf litter decomposed in situ for 1.5 yr.

Elapsed time (yr)	Thurston N (%)	Thurston P (%)	Laupahoehoe* N (%)	Laupahoehoe* P (%)	Kohala N (%)	Kohala P (%)	Kokee N (%)	Kokee P (%)
0.083	75	94	90	88	100	87	...	...
0.25	81	91	97	87	96	82	88	78
0.50	90	97	95	96	83	81	80	90
1.00	89	143	43	55	64	58	119	146
1.50	81	146	39	36	69	66	104	194

* Laupahoehoe site was at 915-m elevation while other sites were at 1200-m elevation.

TABLE 6. Total community basal areas of trees >30 mm in diameter at breast height, % of total community basal area and maximum canopy height of *Metrosideros polymorpha*.

| | Community basal area | | Maximum canopy ht. (m) | |
| | | | | |
Site	Total (m²/ha)	*Metro-sideros* (%)	$\bar{X}$	SE
Thurston	35.8	81	16.5	0.4
Olaa	*	*	20.0	1.0
Laupahoehoe	33.6	83	24.7	1.0
Kohala	35.7	83	11.6	0.3
Kolekole	37.3	86	8.2	0.2
Kokee	38.0	88	13.7	0.4

* No data available.

TABLE 7. Species diversity of the Hawaiian chronosequence sites.

	Thurs-ton	Olaa	Laupa-hoe-hoe	Ko-hala	Kole-kole	Kokee
No. of native species	28	42	41	45	37	64
No. of alien species	6	6	6	8	5	2
Total no. of species	34	48	47	53	42	66

(Thurston) site to the 20 000-yr site (Laupahoehoe), and then increase to the end member of the chronosequence. This pattern reflects changes in the dominant minerals during soil development—from dense primary minerals early, to lighter hydrated amorphous alumino silicates, to more dense crystalline Al and Fe oxides late in soil development (Fox et al. 1991). Thus part of the reason there is less total-P per unit area profile at Laupahoehoe compared to Kohala, or at Kolekole compared to Kokee, is because these former sites have less soil mass. Differences in soil bulk densities, however, do not explain why the total-P maximum occurs at the 150 000-yr Kohala site.

The total-P maximum well into soil development could be due to a parent-material effect. Hawi Volcanics, the source of the Kohala site parent material, consists largely of mugearite, with lesser amounts of benmoreite and hawaiite (Clague and Dalrymple 1987). The total P of alkalic post-shield lavas ranges between 0.2 and 1.1% P_2O_5 (Clague and Dalrymple 1987). In contrast, the P_2O_5 content of tholeiitic shield-building lavas typically fall between 0.17 and 0.35% (Wright 1971). We do not know the original total-P content of the parent material at any of our sites, but one or more

of the four older sites associated with post-shield volcanics may have had higher original P concentrations than the two youngest sites.

A second possible explanation for the peak in total P at the Kohala site is that desilication rates may exceed losses of P throughout early soil development, resulting in P enrichment of the soil profile at mid-soil development. This hypothesis is supported by data of Chadwick and colleagues who observed changes in soil mineralogy across a steep precipitation gradient on a 170 000-yr-old pahoehoe flow of Hawi Volcanics (Chadwick et al. 1994). At a site that received ≈2500 mm rainfall annually, Chadwick found that 64% of the silica content of the original parent material had been leached from the A horizon, while only 18% of the original P content had been lost (O. Chadwick, *unpublished data*). The proportionately greater loss of Si over P was evident to a 163-cm depth in the soil profile, which was the deepest horizon sampled.

The possible influence of Asian dust deposition on the Kohala P maximum is not clear. The lowest total P of all the Kohala mineral horizons was 1.4 mg/g soil dry mass, whereas continental clay minerals average 0.4 mg/g soil dry mass (Ronov and Yaroshevsky 1969). Asian dust deposition may therefore have the effect of diluting, not enriching, the Kohala soil P concentration. However, if silica loss exceeds phosphorus loss through
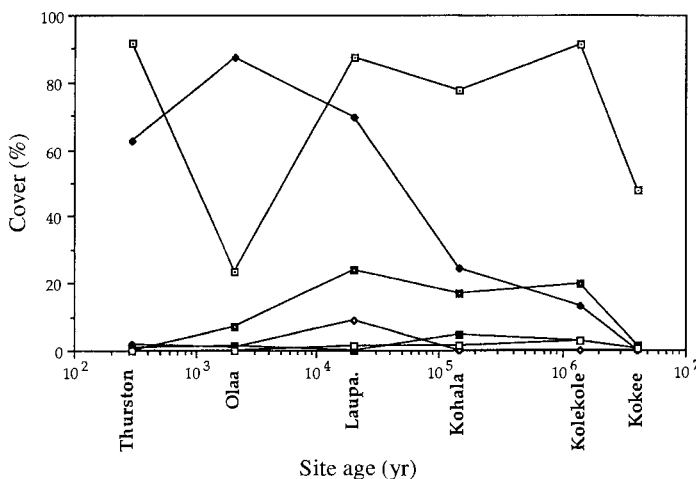

FIG. 6. Changes in percentage cover of six dominant tree and shrub genera at the six Hawaiian chronosequence sites. Genera and number of species (in parentheses) in each genus that grow at one or more sites are: *Metrosideros* (1) –□–; *Cibotium* (3) –♦–; *Cheirodendron* (2) –▣–; *Ilex* (1) –◇–; *Coprosma* (5) –■–; and *Vaccinium* (2) –□–. Note the x-axis logarithmic scale.
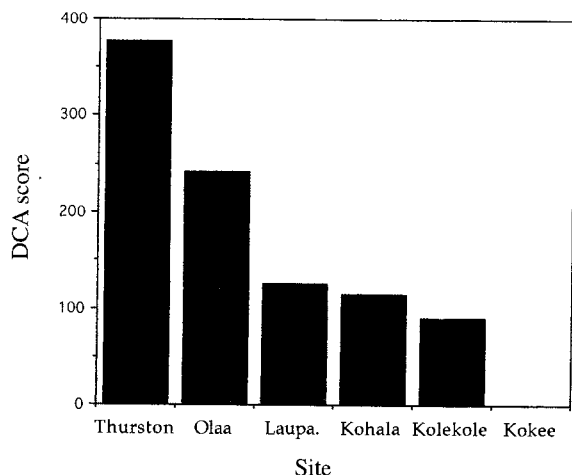
FIG. 7. Detrended correspondence analysis (DCA; Hill 1979: DECORANA) scores on axis 1 of quantitative species composition of chronosequence sites. Eigenvalue = 0.71.

time, as appears to happen in the native soil, then P enrichment from dust inputs may occur.

The largely parallel changes in total profile C, N, and P_o (Table 2) are consistent with the idea that C and N accumulation is regulated by the pool of biologically active P (Walker and Adams 1958, Walker and Syers 1976, Cole and Heil 1981, Tate and Salcedo 1988), and that C, N, and P_o pool sizes increase in early soil development, reach a maximum about when primary phosphate-supplying minerals are depleted, and then decrease through late stages of soil development (Walker and Syers 1976).

The high C to P_o and N to P_o ratios in organic matter at Thurston suggest that P may be in short supply at this early stage in soil development. The wide ratios could be the result of particularly high rates of biochemical mineralization, in which certain soil microbes and plant roots, in response to low P availability, produce extracellular phosphatase enzymes that hydrolytically cleave ester-bound phosphates from organic matter (McGill and Cole 1981).

The low C:N ratio of 16:1 at Thurston at first appears to suggest a relatively high nitrogen status compared to other sites. It may, however, reflect a young, accruing soil organic matter pool that has yet to accumulate significant fractions of materials with high C to N ratios

such as decomposing wood, and stable decomposition products such as fulvic acids (Schnitzer 1978, Fox et al. 1991).

Ecosystem processes

The biotic availability of N and P across the chronosequence largely coincided with the dynamics of the greater, more slowly cycling pools of these elements. Available P measured by buried resin bags (Table 3) was high in the middle period of soil development where the actively cycling P_o and non-occluded P_i pools were highest (Fig. 3A), and low at the beginning and end members of the chronosequence where more P was held in unavailable forms. This unimodal pattern of P availability across the chronosequence was also demonstrated by Vitousek et al. (1995) who reported foliar P concentrations in Metrosideros polymorpha at all six sites (Fig. 9). In parallel with P, resin-available NH_4^+-N (Table 3) and foliar N concentrations (Vitousek et al. 1995) (Fig. 9) are at a maximum in mid-soil development. The low foliar N concentrations at the oldest sites are in contrast to the high resin available NO_3^--N (Table 3) at these sites, suggesting that something other than N availability was limiting N uptake by M. polymorpha.

The high rates of decomposition of M. polymorpha leaf litter measured at Laupahoehoe and Kohala, compared to the low rates measured at Thurston and Kokee, suggest that decomposition rates respond to the fertility gradient across the chronosequence. Does site fertility influence decomposition rates only indirectly, through its effect on leaf tissue quality? Or does the soil environment play a direct role in regulating decomposition rates? Results from the common-site and common-leaf experiments suggest that both effects may be important.

When the soil environment factor was removed by decomposing leaf litter collected from all four sites at one common site, litter from the two intermediate-aged sites was more decomposable than that of the youngest site (Fig. 5). Further, the contrast in decomposition constants (k) of in situ and common leaves decomposed at Kohala and Laupahoehoe show that leaves grown under high-fertility conditions are inherently more decomposable than leaves grown under less fertile conditions.

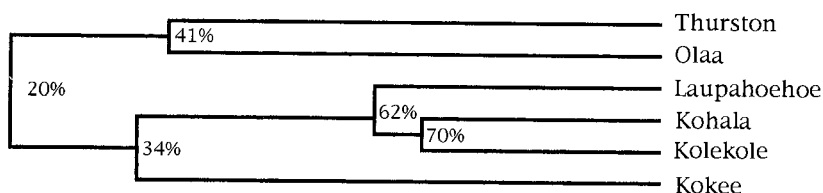The greater nutrient content, greater decomposabil-

FIG. 8. Unweighted pair-group cluster analysis of quantitative species composition of chronosequence sites. Percentage values refer to similarities among sites based on percentage similarity coefficient (Kovach 1990).
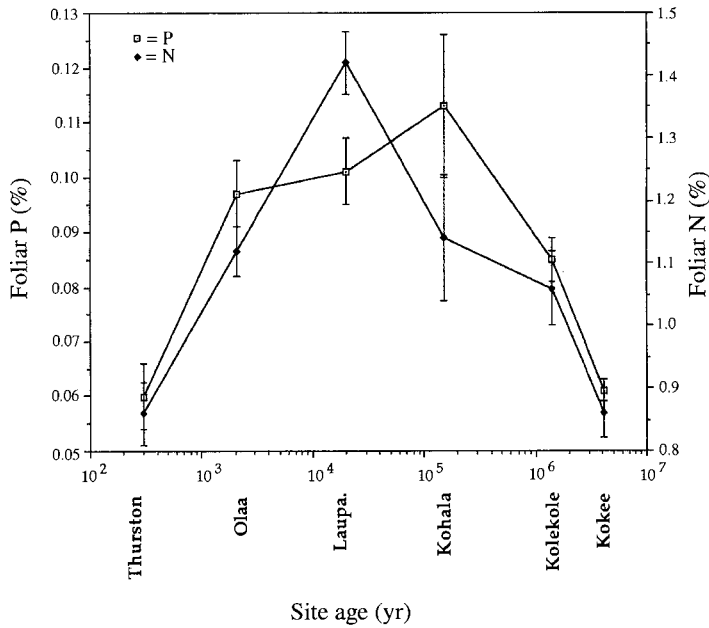
FIG. 9. Changes in the percentage of P and N in foliage of *Metrosideros polymorpha* across the Hawaiian chronosequence sites (modified from Vitousek et al. [1995]). Leaves collected were canopy sun leaves. Bars = ±1 SE. Note the x-axis logarithmic scale.

ity, and more rapid nutrient release from litter in the intermediate-aged sites could contribute to a positive feedback superimposed on the Walker and Syers (1976) pattern, one that accentuates enhanced nutrient availability and circulation in intermediate-aged sites—and decreases nutrient availability and circulation in the youngest and oldest sites (Vitousek 1982, Shaver and Melillo 1984).

The high N_2O emissions we measured at the 20 000 yr intermediate-aged Laupahoehoe site were much higher than fluxes reported by Riley and Vitousek (1995) for the 300, 150 000, and 4.1×10^6-yr-old sites (Table 3). Overall, changes in soil N_2O emissions from early to middle soil development appear to reflect an increase in the quantity of N cycling in these ecosystems. Riley and Vitousek (1995) suggested that from middle to late soil development the differences in N_2O emissions between sites are probably more related to changes in soil water content that affect the diffusivity of O_2, rates of nitrification and denitrification, and possibly consumption of N_2O within the soil. In addition, amorphous minerals, which are in greatest abundance at the intermediate-aged sites (Fox et al. 1991), have extremely high water-holding capacities (Wada 1989), which could further increase N_2O emissions (Riley and Vitousek 1995).

Vegetation patterns

While *Metrosideros polymorpha* dominates the overstory at all sites, maximum tree height increases from the youngest site, Thurston, to a maximum at Laupahoehoe, and then declines late in soil development (Table 6). We do not know the frequency or extent of natural disturbances that has affected these sites, and cannot interpret this pattern of tree stature other than

to say that the stature of *M. polymorpha* closely and positively corresponds to measurements of N and P fertility across the chronosequence.

Changes in species richness across the chronosequence (Table 7) reflect the variation in the islands' regional floristic richness. The highest native species count of our sites was at the oldest one, Kokee (64 species) reflecting an evolutionary component to the biological diversity of the oldest major island; indeed, the uniquely diverse flora of Kauai allowed it to be identified as the oldest island before the geological ages of the Hawaiian Islands were understood (Hillebrandt [1887] referenced in Clague and Dalrymple [1987]). Conversely, low native species richness (28 species) at the youngest site was expected given the short amount of time for colonization or speciation.

Results from the DECORANA and cluster analyses (Figs. 7 and 8) suggest that factors related to soil development, such as site fertility, are important in determining the abundance and coverage of dominant species at different sites. The strong relationship between site age and plant community composition could be attributed to the almost linear southeast to northwest geographic relationship of the chronosequence sites (Fig. 2). However, we found Kohala (on the island of Hawaii) and Kolekole (on Molokai) to have the highest floristic similarity, in spite of the long distance between them. Moreover, Laupahoehoe formed a more cohesive cluster with Kolekole and Kokee, which are all on different islands, than with Thurston and Olaa, which are both on the same island as Laupahoehoe (Fig. 8). The results of the cluster analysis, therefore, support the idea that changes in community composition are driven by soil development as well as by geographic proximity of the sites.

*Changes in N and P dynamics through
ecosystem development*

Full-factorial fertilization experiments have been carried out at the youngest and oldest sites on the chronosequence to evaluate nutrient limitation (Vitousek et al. 1993, Herbert and Fownes, *in press*). Treatments (four plots per treatment) included N, P, all essential macro- and micronutrients other than N and P (termed "OE"—other elements), and all combinations of N, P, and OE additions. At the young Thurston site, N and only N was found to limit rates of aboveground net primary production (ANPP) after 2 yr of fertilization (Vitousek et al. 1993). At the oldest site, Kokee, P fertilization significantly increased ANPP, while applications of OE magnified the P effect. N applications affected leaf turnover but did not significantly increase ANPP (Herbert and Fownes, *in press*). These results suggest that over the course of 4×10^6 yr of ecosystem development, there is either a gradual shift from N to P limitation, or a transition time where neither N or P chiefly limit rates of productivity.

The Thurston site, being only 300 yr old, is in an early stage of ecosystem development during which N is accumulating (Table 2). Rates of nitrogen accumulation are impeded by the absence of N-fixing vascular plant symbioses; thus the only N inputs to the biota are through roughly equal contributions from atmospheric deposition and N fixation by free-living bacteria, neither of which approach N input rates of vascular N-fixers (Vitousek and Walker 1989, Vitousek 1994). Although additions of P did not significantly increase ANPP at Thurston during the 2-yr fertilization study (Vitousek et al. 1993), very low resin-available P (Table 3), a high C to P_o ratio in soil organic matter (Table 2), low foliar P concentrations (Fig. 9), and high rates of P immobilization during decomposition (Table 5) together suggest that P availability could have indirect effects on ANPP, perhaps through regulation of N-fixation rates or N release from decomposition.

At the Laupahoehoe and Kohala sites, which represent the middle stage of ecosystem development, N and P fertility is relatively high. Of all the chronosequence sites, these two have the largest pools of non-occluded P and P_o (Fig. 3A), as well as total soil N (Table 2), intermediate to very high resin-available N and P (Table 3), high foliar N and P (Fig. 9), high N_2O emissions (Table 3), and high rates of N and P mineralization during 1.5 yr of in situ decomposition (Table 5).

The fertile conditions at Kohala and Laupahoehoe could be partly a consequence of high decomposition rates (Vitousek 1982) that themselves are driven by high soil fertility. When net mineralization is rapid, a relatively small proportion of nutrients is held unavailable in slowly decomposing leaf litter, and a larger proportion of nutrients is actively cycling. This is in contrast to the Thurston site where the actively cycling

pool of N (and other nutrients) could be reduced because a higher proportion of N is held unavailable in slowly decomposing leaf litter.

Measurements at Kokee of low resin-available P (Table 3) and soil-P_o (Table 2), low foliar P concentrations (Fig. 9) and high rates of P immobilization during 1.5 yr of decomposition (Table 5) are all indicative of a P-impoverished site. P limitation of primary productivity at this site (Herbert and Fownes, *in press*), appears to be caused by a reduction in P availability through occlusion into secondary iron minerals (Fox et al. 1991; Fig. 3B). The percentage of organic P that is recalcitrant is also at its highest late in soil development. Aluminum, manganese, or other elemental toxicities associated with highly weathered soils, may also play a role in limiting productivity at older chronosequence sites.

In contrast to the Laupahoehoe and Kohala sites, low soil fertility at Kokee could set in motion a feedback whereby low rates of decomposition further intensify nutrient limitation. Because of pedogenic transformations, the percentage of total soil P that is actively cycling at Kokee is reduced compared to intermediate-aged soils; we suggest that any process that further reduces this pool will act to further intensify nutrient limitation. Decomposition may be such a process, since long periods of microbial immobilization (Table 5) effectively remove P and other nutrients from active cycling. We understand that immobilized P will eventually be mineralized, but the salient point is that at any moment in time, a greater proportion of actively cycling P will be rendered unavailable in decomposing organic matter at Kokee (where its demand is greatest) than at Laupahoehoe or Kohala.

Atmospheric deposition of dust from other parts of Hawaii or Asia may prevent the highly weathered Kolekole and Kokee soils from becoming as infertile as they otherwise might (Jackson et al. 1971). However, Oxisols generally have enormous P sorption capacities because of their high gibbsite and goethite contents (DeDatta et al. 1963, Fox et al. 1991). It therefore seems unlikely that these soils will actually rejuvenate, but instead maintain an equilibrium between rates of atmospheric deposition, occlusion, and ultimately erosion.

Although the dominant vegetation of the Hawaiian montane rainforest remains largely constant across the chronosequence, we recognize a critical shift in biogeochemical controls on ecosystem functions between early and late stages of soil development. Early in soil development, the factors that regulate N availability to the biota ultimately control productivity of the rainforest, whereas late in soil development, the factors that regulate P availability control productivity. The general pattern of decreasing N limitation as soil fertility increases early, followed by increasing P limitation as soil fertility declines late, is a function of (1) the biogeochemical controls on net inputs and outputs

of these two elements at different stages of ecosystem development and (2) a possible decomposition feedback that intensifies the fertility or infertility of the different aged sites.

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