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Cover Photo: Forest nutrient cycles emerge from the interaction of atmosphere, rock, biota, and time in native tropical forests of the Hawaiian Islands. In the foreground, a young lava flow is colonized by crusts of nitrogen fixing lichens (*Stereocaulon vulcanai*), ohelo shrubs (*Vaccinium reticulatum*), and tree ferns (*Sadleria spp.*). In the background, a dense ohia forest (*Metrosideros polymorpha*) has emerged on a 3,500-year-old lava flow. On page 2231, Lars Hedin and colleagues explore how cycling and losses of nutrients change across four million years of forest development throughout the Hawaiian archipelago. Photo by Lars Hedin.

PERSPECTIVES

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NUTRIENT LOSSES OVER FOUR MILLION YEARS OF TROPICAL FOREST DEVELOPMENT

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Abstract. Biological, atmospheric, and geochemical processes interact to shape how element cycles and nutrient losses develop within newly formed landscapes. We examined losses of nitrogen (N), phosphorus (P), and base cations across a four-million-year substrate age gradient of Hawaiian montane tropical forests, with the goal of understanding how losses depend on changes in biotic demand, weathering, and atmospheric sources. We were particularly interested in whether losses of nutrients that are not subject to traditional mechanisms of *biotic availability* could influence ecosystem fertility and nutrient limitation over time. Over a three-year period we sampled nutrient outputs in soil solutions below the active plant–soil system and small streams, gaseous N losses (NO, N₂O, and N₂), and pools and transformations of N in soils.

Weathering was the major determinant of ecosystem losses of P, of base cations and Si, and of ecosystem acid–base status. Sharp reductions in weathering inputs after 20 000 years of forest development caused dramatically lower outputs of P (~65% reduction), Ca²⁺ (~99%), and Si (~94%), to rates that matched inputs from dilute sea-salt and dust aerosols. Internal production of organic acids, in combination with low weathering, caused highly acidic soil waters (pH < 5.0) with elevated Al (up to 300 µg/L) and Ca:Al ratios (<0.3) below values considered critical thresholds for many plant species.

Long-term N and P interactions were more complex than predicted by the Walker and Syers model, with important influences of N and P loss pathways that were not subject to direct biotic availability. While losses of available forms of dissolved N and P, and N gases followed (as predicted) ecosystem nutrient availability, significant dissolved organic N (DON) and dissolved organic P (DOP) losses occurred independent of ecosystem N or P status. DON losses were not sufficient (relative to external inputs) to sustain N limitation beyond 20 000 years, while dissolved P losses remained large enough to maintain P limitation in older forests. Forests developed high N:P loss ratios over time (>300 on mass weight basis) due to efficient P recycling and unexpectedly high N throughputs (4–9 kg N·ha⁻¹·yr⁻¹) by either N fixation and/or N deposition.

Key words: *acidity, soil waters; base cations; calcium; ecosystem evolution over geologic time; forest ecosystems and biogeochemical processes; Hawaiian montane tropical forests; nitrogen and nitrogen oxide; nutrient cycles and nutrient limitations; phosphorus; silicon; tropical forest development; watershed losses.*

INTRODUCTION

Forests are complex biogeochemical systems in which local organism–nutrient interactions depend on, and feed back upon, ecosystem nutrient cycles that develop over centuries, millennia, and longer. Walker and

Syers (1976) proposed a conceptual model for changes in cycles of P, N, and base cations as forests develop over geologic time. Their model can be summarized as follows: (1) weathering is the major source of P to terrestrial ecosystems; (2) over time, some weathered P is lost via leaching and more is irreversibly adsorbed and “occluded” by iron and aluminum sesquioxide clays; (3) weathering inputs of P decline and eventually virtually disappear, as primary minerals are depleted (at which point P input is maintained by dilute aerosol

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deposition [Newman 1995, Chadwick et al. 1999]); (4) as P inputs decline, weathering inputs of other essential nutrients (Ca^{2+} , Mg^{2+} , and K^+) also decline, as does soil pH; (5) in contrast to weatherable P and base cations, fixed N is nearly absent from most geologic parent materials (but see Dahlgren 1994); (5) N supply should limit plant growth on young soils, and plants with N-fixing symbioses should be favored; and (6) over time (and in the absence of recurring fires, landslides, or similar large-scale disturbances) the quantity of N in circulation should equilibrate with that of P or other potentially limiting nutrients. Physiological-based models suggest that N fixation should be energetically favored only as long as N remains limiting (Pate 1986, Hartwig 1998, Vitousek and Field 1999); fixation therefore ought to adjust any deficit in N relative to P (or other resources) over time (Smith 1992, Schimel et al. 1997), but should cease once N and P become equally limiting. This model is analogous to the long-term equilibration of marine N and P cycles described by Redfield (Redfield 1958), or of lake N and P cycles described by Schindler (Schindler 1977).

In the case of developmentally young forests (i.e., forests that grow on young geologic substrates), there is considerable empirical support for this model. Such forests generally display narrow soil N-to-P ratios (Walker and Adams 1958, 1959, Stevens and Walker 1970, Vitousek and Sanford 1986, Bormann and Sidle 1990, Crews et al. 1995), presence of symbiotic N fixers (Lawrence 1951, Vanclve et al. 1991, Binkley et al. 1992, Bormann et al. 1993, Cleveland et al. 1999, Crews et al. 2001, Kurina and Vitousek 2001), and N limitation on plant growth (Silvester 1989, Vitousek and Howarth 1991, Vitousek and Farrington 1997, Tanner et al. 1998).

In contrast, studies have not supported the prediction that N and P cycles ought to equilibrate at or near equal availability as forest ecosystems age further. Instead, humid tropical forests appear to become rich in N, but increasingly poor in P and base cations over geologic time, while N limitation appears to be sustained in many temperate ecosystems. For example, lowland tropical forests on old substrates display wide N-to-P ratios (Vitousek and Sanford 1986, Tanner et al. 1998, Martinelli et al. 1999) and an abundance of potentially N-fixing symbioses (Jenny 1950, Cleveland et al. 1999, Crews 1999, Martinelli et al. 1999), suggesting that they accumulate N well beyond equilibration with P supply. Moreover, experimental nutrient additions have shown singularly strong P limitation to plant growth in humid Hawaiian forests on old and highly weathered substrates, with soil N availability greatly exceeding P when compared to N:P ratios in plant biomass growth (Crews et al. 1995, Herbert and Fownes 1995, 1999, Vitousek and Farrington 1997).

We suggest that an understanding of how ecosystem-level element inputs and outputs are regulated could resolve some of these observations, and thereby con-

tribute to understanding long-term controls of nutrient cycling and limitation in forested ecosystems. Traditional models of ecosystem nutrient cycles (e.g., Vitousek and Reiners 1975, Walker and Syers 1976, Gorham et al. 1979, Ågren and Bosatta 1988, Stoddard 1994, Likens et al. 1995, McGuire et al. 1997, McKane et al. 1997, Schimel et al. 1997, Aber et al. 1998, Rastetter et al. 2001) focus on inorganic forms of nutrients that are immediately available to biotic uptake, such as NO_3^- , PO_4^{3-} , or Ca^{2+} . These models predict efficient retention and minimal losses of any nutrient that is limiting to biological processes, but that losses should increase to match inputs once enough of the nutrient has accumulated so that it no longer is limiting (e.g., Vitousek and Reiners 1975, Stoddard 1994, Aber et al. 1998). Barring recurring major disturbances such as hot fires or landslides, single-nutrient limitation should therefore be a transient phenomenon in natural forests, and internal supplies of potentially limiting nutrients should over time equilibrate at or near co-limitation. To the extent that losses depend upon nutrient availability within ecosystems, we are no closer to explaining why empirical observations differ from predictions of traditional models.

Hedin et al. (1995) suggested a different class of mechanisms that could influence the long-term development of nutrient cycles in forests. They argued that losses of nutrients that do not depend on immediate availability to the biota (i.e., are not subject to traditional mechanisms of biotic retention) can, over time, act to constrain nutrient accumulation and sustain nutrient limitation at the ecosystem level (Hedin et al. 1995, Vitousek et al. 1998, Perakis and Hedin 2002). The observation of substantial outputs of dissolved organic N (DON) from N-poor and unpolluted old-growth forests throughout temperate South America (Hedin et al. 1995, Perakis and Hedin 2001, 2002) led Hedin and colleagues to propose that DON could constitute a vector of N loss that occurs independently of ecosystem N availability—a loss or “leak” that is uncontrollable by traditional mechanisms of biotic uptake (Hedin et al. 1995).

This “leak” hypothesis offers a mechanism by which losses of biotically unavailable, yet hydrologically mobile, forms of nutrients can indefinitely sustain nutrient limitation, thereby counteracting the propensity for single-nutrient limitation to disappear (due to efficient nutrient retention) as nutrient cycles develop over time. We operationally define nutrients as “unavailable” if they occur in dissolved forms (e.g., humic complexes of DON) for which rates of biotic turnover are slower than rates of hydrologic export from the active plant-soil system to deeper soil water (Hedin et al. 1995). While substantially less abundant, organic forms such as amino acids and urea turn over rapidly (Näsholm et al. 1998) and, in the context of this study, are subject to “direct biotic control” in a manner similar to NO_3^- and NH_4^+ .

It is less clear, however, whether such fertility-independent mechanisms of DON loss also apply to dissolved forms of organic P (DOP), or gaseous forms of N that are produced during the soil N transformations of nitrification and denitrification. Plants and microbes have evolved elaborate mechanisms to increase the availability of organic P in soils, including release of extracellular phosphatases (McGill and Cole 1981) and symbiotic relationships with P-mining microbes (Rausch and Daram 2001). In addition, Walker and Syers (1976) argued that in highly weathered soils P could be made unavailable by abiotic sorption to Fe and Al sesquioxide clays (which are abundant in many old soils), even in shallow soil horizons with high root and microbial activity. It is not known whether—despite such biotic “retention efforts” and abiotic sorption—losses of DOP remain significant, or whether these losses are large enough to contribute to the maintenance of P limitation in old tropical soils. In contrast, our present understanding of gaseous N losses suggests that these depend on ecosystem N availability. Losses of nitric oxide (NO) and nitrous oxide (N₂O) are linked to high rates of nitrification (Firestone and Davidson 1989), while losses of N₂O and dinitrogen (N₂) occur primarily under high levels of NO₃⁻, organic carbon, and soil moisture in N-rich soils (Davidson et al. 1996, Hall and Matson 1999, Duan and Xiao 2000).

We also expect important interactions between base cations (Ca²⁺, Mg²⁺, Na⁺, and K⁺) and changes in N and P cycles as forest nutrient cycles develop over geologic time (see Walker and Syers 1976). Weathering is critical since—in addition to supplying P and base cations—it influences the formation and stability of secondary minerals (and associated ion-exchange sites), consumes acidity and generates alkalinity in soils and drainage waters, and consumes atmospheric CO₂ if carbonic or organic acids are the primary acids (or “weathering agents”) that mediate the weathering process (Bernier and Berner 1996). Recent studies of humid Hawaiian forests have shown that weathering dominates as a source of both P and base cations in young soils, and that dilute atmospheric inputs of Asian dust (P) and sea-salt aerosols (base cations) become increasingly important sources for forests on highly weathered substrates (Crews et al. 1995, Kennedy et al. 1998, Chadwick et al. 1999; also see Kennedy et al. 2002). It is not clear, however, how these long-term trends in weathering vs. atmospheric inputs translate into changes in ecosystem acid–base status and, in turn, export of P, individual base cations, and aluminum (Al) during the course of forest ecosystem development.

In this paper we examine how hydrologic and gaseous losses of nutrients change across a 4.1-million-year substrate age gradient of Hawaiian montane tropical forests, along which nutrient limitation shifts from N in young sites to P in the oldest (Crews et al. 1995, Vitousek and Farrington 1997). We approach this analysis from three different perspectives. First, we ask

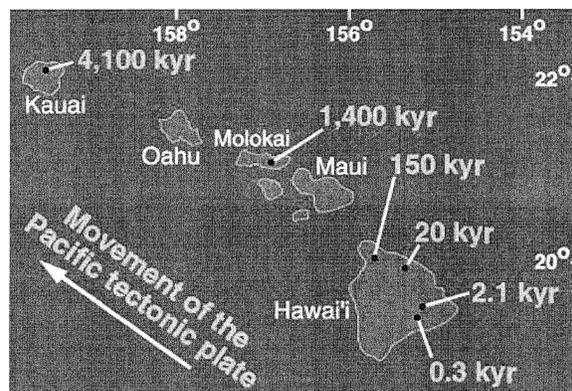


FIG. 1. Location of the age gradient of study sites across the Hawaiian Islands. The 300- and 2100-year-old sites are on the still-active Kilauea volcano, the 20 000-year-old site is on Mauna Kea, the 150 000-year-old site is on Kohala, the 1 400 000-year-old site is on East Molokai, and the 4 100 000-year-old site is on Kauai. (On the figure “kyr” stands for 10³ years.)

whether losses of base cations and P follow known trends in weathering vs. atmospheric inputs (Chadwick et al. 1999), and how these changes affect the overall acid–base status of these forest ecosystems. Second, we seek to understand whether losses of different forms of nutrients are controlled by long-term changes in nutrient availability or—in the case of DON and DOP—independent of ecosystem nutrient availability following the “leak” hypothesis. Third, we ask whether ecosystem N and P cycles equilibrate over geologic time scales and, if not, whether losses of DON and DOP act to sustain single-element limitation.

CONCEPTUAL AND EXPERIMENTAL APPROACH

Our work focuses on montane tropical forest ecosystems distributed along the 4.1-million-year Hawaiian substrate age gradient first described by Crews et al. (1995), and which has been formed by the northwest movement of the Pacific lithospheric plate over a stationary convective lava plume (hot spot) (Clague and Dalrymple 1987, Moore and Clague 1992). Our study considers six well-characterized forested sites (Fig. 1) on volcanic shield surfaces that originated as basaltic tephra or lava flows, with substrate ages ranging from 300 (Thurston) to 2100 (Ola’ a), 20 000 (Laupahoehoe), 150 000 (Kohala), 1 400 000 (Kolekole), and to 4 100 000 years (Kokee).

While our sites differ markedly in age and history, they share similar current climates (mean annual temperature of ~16°C and precipitation of ~2500 mm), plant communities (dominated by varieties of the native tree species *Metrosideros polymorpha*), and basaltic parent material (Table 1; Crews et al. 1995, Vitousek and Farrington 1997, Chadwick et al. 1999). The chemical and mineral composition of Hawaiian basalts has changed only slightly between early and late volcanic stages (Macdonald et al. 1983). Despite these similar-

TABLE 1. Site characteristics including information on soils and lysimeter installations along the substrate age gradient for the six Hawaiian montane tropical-forest sites studied.

Site	Substrate age (yr)	Elevation (m)	Approximate mean annual temperature (°C)	Approximate mean annual precipitation (mm)	Soil classification	Number of lysimeters†	Mean lysimeter depth (cm)
Thurston	300	1176	16	2500	isomesic amorphous ashy Lithic Hapludand	6	20
Ola'a	2100	1200	16	2500	isomesic glassy ashy Thaptic Udivitrand	2 + 6 ^Q	22
Laupahoehoe	20 000	1170	16	2500	isomesic ferrihydritic hydrous Hydric Hydrudand	6	32
Kohala	150 × 10 ³	1122	16	2500	isomesic amorphous hydrous Hydric Hydrudand	6	36
Kolekole	1400 × 10 ³	1210	16	2500	isomesic amorphous medial Hydric Hydrudand	6	25
Kokee	4100 × 10 ³	1134	16	2500	isomesic ferruginous very-fine Plinthic Kandiudox	6 + 6 ^Q	35

Note: Data are from Crews et al. (1995), Chadwick et al. (1999), Neff et al. (2000), and this study.

† A superscript Q indicates lysimeters installed with quartz slurry.

ities, the vast difference in age means that sites have been exposed to different histories of climate, vegetation, dust inputs, and isostatic and thermal subsidence (Moore and Clague 1992, Chadwick et al. 1999, Hotchkiss et al. 2000). Our analysis assumes that the residual effects of such historical differences among sites are small compared to consequences of substrate age for present day plant–soil–nutrient relations. From this perspective, the sites define a sequence of montane tropical forests assembled from similar species pools, but subject to substantially different degrees of weathering of soils and parent materials. In fact, soils and mineralogy change dramatically across the gradient, from relatively unweathered Hapludands rich in primary minerals, to Hydrudands characterized by accumulation of noncrystalline secondary minerals (e.g., imogolite and allophane), to Kandiudox (Oxisols) rich in highly weathered iron and aluminum sesquioxides (Table 1; Torn et al. 1997, Chadwick et al. 1999).

We could not employ the small-watershed approach (Bormann and Likens 1967) to study nutrient losses because constructional volcanic surfaces can occur only in locations with shallow to nonexistent slopes, because the geologic substrate is not hydrologically watertight at scales of small watersheds, and because the depth of weathering processes (>10 m in the oldest site) causes stream water to be influenced by deep geochemical processes that are biologically irrelevant to the shallow plant–soil system. Our approach was therefore to install lysimeters (collection devices for soil water) to intercept soil water that had moved through, and interacted with, the plant–soil system defined by the biologically active rooting zone. We installed these lysimeters below the layer of active root turnover (20–36 cm depth; Table 1), as inferred from distributions

of roots (Herbert and Fownes 1999, Ostertag and Hobbie 2000) and bomb-derived ¹⁴C throughout the soil profile (Torn et al. 1997). It should be noted, however, that while our measures in this sense characterize losses from the forest ecosystem, additional processes (e.g., sorption, desorption, microbial decomposition) may further influence water chemistry and element transport along flow paths from lysimeters to streams.

METHODS

Collection of soil solutions

At each site we installed 6 to 12 lysimeters randomly throughout an area 10 m in radius. After an initial 2–5 month equilibration period, we sampled lysimeters roughly monthly between August 1995 and May 1998, depending on site accessibility: Thurston (20 monthly events), Ola'a (15 events), Laupahoehoe (22 events), Kohala (15 events), Kolekole (10 events), and Kokee (16 events).

Lysimeters consisted of a cylindrical Teflon frame (2-cm diameter; 5-cm length of collection area) covered by 0.2 μm pore size quartz-gel (PRENART Corporation, Copenhagen, Denmark). We used a clean and sharpened steel tube corer (2.2-cm inner diameter) to create a 45°-angle access hole at the soil surface. The lysimeter was lowered through the steel tube (to prevent contact with the soil matrix) and pushed fully into the fresh undisturbed soil at the bottom of the access hole; the hole was then refilled with native soil material. Each lysimeter was connected by a 3-mm outer-diameter Teflon tube to a 1.5-L high-density polyethylene (HDPE) vacuum bottle. The access hole, tubing, and vacuum container were located down-slope of the lysimeter, thus minimizing any effects on soil water

flow paths. Lysimeters and collection vessels were acid washed, rinsed with copious amounts of deionized water, and tested for chemical contamination in our laboratory before installation.

In soils with high porosity (Ola'a), or where fine clay particles clogged the quartz-gel pores over time (Kokee), we improved capillary contact by installing additional lysimeters within slurries of clean and well-rinsed silica flour (Sibelco Corporation, Antherp, Belgium). At Kokee, where ambient Si and Ca²⁺ levels were exceedingly low, these slurry-based lysimeters yielded slightly higher Ca²⁺ and Si levels than non-slurry lysimeters; we therefore based all measures of Ca²⁺ and Si at Kokee solely on samples from non-slurry lysimeters.

We sampled soil solutions by applying 35 kPa vacuum to the collection containers over 1–3 days. We used a clean HDPE syringe to withdraw soil solutions via a small-diameter Teflon access tube that extended to the bottom of the collection vessel; this approach permitted us to withdraw samples without opening the sealed vacuum bottle. Samples from lysimeters and nearby small streams (at Laupahoehoe, Kohala, Moloai, and Kokee sites) were immediately filtered through a pre-rinsed Gelman type A/E glass fiber filter (<1- μ m nominal pore size, tested in our laboratory), stored in thoroughly rinsed clean HDPE bottles, kept on ice for up to six hours, and shipped by refrigerated air express for analysis at Cornell University (Ithaca, New York, USA). A fraction (13%) of all samples were collected in duplicate, with high-pressure-liquid-chromatography-grade chloroform (0.5% of final volume) added as a preservative to one sample. This treatment allowed us to examine the effectiveness of filtration and refrigeration for stabilizing the chemistry of water samples.

Dissolved nutrients

We analyzed the most sensitive dissolved species first, with average time elapsed between field sample collection and start of analyses ranging from 5.2 ± 2.6 d (mean ± 1 SD) at Ola'a) to 8.4 ± 6.9 d at Laupahoehoe). We immediately analyzed NH₄⁺ after opening each sample bottle to minimize entry of atmospheric NH₃. Preservation tests indicated that samples remained stable after collection and filtration. Correlations between duplicate samples with vs. without chloroform ($n = 45$ – 49 samples) were uniformly strong ($r > 0.97$) for all elements, with the exception of NH₄⁺, and displayed slopes that approximated unity (0.97–1.09). The correlation was weaker for NH₄⁺ ($r = 0.27$; $n = 47$ samples) because NH₄⁺ levels remained exceedingly low in nearly all samples; the slope did not differ significantly from unity ($P > 0.2$; $n = 47$ samples) although the scatter was considerable. Our tests further show that when filtered immediately in the field, representative solutes (NO₃⁻, PO₄³⁻, SO₄²⁻, and Cl⁻) were stable for at least three

weeks in capped and refrigerated bottles, with correlations between repeated analyses of $r > 0.93$ and slopes near unity (0.91–1.00); we found no evidence for contamination of NH₄⁺ or sorption of PO₄³⁻ within sample or lysimeter bottles. Our interpretation of Al chemistry assumes that we measured only dissolved Al, even though filtration through glass-fiber filters may not remove all particulate Al.

Analytical methods were: NO₃⁻-N, SO₄²⁻, and Cl⁻ by Dionex (Marlton, New Jersey, USA) chemically suppressed ion chromatography using AS4A column and pre-concentration for NO₃⁻ (Hedin et al. 1995); NH₄⁺-N, Si, and orthophosphate (referred to as PO₄³⁻) by Alpkem (OI Analytical, College Station, Texas, USA) and automated colorimetry (PO₄³⁻ was corrected for colorimetric Si interference by the empirically determined correction factor of $[\text{Si}] \times (8.8 \times 10^{-5})$; pH by potentiometry using a Ross electrode (Orion Research, Boston, Massachusetts, USA); Ca²⁺, Mg²⁺, K⁺, and Na⁺ by Perkin-Elmer (Shelton, Connecticut, USA) flame atomic absorption spectrophotometry (AAS); total Al by Perkin Elmer inductively coupled plasma emission spectroscopy; DOC (dissolved organic C) by Shimadzu (Tokyo, Japan) 5000 high-temperature (850°C) platinum catalyst combustion; DON (dissolved organic N) and DOP (dissolved organic P) by high-temperature (120°C) persulfate combustion, followed by colorimetric analyses of NO₃⁻ and PO₄³⁻ as described above (Alpkem; Hedin et al. 1995). We tested persulfate digestion efficiency against glycine, NO₃⁻, and NH₄⁺ standards, and by testing for residual DOC (after digestion) using high-temperature (850°C) platinum catalyst combustion. HCO₃⁻ and CO₃²⁻ were estimated from Gran-titrations of selected samples (Gran 1952). Method detection limits were: NO₃⁻-N, <0.045 μ g/L; NH₄⁺-N, <1.0 μ g/L; DON, <10 μ g/L; PO₄-P, <0.5 μ g/L; DOP, <1.0 μ g/L; Ca²⁺, <0.01 mg/L; Mg²⁺, <0.01 mg/L; K⁺, <0.005 mg/L; Na⁺, <0.1 mg/L; SO₄²⁻, <0.1 mg/L; Cl⁻, <0.01 mg/L; Si, <0.1 mg/L; total Al, <5 μ g/L; and DOC, <0.05 mg/L. For concentrations below these detection limits, we assigned a value of half the detection limit.

Trace-gas fluxes

We quantified N₂O-N and NO-N emissions at the soil-air interface using two-piece portable flux chambers. At each sampling time 8–12 polyvinyl chloride (PVC) rings (25-cm diameter) were placed in the soil (to 10-cm depth) and allowed to equilibrate for 15 min. After sealing 5-L chambers onto the rings, gas samples were removed from the headspace at 0, 10, 20, and 30 minutes using nylon syringes (Matson et al. 1996). Air samples and standards were analyzed for N₂O-N at the Hawai'i Volcanoes National Park (HVNP) laboratory (Hawaii, USA) within 30 h after sampling, using a gas chromatograph equipped with a ⁶³Ni electron capture detector (ECD). The same rings were used for NO-N flux measurements, which were taken within 1 h of the

N₂O-N sampling, and measured in situ using a portable Scintrex (Concord, Ontario, Canada) LMA-3 chemoluminescence detector (Matson et al. 1996). This detector was calibrated several times per day with a known standard in the field and further compared to a NO-N standard in the laboratory. Minimum detectable flux was $\sim 0.05 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$. Air temperature was taken in the shade and soil temperature was measured at 2-cm depth at the time gases were sampled.

Because gas emissions showed no discernable seasonality and other studies in Hawaii showed low diel variability (Matson et al. 1996), we estimated annual N gas emissions by assuming a constant flux over 24 h, and extrapolated to an annual basis by multiplying the average daily flux over all sampling dates by 365 days. To estimate N₂ lost from these soils, we carried out acetylene inhibition experiments (Davidson 1992) two times in each site. We applied high (10 kPa) C₂H₂ concentrations to block the reduction of N₂O to N₂. For each sample (4–8 samples per site, per time), an intact soil core was removed and clumps of intact soil ($\sim 25 \text{ g}$ wet mass) were placed in paired 0.475-L mason jars and sealed with lids fitted with rubber septa; 250-mL headspace air was thus removed from each jar. In one jar of each pair, 50 mL of C₂H₂ was injected into the headspace and allowed to sit for 5 min before venting; the second jar was vented at the same time and treated as the control. Five milliliter subsamples were removed after 1 and 6 h of incubation, and analyzed for N₂O as described above. The rate of production was calculated for both controls and C₂H₂-treated samples, and we inferred N₂ production by subtracting the C₂H₂ treatment from the control. We calculated the ratio of N₂:N₂O in samples where both gases were produced, and applied that ratio to the annual measures of N₂O fluxes as a rough estimate of annual N₂ fluxes.

Soil nutrients and transformations

Soil nitrogen (N) transformations and pools of inorganic N were measured each time gases were sampled. Mineral soils were sampled to 10-cm depth; where present, organic layers were sampled separately. Samples were transferred on ice to the HVNP laboratory, where they were processed within 24–48 h of sampling. Soils were hand-mixed and rocks and roots to 4-mm diameter were removed. One 10-g subsample was immediately placed in 50 mL of 2-mol/L KCl, shaken for 1 min, allowed to equilibrate for 18–24 h, filtered through pre-leached filters, and stored frozen until analyzed for NH₄⁺-N and NO₃⁻-N on a continuous-flow autoanalyzer (Matson et al. 1996). An additional 10-g subsample was placed in a covered cup and incubated in the dark at $\sim 20^\circ\text{C}$ for 7–10 d, then extracted and analyzed as described above. Net N mineralization (NH₄-N plus NO₃-N production) and net nitrification (NO₃-N production) were calculated as incubated minus initial inorganic N concentrations, and expressed as rates per day. Additional soil samples

($\sim 50 \text{ g}$) were dried at 105°C for determination of soil moisture and bulk density.

Tests of lysimeter collections

We used two approaches to examine how well the lysimeter collections approximated dissolved nutrient outputs from these forests. First, we compared the chemistry of soil waters against first-order streams that drained four of our six sample sites (Appendix A). We assumed that Cl⁻ behaves as a hydrologic tracer of sea-salt aerosol (see *Methods: Atmospheric sea-salt corrections*). We found a strong and linear relationship between coincident samples of Cl⁻ in stream vs. soil waters across all sites, with a slope near unity ($P < 0.001$; $r^2 = 0.88$; slope = 0.9; intercept is nonsignificant at $P > 0.6$; $n = 28$ samples). We interpret this similarity to show that lysimeter and stream waters were closely coupled across sites, and that effects of evapotranspiration (ET) on Cl⁻ concentrations did not differ substantially between the two water sources. Comparison of other solutes showed: (1) close similarities of major sea-salt-derived elements between lysimeters and streams (Cl⁻, Na⁺, SO₄²⁻, Mg²⁺); (2) a tendency for higher Si and pH, and substantially higher Ca²⁺ and PO₄³⁻ in streams than in lysimeters, particularly in younger sites; and (3) sometimes similar and sometimes lower NO₃⁻ levels in streams vs. lysimeters. We interpret these patterns to reflect: little evidence for differences in ET between lysimeters and streams (thus observation 1, above); some (but limited) influence by deeper flow paths in contact with weathering zones (thus observation 2, above); and evidence of denitrification and/or other NO₃⁻ losses along flow paths from soils to streams (thus observation 3, above).

Second, we examined how well lysimeters collected gravity-flow soil water at sites with the most different soil structure: Thurston (300 yr old), characterized by coarse and unweathered tephra with little clay content, and Kokee (4 100 000 yr old), characterized by fine and highly weathered Fe and Al clays. We added a NaBr tracer solution (at 0.5 mg Br⁻/L) throughout a 1-m-diameter soil area above a randomly selected lysimeter. We maintained addition rates at 2.5 cm/h, below the soil infiltration capacity. Lysimeter Br⁻ responded following a standard “breakthrough curve” (Freeze and Cherry 1979) from which we could estimate vertical travel velocity and dispersion.

At Thurston, the Br⁻ tracer moved faster (4.0 cm/h) through the soil matrix than the tracer addition rate (2.5 cm/h), indicating the existence of preferential paths of soil water flow. Nevertheless, lysimeters sampled close to 90% of the added Br⁻ concentration at peak Br⁻ levels. In contrast, we found no evidence of preferential flow at Kokee, with the average travel time (2.5 cm/h) indistinguishable from the tracer addition rate (2.5 cm/h). It took longer for the breakthrough curve to equilibrate at Kokee, and lysimeter Br⁻ was still increasing after 38 h, at which point lysimeter Br⁻

equaled 56% of the addition solution. This slow equilibration at Kokee likely reflects one or more of the following: (a) the relatively deep (35 cm) location of lysimeters in the soil profile integrates water flow that occurs over scales greater than the 1-m-diameter tracer addition; (b) slow exchange of Br^- between gravity-flow water and water held more tightly within the soil matrix (i.e., dispersion); or (c) sorption of Br^- onto variable-charge sites that occur in the highly weathered soils at Kokee.

Calculation of hydrologic fluxes

We measured precipitation volumes directly at four of six sample sites. At Laupahoehoe, Kolekole, and Kokee we used manual integrating precipitation collectors that were emptied at each lysimeter sample effort. At Thurston we used an automated tipping bucket collector, operated by B. J. Huebert of the University of Hawaii (*personal communication*); we also used this record as a proxy for the nearby Ola'a site. We could not maintain a collector at the Kohala site, and therefore only report expected precipitation volumes from this site, as interpolated from Giambelluca et al. (1986); earlier observations by Herbert (1995) yielded ~ 2500 mm/yr.

We used the Thornthwaite-Mather technique to calculate soil water balances and to estimate losses of soil water moving below the lysimeter depth of each site (Table 1; Thornthwaite and Mather 1955, Steenhuis and van der Molen 1986). We used -200 vs. -1500 kPa water content (O. Chadwick, *personal communication*) to approximate available water capacity for layers between the soil surface and 5-cm, 20-cm, 30-cm, and 35-cm depth. While we did not have measures at -33 kPa, at which field capacity is traditionally defined, we used standard power-law relationships between the -200 and -1500 kPa measures vs. volumetric water content to estimate field capacity at -33 kPa. By recalculating water balances based on these adjusted estimates, we found that our use of -200 kPa measures had only a small (0.9–4.6% decrease in ET) effect on overall water budgets at the depth of lysimeters, across all sites. We adopted a mean potential ET of 3.5 mm/d, which we varied to fit empirically observed seasonality. Because precipitation volumes during our study period were greater than the expected long-term mean volumes at each site, we calculated soil water losses in two ways: (1) using the volumes obtained during this study period, and (2) using long-term average volumes at each site. We then estimated hydrologic nutrient losses by multiplying the average annual concentration of a nutrient/solute times the annual calculated soil water flux at the lysimeter depth in each site. We did not stratify our flux calculations by season or event, since we observed no seasonal variations in nutrient concentrations. The resulting values represent best-effort estimates of hydrologic nutrient losses, giv-

en the limits of our lysimeter-collection approach and hydrologic budget (Steenhuis and van der Molen 1986).

Atmospheric sea-salt corrections

We used Cl^- as a hydrologic tracer to calculate net ecosystem retention vs. release of nutrients relative to inputs of atmospheric sea-salt aerosols (Hedin et al. 1995). This approach assumes that Cl^- originates predominantly from sea-salt aerosol inputs, and that Cl^- acts conservatively along hydrologic flow paths within the ecosystem. All our sites receive orographic precipitation from northeast trade winds that bring marine air masses dominated by sea-salt aerosols; each site is located in close downwind proximity to the ocean (Thurston ~ 38 km, Ola'a ~ 35 km, Laupahoehoe ~ 13 km, Kohala ~ 14 km, Kolekole ~ 14 km, and Kokee ~ 7 km). Thurston and Ola'a are influenced by local volcanic SO_2 and NO_x emissions (Huebert et al. 1999), and possibly by Cl_2 or HCl produced as lava enters the ocean south of both sites (McGee and Gerlach 1998). The use of Cl^- as a conservative tracer was supported by a strong decrease in soil water Cl^- with distance of sites from the ocean, by low Cl^- abundance in basalts (Berner and Berner 1996), and by Cl^- outputs ($30\text{--}160$ $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$) that were orders-of-magnitude greater than any possible internal net biotic sink or source.

Other sea-salt elements (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and SO_4^{2-}) occur in strict ratios relative to Cl^- in sea-salt aerosols (Keene 1986). By comparing observed element: Cl^- ratios in hydrologic losses against these theoretical sea-salt ratios, we can quantify net retention or release of individual elements within the forest ecosystem. We corrected soil solutions for the influence of sea-salt aerosols using the following sea-salt mass ratios (R_{ss}) relative to Cl^- (Keene et al. 1986): $\text{Na}^+ = 0.559$, $\text{K}^+ = 0.0207$, $\text{Mg}^{2+} = 0.0672$, $\text{Ca}^{2+} = 0.0214$, and $\text{SO}_4^{2-} = 0.141$. Net element release within the ecosystem would produce element: Cl^- ratios in outputs that were greater than the theoretical sea-salt aerosol ratio ($R_{\text{out}} > R_{\text{ss}}$); conversely, net retention would produce output ratios that were lower than sea-salt aerosols ($R_{\text{out}} < R_{\text{ss}}$).

RESULTS AND DISCUSSION

We summarize in Appendices A, B, and C our measures of dissolved nutrients in soil solutions and streams, soil N gas fluxes, soil N pools, soil N mineralization, and soil nitrification across the age gradient of study sites. In Appendices B and C we also provide two measures of temporal and spatial variability at each site: the range in monthly mean values, and the range in standard errors of the replicate samples that compose each monthly mean. For virtually all parameters of interest, trends across the age gradient were substantially greater than within-site variability. For example, error bars in Figs. 2, 3 and 5 are small and even indistinguishable from the symbols that denote average trends across sites.

Losses of weathering- vs. aerosol-derived nutrients

Our results are consistent with the idea that developmentally young forests are subject to strong weathering inputs of P and base cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+), while older forests increasingly depend on atmospheric sources of these nutrients (Walker and Syers 1976, Gorham et al. 1979, Kennedy et al. 1998, 2002, Chadwick et al. 1999). Subtraction of the influence of sea-salt aerosols (hereafter indicated by “*” before the solute formula, e.g., $^*\text{SO}_4^{2-}$) revealed that hydrologic losses of all non-sea-salt base cations (Fig. 2A), PO_4^{3-} (Fig. 3B), Si (Fig. 2B), and to some extent $^*\text{SO}_4^{2-}$ (Fig. 2B), followed a very similar pattern across the age gradient: high levels in the two youngest forests (300 and 2100 years old), a marked decrease in the 20 000-year-old forest, and a further drop to near or even below zero in forests older than 20 000 years. The trend in $^*\text{SO}_4^{2-}$ followed these trends with the exception of a more gradual decline in $^*\text{SO}_4^{2-}$ than any of the base cations over the first 20 000 years.

These patterns are consistent with the existence of a strong weathering source for these elements in the two youngest forests, a steep reduction in this source between 2000 and 20 000 years, and low or negligible weathering input above the depth of the lysimeters in forests older than 20 000 years. The lack of significant Si in sea-salt aerosols (Keene et al. 1986) permitted us to use dissolved Si as a proxy tracer of silicate weathering within our soil profiles; the trend in Si losses across the gradient supports the idea that weathering inputs dropped dramatically between the 2000- and 20 000-year-old forests (Fig. 2B). The existence of uniformly strong correlations between concentrations of individual sea-salt corrected base cations and Si ($r = 0.69\text{--}0.98$; $P < 0.001$; $n = 83\text{--}87$ monthly averages), and between PO_4^{3-} and Si ($r = 0.71$; $P < 0.001$; $n = 89$ monthly averages), provide further evidence of a close link between weathering and hydrologic nutrient losses, both within and across sites. These trends are consistent with observed changes in soil composition across the age gradient: apatite-bound weatherable P (Table 2), exchangeable cations (indicated by Ca^{2+} in Table 2), integrated (relative to parent material) losses of P and Si, and Sr isotopes across the same Hawaiian substrate age gradient (Crews et al. 1995, Kennedy et al. 1998, Chadwick et al. 1999). Weathering thus constitutes a dominant control on changes in hydrologic losses of base cations and PO_4^{3-} over the course of Hawaiian forest development.

Retention of rock-derived nutrients

We used slopes of the linear regressions between sea-salt-corrected base cations vs. Si, and PO_4^{3-} vs. Si, to quantify the average ratios of each element vs. Si in hydrologic losses, relative to ratios observed in Hawaiian basalt parent material (Moore and Fabbi 1971; O. A. Chadwick, *personal communication*); these

slopes and regression statistics are summarized in Table 3. We show in Fig. 4 that ratios of $^*\text{Ca}^{2+}$, $^*\text{K}^+$, and $^*\text{Na}^+$ vs. Si deviated less than 30% from their abundance ratios in bulk parent material, suggesting that hydrologic losses were roughly consistent with congruent release of those elements by weathering. In contrast, soil solution $^*\text{PO}_4^{3-}$ was reduced by as much as 97% below expected concentration ratios relative to Si. Since P is primarily found in apatite and other highly weatherable minerals (Crews et al. 1995, Berner and Berner 1996), we conclude that P released by weathering was strongly retained within our young forests, and did not accompany Si in soil water losses below the active rooting zone. Chadwick et al. (1999) estimated a *net* loss of total P from the soil as a whole—that is, weathering release corrected for retention by biotic uptake and the formation of occluded forms of soil P—of $\sim 10 \text{ mg}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ over the first 2000 years of soil development (scaled to a depth of 20 cm), which corresponds to a volume-weighted concentration loss of $\sim 5.8 \mu\text{g P/L}$. This predicted value agrees well with our measures of 3.6–4.9 $\mu\text{g/L}$ total P in soil solutions draining the 300- and 2000-year-old sites (Fig. 3B and Appendix B).

We conclude that most P released by primary mineral weathering was efficiently retained by plant and microbial uptake, with P accumulating over time in more refractory soil organic pools and “occluded” inorganic pools (Table 2; cf, Crews et al. 1995). Despite such strong retention, available P was not completely retained within the plant–soil–microbe system, causing significant hydrologic loss of PO_4^{3-} and dissolved organic P (DOP).

In contrast, losses of $^*\text{Mg}^{2+}$ were elevated by 87% above the ratio to Si in parent rocks, likely due to preferential weathering of the Mg^{2+} -rich minerals olivine and pyroxene that is known to take place in young Hawaiian basalts (Wasklewitz 1994). Perhaps most remarkably, loss ratios of $^*\text{SO}_4^{2-}$ vs. Si were elevated 550-fold above the ratio expected from congruent weathering alone (Fig. 4), equivalent to as much as 11 mg/L SO_4^{2-} over and above sea-salt contributions (Fig. 2B and Fig. 5). Such dramatically high $^*\text{SO}_4^{2-}$ levels can only be explained by an additional external source, such as the deposition of acidic sulfur gases and aerosols emitted from the nearby ($\sim 6\text{--}7 \text{ km}$ from our two youngest sites) and active Kilauea Volcano (McGee and Gerlach 1998). The close correlation between $^*\text{SO}_4^{2-}$ and Si across sites and months (Table 2; $r = 0.79$; $P < 0.001$; $n = 89$ samples) likely reflects the influence of volcanic-derived sulfuric acid as a dominant weathering agent in young soils.

Differing source relationships among elements

Despite the generally similar loss patterns of rock-derived elements, we found diagnostic differences among monovalent base cations, divalent base cations, and SO_4^{2-} across the age gradient. We show in Fig. 2D

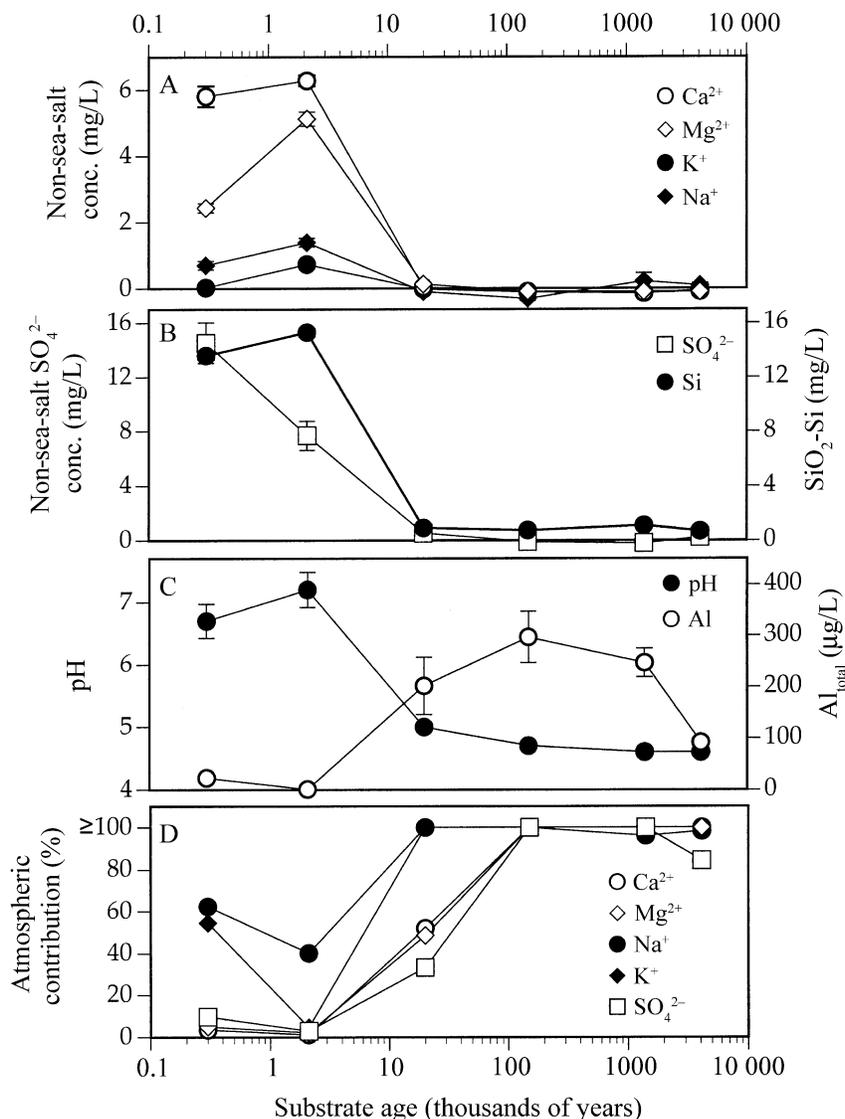


FIG. 2. Nutrient and element concentrations, free acidity, and atmospheric sea-salt contribution in soil waters below the active rooting zone across the age gradient of study sites. Each value is the long-term arithmetic mean based on 10–22 monthly sample efforts, from 6–12 lysimeters at the different sites (see Appendix B). Values for Al_{total} are based on fewer samples and replicates. Error bars identify 1 SE of the mean; the absence of error bars indicates that errors were too small to be differentiated from individual symbols. (A) Sea-salt-corrected concentrations of Ca^{2+} , Mg^{2+} , K^+ , and Na^+ . (B) Concentrations of dissolved Si, and of sea-salt-corrected SO_4^{2-} . (C) The pH and concentrations of total dissolved aluminum (Al_{total}). (D) Percentage contribution by atmospheric sea salts to concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and SO_4^{2-} ; “ $\geq 100\%$ ” indicates that our Cl-based sea-salt correction could explain 100% or greater of the observed lysimeter concentrations. Note the x-axis logarithmic scale.

that SO_4^{2-} and the divalent cations Ca^{2+} and Mg^{2+} shifted sharply from $<5\%$ sea-salt aerosol contribution in the 300- and 2100-year-old sites, to near 100% aerosol contribution in sites 150,000 years and older. In contrast, the monovalent cations K^+ and Na^+ were more strongly influenced by sea-salt aerosols even in young sites; as much as 55–65% of losses were due to sea salts even at 300 years of substrate age. These differences extended to the 20,000-year-old forest, in which atmospheric sources contributed nearly 100% to losses

of K^+ and Na^+ , but only 48 vs. 51%, respectively, to losses of Ca^{2+} and Mg^{2+} (Fig. 2D). These differing source relations are consistent with the observation of low ratios of divalent to monovalent base cations in sea salt and by high ratios in primary rocks (Clague and Beeson 1980, Keene et al. 1986, Clague and Dalrymple 1988, West et al. 1988). In addition, the low influence of aerosols on SO_4^{2-} losses from young sites is consistent with high inputs of sulfur from volcanic aerosols.

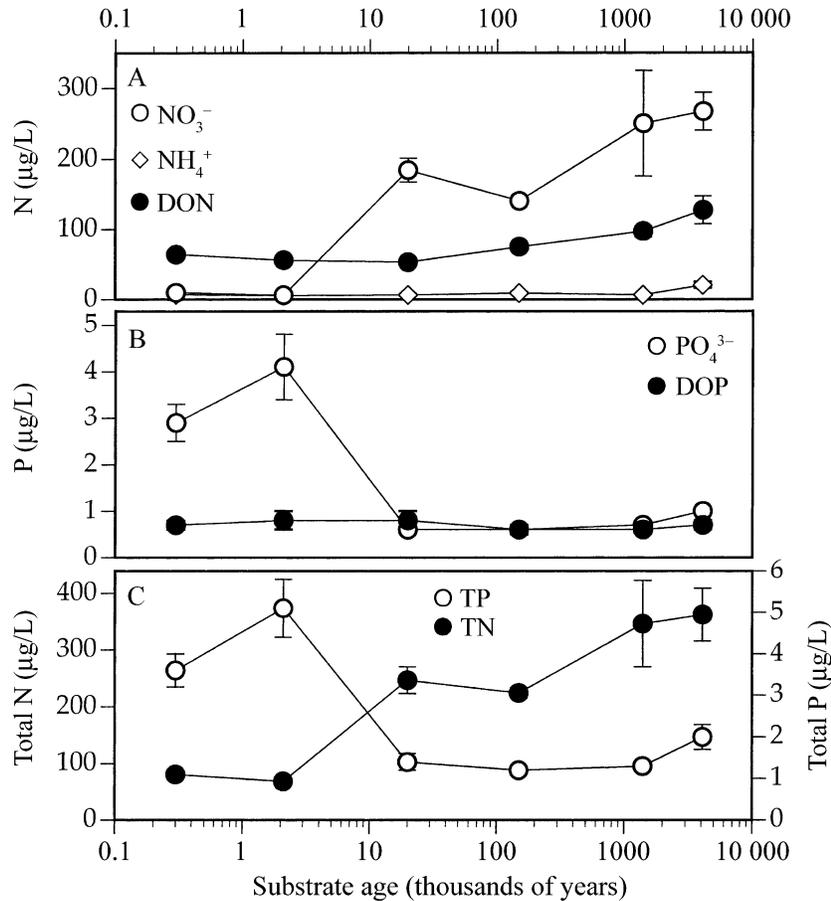


FIG. 3. Concentrations of different forms of N and P in soil waters below the active rooting zone across the age gradient of study sites. Each value is the long-term arithmetic mean based on 10–22 monthly sample efforts, from 6–12 lysimeters at the different sites (see Appendix B). Error bars identify 1 SE of the means; the absence of error bars indicates that errors were too small to be differentiated from individual symbols (A) Concentrations of NO_3^- , NH_4^+ , and DON (dissolved organic nitrogen). (B) Concentrations of PO_4^{3-} and DOP (dissolved organic phosphorus). (C) Concentrations of total N (sum of NH_4^+ , NO_3^- , and DON) and total P (sum of PO_4^{3-} and DOP) Note the x-axis logarithmic scale.

TABLE 2. Summary of soil nutrient contents, cation exchange properties, and soil pH across the Hawaiian forest age gradient.

Site	Depth sampled (cm)	Organic C (kg/m ²)	Total N (kg/m ²)	P			CEC (cmol/kg)	Exchangeable Ca ²⁺ (cmol/kg)	Exchangeable Al ⁿ⁺ (cmol/kg)	Base saturation (%)	pH¶
				Total P (kg/m ²)†	Weatherable P (%)‡	Refractory P (%)§					
Thurston	35	12.0	0.7	0.45	82	16	25.2	2.7	0.57	19	5.1
Ola'a	45	11.9	0.8	0.43	60	32	27.6	4.4	0.22	26	5.6
Laupahoehoe	39	23.3	1.2	0.34	1.3	72	80.0	1.5	2.8	5.5	4.0
Kohala	48	31.9	1.4	0.54	<1	68	76.4	1.1	5.3	3.4	4.3
Kolekole	38	14.6	0.7	0.35	<1	80	52.6	0.66	4.9	4.3	4.3
Kokee	49	20.5	1.0	0.47	<1	72	43.3	0.98	3.5	6.6	4.3

Notes: Data are averages integrated to depths at or near the location of soil lysimeter in each profile, with the exception of P (see †). All values are courtesy of Oliver Chadwick (*personal communication*), except those for P, which are from Crews et al. (1995).

† Total P is based on a uniform depth of 50 cm at all sites.

‡ Weatherable = P bound in apatite minerals.

§ Refractory P is the sum of organic and occluded pools of P (cf. Crews et al. 1995).

|| CEC = cation exchange capacity.

¶ Measured in 1:1 ratio soil and distilled water.

TABLE 3. Ratios of non-sea-salt elements vs. silica in soil solutions (mean \pm 1 SE) calculated from least-square regression fits between monthly average concentrations from each sample site.

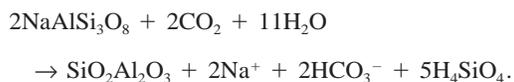
Element ratio	Ratio in soil solutions†	<i>n</i>
*Ca ²⁺ :Si	0.45 \pm 0.009	87
*Mg ²⁺ :Si	0.28 \pm 0.013	86
*Na ⁺ :Si	0.080 \pm 0.008	84
*K ⁺ :Si	0.031 \pm 0.004	83
*SO ₄ ²⁻ :Si	0.82 \pm 0.068	89
PO ₄ ³⁻ :Si	0.00021 \pm 0.00002	89

Notes: Ratios are influenced by high inputs of base cations, SO₄²⁻, and PO₄³⁻ at the two youngest sites (Thurston and Ola'a). We did not apply a sea-salt correction for PO₄³⁻ as it is not significantly present in sea-salt aerosol and marine precipitation. For the last column, *n* = number of monthly averages used in the regression.

† All data are statistically significant at $P < 0.001$.

Weathering mechanisms and fate of CO₂ over geologic time

Mechanisms of weathering matter not only for understanding how nutrients enter forests from rocks, but also for whether soils can act as sinks for atmospheric CO₂ as they develop over geological time (Berner 1992, Chadwick et al. 1994). In the case of silicate minerals (which make up the great majority of Hawaiian basaltic parent material), all weathering processes mediated by either carbonic (i.e., CO₂ + H₂O) or organic (i.e., RCOO⁻ + H⁺) acids result in net removal of CO₂ from the atmosphere, such as in albite (NaAlSi₃O₈) weathering to imogolite (SiO₂Al₂O₃):



In this case, consumption of carbonic acid transfers atmospheric C to dissolved bicarbonate (HCO₃⁻). Bicarbonate, in turn, accompanies cations (in this case Na⁺) as soil water drains into streams, rivers, and—eventually—the ocean. Half of C captured within this HCO₃⁻ eventually precipitates as carbonates in ocean sediments (the other half returns as CO₂ to the atmosphere; Berner 1992), causing net removal of C from the atmosphere–biosphere cycle, which operates over decades to millennia, and net addition of C to the tectonic atmosphere–lithosphere cycle, which operates over hundreds of millions of years (Berner 1992, Van Capellen and Ingall 1996). Organic acid-mediated weathering can similarly remove atmospheric CO₂ over long time scales, if organic anions (RCOO⁻) are either decomposed to HCO₃⁻ (Berner and Berner 1996) or deposited in environments that offer long-term protection from decomposition (e.g., clay-rich soils; Torn et al. 1997). In contrast, weathering by strong mineral acids does not affect the atmospheric CO₂ balance, as the weathering reaction does not involve any net transfer of atmospheric C to either RCOO⁻ or HCO₃⁻.

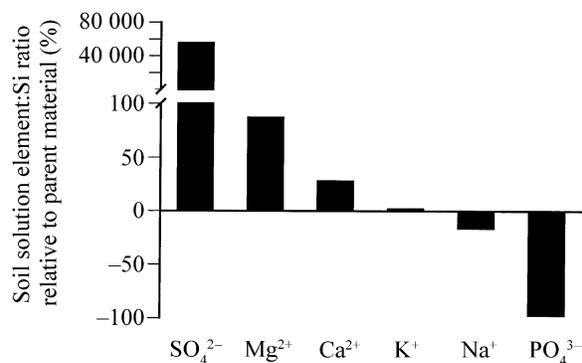


FIG. 4. Element-to-Si concentration ratios in soil solutions relative to the ratio of element-to-Si expected from the congruent weathering of geologic parent materials. The y-axis indicates the percentage increase (or decrease) of elements in soil solutions compared to concentrations expected from congruent weathering. Positive values indicate net enrichment, and negative values indicate net retention of an element relative to weathering input. Elements were corrected for the influence of sea-salt deposition (see *Methods: Atmospheric sea-salt correction*).

In Fig. 5 we examine each of these weathering mechanisms by evaluating contributions of HCO₃⁻, RCOO⁻, SO₄²⁻ (anion of sulfuric acid), and NO₃⁻ (anion of nitric acid) to total anionic charges in soil water below the active rooting zone in the 300-, 20 000- and 150 000-year-old forests. This analysis shows that weathering was predominately mediated by sulfuric acid in the youngest Hawaiian forests (Fig. 5A). After correcting for sea salts, *SO₄²⁻ was the dominant (66%) contributor to anionic charges, with only minor contributions from HCO₃⁻ (13%) and RCOO⁻ (5%). We conclude that volcanic emissions of acidic sulfur can substantially influence local weathering regimes, without causing a corresponding effect on atmospheric CO₂ uptake.

Total dissolved elements were distinctly lower at the 20 000- and 150 000-year-old sites (Fig. 5B and C), a pattern consistent with reduced deposition of acidic sulfur (as indicated by lower *SO₄²⁻ levels in Fig. 2B), reduced overall weathering rates (as indicated by lower non-sea-salt base cations in Fig. 2A), and greater influence of dilute atmospheric sea salts (Fig. 2D). Organic acids contributed most to total non-sea-salt anion charges at both 20 000 and 150 000 years (71 and 82%, respectively). Contributions from NO₃⁻ (14 and 18%, respectively) and *SO₄²⁻ (15 and 0%, respectively) remained relatively low, and pH was too low (pH < 5) to permit any significant HCO₃⁻. These results lead us to infer that organic acids and NO₃⁻ (produced by nitrification) were the dominant sources of acidity in forests older than 20 000 years. Export of this acidity to deeper and less weathered soil horizons can sustain weathering processes along deep hydrologic flow paths and, in the case of organic acids, cause sustained net uptake of atmospheric CO₂.

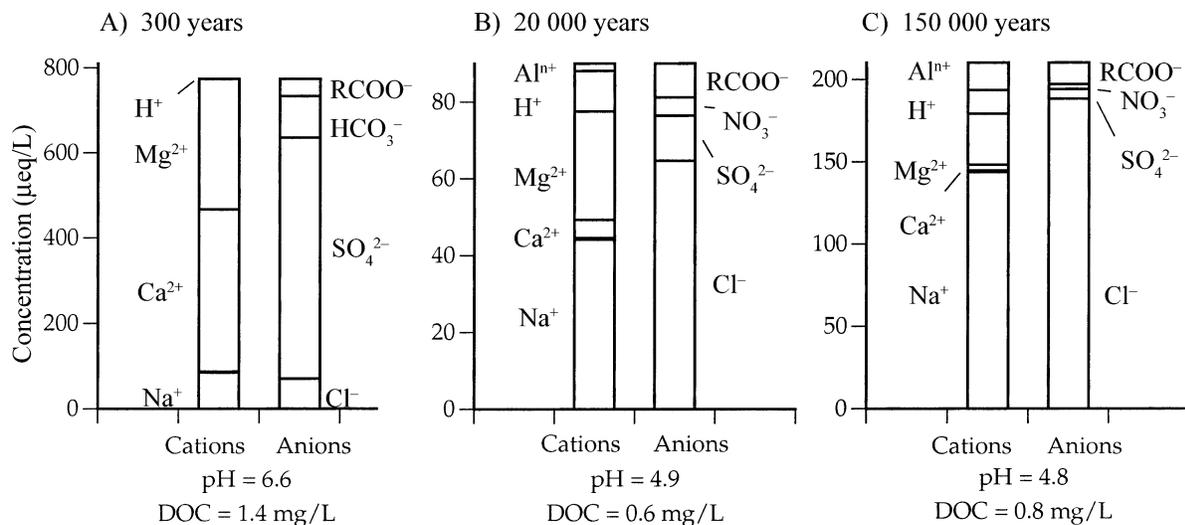


FIG. 5. Complete anion-cation charge balance of major solutes in soil waters below the active rooting zone at three of the study sites ($n = 3$ samples, each site). Note the reduction in scale between the youngest vs. two older sites, due to diminished influence of H_2SO_4 -driven weathering (see *Results and discussion: Retention of rock-derived nutrients*); the increase in scale between 20 000 and 150 000 years reflects higher contributions by sea-salt aerosols at the latter site (see *Methods: Atmospheric sea-salt corrections*). Solute concentrations are presented as micro-equivalents of charge per liter of solution ($\mu\text{eq/L}$), which represents molar concentrations multiplied by the equivalent charge of each solute. Contributions of organic acids (RCOO^-) were calculated from the charge discrepancy of cations minus anions. Al^{n+} represents the charge of inorganic and organic Al, determined by applying a chemical equilibrium model to measures of total dissolved Al (see *Methods and discussion: Natural ecosystem acidification*). Bicarbonate (HCO_3^-) was determined from Gran alkalinity titrations (see *Methods: Dissolved nutrients*). Dissolved Al_{total} was insignificant at the 300-year-old site, while HCO_3^- was insignificant at the 20 000 and 150 000-year-old site. DOC = dissolved organic carbon.

Natural ecosystem acidification

This Hawaiian-forest age gradient offers a striking example of natural ecosystem acidification over geologic time. Acidity (pH) and total dissolved aluminum (Al_{total}) showed strong and diagnostic trends across the age gradient (Fig. 2C). Soil solutions were circumneutral (pH 6.7–7.2) in the two youngest forests, which—in combination with accumulation of non-sea-salt base cations (Fig. 2A) and HCO_3^- (Fig. 5A)—indicates that weathering was rapid enough to consume all inputs of acidity to the soil profile. However, the acid-base status of soil solutions changed dramatically and nonlinearly between 2000 and 20 000 years of age, as evidenced by a two-order-of-magnitude increase in acidity (from pH 7 to <5.0), by sharp drops in non-sea-salt base cations and Si (Fig. 2A and B), and by an abrupt increase in dissolved Al (Fig. 2C). We show in Table 2 that in parallel with these dramatic changes in solution chemistry, pools of exchangeable cations dropped from high base saturation (18–26%) and dominance by essential plant nutrients (e.g., Ca^{2+} , Mg^{2+} , and K^+) in young soils, to <5% base saturation and dominance by free acidity and exchangeable Al in soils older than 20 000 years (data provided by O. Chadwick, *personal communication*).

This natural progression of forest acidification is consistent with a sharp drop in weathering rates after 20 000 years of forest development, to levels at which

weathering no longer can neutralize internal production of organic (from soil and/or plant organic matter) and nitric acids (from nitrification). This intimate coupling between forest acid-base status, silicate weathering, and supplies of base cations is further evidenced by strong correlations between monthly average soil solution pH from all sites and dissolved Si ($r = 0.94$; $P < 0.001$; $n = 87$ monthly averages) or $^*\text{Ca}^{2+}$ ($r = 0.98$; $P < 0.001$; $n = 87$ monthly averages), and by the observation that weatherable silicate minerals are exhausted in soil profiles older than 20 000 years (Chadwick et al. 1999).

Our results show that while dissolved Al remained low (<20 $\mu\text{g/L}$) in the two youngest sites, concentrations increased about 10-fold (to $\sim 200 \mu\text{g/L}$) at the 20 000-year-old site (pH 5.0), and reached exceedingly high levels (up to 300 $\mu\text{g/L}$) in developmentally older forests (Fig. 4C). These changes were paralleled by increases in exchangeable Al across the age gradient (Table 2). This dramatic Al trend is consistent with dissolution of imogolite and similar noncrystalline Al minerals under highly acidic conditions, in which neutralization of acidity by weathering and cation exchange has been largely exhausted (Driscoll and Schecher 1988, Sposito 1989). The close link between soil acidity and Al dissolution is further indicated by an inverse correlation of dissolved Al and pH across the age gradient ($r = -0.65$; $P < 0.001$; $n = 25$), and

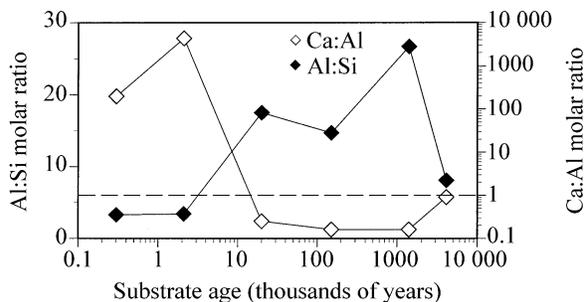


FIG. 6. Changes in dissolved molar ratios of Ca:Al and Al:Si in soil solutions across the age gradient. The dashed line indicates the 1.0 critical Ca:Al ratio below which damage to temperate tree species is common (Cronan and Grigal 1995). Note the logarithmic scales for the x-axis and the right-side y-axis.

by high exchangeable Al^{n+} in older sites (Table 2). However, soil solution levels of Al_{total} in the oldest forest remained moderate ($\sim 90 \mu\text{g/L}$) despite persistently low solution pH of ~ 4.6 ; this pattern is associated with a nearly complete exhaustion of soluble secondary Al minerals at this site (Torn et al. 1997, Chadwick et al. 1999) and with a parallel drop in exchangeable Al^{n+} (Table 2).

We used the chemical equilibrium model MINEQL+ (Schecher and McAvoy 1998) to further investigate controls on dissolved Al across the forest age gradient. We estimate that dissolved Al predominately (89–93%) occurred as organic complexes (Al_{org}) across all sites, with only ~ 7 –11% occurring as free inorganic Al^{n+} —the form thought to be most toxic to organisms (Driscoll et al. 1980, Cronan and Grigal 1995). We also found a dramatic drop in the ratio of dissolved Ca^{2+} : Al^{n+} , and increase in Al:Si across the age gradient (Fig. 6). In our most acidic soils, molar ratios of Ca: Al_{total} (< 0.3) were substantially below ratios considered as “critical thresholds” for tree species in temperate regions (Cronan and Grigal 1995). However, we do not know the biological implications of such low Ca: Al_{total} ratios in these Hawaiian forests, or whether the apparent complexation by organic acids renders Al less toxic to *Metrosideros polymorpha* and other plant species.

Hydrologic losses of N and P

Dissolved losses of NO_3^- and PO_4^{3-} differed markedly across the age gradient, following the shift from N limitation in young forests, to N sufficiency and P limitation in developmentally old forests (Vitousek and Farrington 1997). Levels of NO_3^- (Fig. 3A) were exceedingly low ($< 10 \mu\text{g N/L}$) in the youngest sites where N limits plant growth, increased sharply at 20 000 years where forests are co-limited by N and P, and reached a maximum of $270 \mu\text{g N/L}$ in the oldest site where plant growth is singularly limited by P. Directly opposite to these NO_3^- variations, losses of PO_4^{3-} were highest in the N-limited young forests, and ex-

ceedingly low ($< 0.5 \mu\text{g P/L}$) in the P-limited older sites (Fig. 3B).

In contrast, losses of NH_4^+ , dissolved organic N (DON), and DOP did not closely follow changes in nutrient limitation across the age gradient. Losses of NH_4^+ remained uniformly low across all sites ($< 10 \mu\text{g N/L}$), with the exception of a slight increase in the oldest site. Significant amounts of DON were lost even from young N-limited forests, and DON levels increased only gradually from 50 – $60 \mu\text{g N/L}$ in the first 20 000 years to a high of $130 \mu\text{g N/L}$ in the oldest forest. Losses of DOP remained even more consistent across the entire age gradient, with little to no differences between N-limited vs. P-limited forests (Fig. 3B).

When taken together, these rather complex trends in inorganic and organic nutrient losses combine to form total dissolved losses of N and P that are roughly opposite in pattern across the age gradient (Fig. 3C). That is, N-limited forests were characterized by low N but high P output, and P-limited forests by low P but high N output. We conclude that NO_3^- and PO_4^{3-} losses were primarily controlled by the nutrient-limitation status of biota, while “leaks” of DON (and to a lesser extent DOP) remained significant despite dramatic shifts in nutrient limitation—as expected in the case of forms of nutrients that are not immediately available for biotic uptake and retention.

Soil N pools, transformations, and gaseous N fluxes

We found consistent patterns in soil exchangeable pools of NO_3^- and NH_4^+ over two years of sampling. In the younger soils, NO_3^- concentrations were low relative to NH_4^+ (Fig. 7C). However, by 20 000 years, exchangeable NO_3^- increased (on basis of mass or area) and remained high in all forests older than 20 000 years. Similarly, net nitrification rates increased dramatically at 20 000 years (Fig. 7A), and became a greater proportion of total net mineralization in sites 20 000 years and older. Nearly 100% of mineralized N was converted to NO_3^- in these older sites. These trends were broadly consistent with changes in hydrologic losses of NO_3^- and NH_4^+ (Fig. 3A); forests began to export dissolved NO_3^- after 20 000 years, at which time nitrification and exchangeable NO_3^- had increased substantially.

Emissions of N_2O and NO (averaged over all sample dates) followed these changes in soil extractable NO_3^- (Fig. 7B), nitrification, and dissolved NO_3^- export. Rates were extremely low before 20 000 years, but remained elevated in forests older than 20 000 years. The acetylene block experiments indicated that little N_2 was produced by denitrification, except in the 300- and 1 400 000-year-old forests; such results are consistent with observations in other forest soils (Robertson and Tiedje 1984, Merrill and Zak 1992). At the youngest site, 7 of 12 samples displayed positive N_2 flux, with a $N_2:N_2O$ ratio of 25.6 ± 44.9 (mean ± 1 SD), while at 1 400 000 years we measured positive N_2 flux in 8 of 19 samples, and an $N_2:N_2O$ ratio of 4.28 ± 9.33 . If we

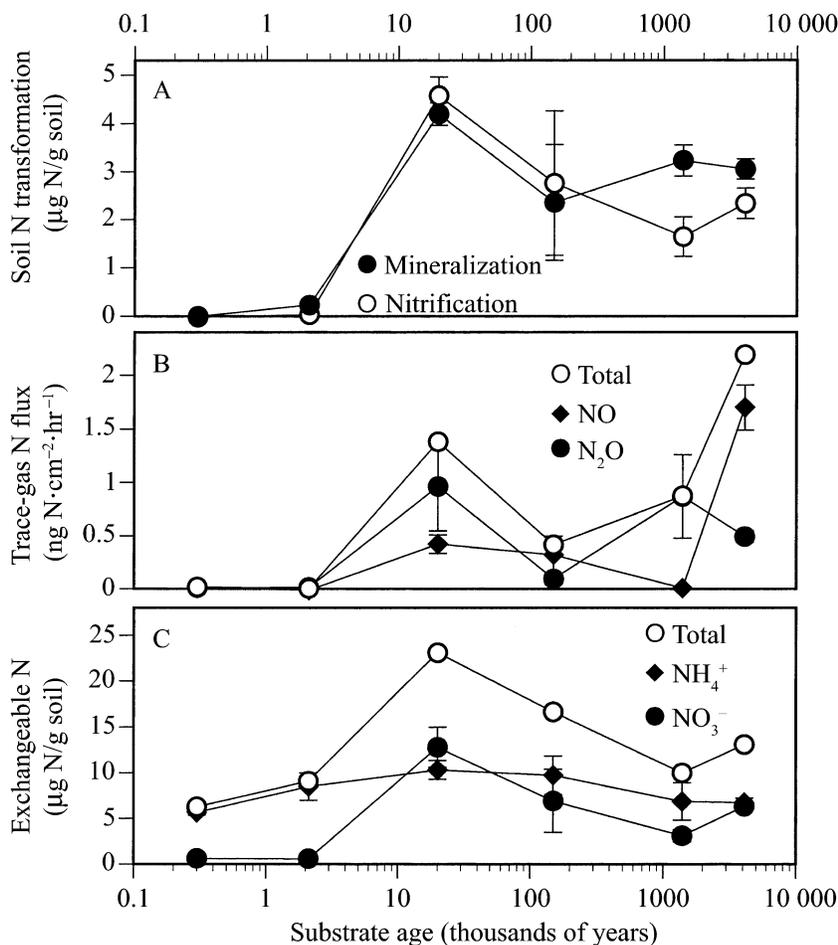


FIG. 7. Transformations and pools of inorganic N across the age gradient of study sites: (A) N mineralization and nitrification; (B) net fluxes of NO and N₂O trace gases between soils and the atmosphere; (C) pools of exchangeable NH₄⁺, NO₃⁻, and total inorganic N (sum of NH₄⁺, and NO₃⁻). Note the x-axis logarithmic scale.

apply these ratios to the mean N₂O fluxes from these two sites, we estimate annual N gas fluxes (NO + N₂O + N₂) of 0.27 kg/ha at the youngest site, and 4.1 kg/ha at the 1 400 000-year-old site. However, given the large uncertainty in our N₂:N₂O ratios, we do not include these values in the following statistical analyses nor in our analyses of ecosystem N fluxes.

Total trace-gas fluxes were significantly correlated with changes in net nitrification ($r = 0.65$; $P < 0.17$) and soil exchangeable NO₃⁻ ($r = 0.62$; $P < 0.19$), but more closely associated with dissolved NO₃⁻ losses ($r = 0.86$; $P < 0.03$) across the age gradient. In the youngest sites, N₂O fluxes were low but relatively more important than NO fluxes while, in older sites (except at 150 000 years), NO fluxes were as important or more important than N₂O fluxes. Fluxes of N₂O were most strongly correlated with N mineralization ($r = 0.88$; $P < 0.02$), dissolved NO₃⁻ losses ($r = 0.77$; $P < 0.07$), and nitrification ($r = 0.70$; $P < 0.13$). In contrast, NO fluxes were highly variable and not strongly related to

N mineralization, NO₃⁻ loss, or nitrification across the gradient ($P > 0.20$).

N losses during forest ecosystem development

In aggregate, total N losses increased roughly linearly with the logarithm of substrate age, reaching 7–9 kg N·ha⁻¹·yr⁻¹ in the oldest sites (Table 4; Fig. 3B and 7B). Using a linear time axis, most of this increase occurred relatively early in the four-million-year gradient. In the case of hydrologic losses, total dissolved N export increased to roughly 58% of maximum at 20 000 years, and 83% of maximum at 1 400 000 years. Gaseous losses also increased rapidly over the first 20 000 years (63% of maximum), but were more variable across sites older than 20 000 years.

Patterns of N loss would be expected to differ from those of cations and P, given the lack of a weathering source of N (Walker and Syers 1976)—but *why* this particular pattern, and why does it develop over scales of millennia or longer? We believe that the N loss pat-

TABLE 4. Summary of hydrologic and gaseous losses of nutrients and elements along the substrate age gradient.

Site	Substrate age (10 ³ yr)	Hydrologic losses (kg·ha ⁻¹ ·yr ⁻¹)					Gaseous losses, N ₂ O + NO (kg N·ha ⁻¹ ·yr ⁻¹)	Total N loss (kg N·ha ⁻¹ ·yr ⁻¹)	
		N	P	Ca ²⁺	K ⁺	Si		Sum	Gas fraction (%)
Thurston	0.3	1.4 (1.3)	0.06 (0.06)	100 (95)	1.2 (1.1)	233 (220)	0.01	1.4	1
Ola'a	2.1	1.2 (1.1)	0.08 (0.08)	109 (103)	13.2 (12.4)	263 (248)	0.00	1.2	0
Laupahoehoe	20	4.2 (6.8)	0.03 (0.04)	1.3 (2.0)	0.3 (0.4)	16 (25)	1.21	5.4	22
Kohala	150	3.9 (N/A)	0.02 (N/A)	1.2 (N/A)	0.7 (N/A)	13 (N/A)	0.36	4.3	9
Kolekole	1400	6.0 (9.0)	0.02 (0.03)	1.0 (1.5)	0.7 (1.0)	18 (27)	0.76	6.8	11
Kokee	4100	7.2 (6.1)	0.03 (0.03)	2.1 (1.8)	1.9 (1.6)	12 (10)	1.9	9.1	21

Notes: Hydrologic losses are based on long-term average precipitation amounts (2500 mm/yr) and modeled evapotranspiration losses (30–32% of total precipitation input) at each site. Values in parentheses are based on direct measures of precipitation inputs for the period January 1996–August 1998, and modeled evapotranspiration losses over the same period; for Kohala there was insufficient hydrologic information available.

tern makes sense if: (1) inputs of N are fairly large, in the range of 5–8 kg N·ha⁻¹·yr⁻¹, in all of the sites; (2) the development of a plant and soil N pool represents a substantial sink for N in young sites; and (3) losses of DON are significant, but not large enough to indefinitely maintain N limitation.

The first point—relatively high N inputs—is surprising, given the remoteness of Hawaii from sources of anthropogenic fixed N (Holland et al. 1999, Gallo-way and Cowling 2002) and the lack of symbiotic N-fixing trees within or near most sites. Nonsymbiotic N fixation in leaf litter of developmentally young (300 years) forests has been estimated to be relatively low, 1–2 kg N·ha⁻¹·yr⁻¹ (Vitousek 1994, Crews et al. 2001), and declines to very low levels (<0.2 kg N·ha⁻¹·yr⁻¹) in forests older than 2100 years (Crews et al. 2000). Epiphytic bryophytes, lichens, and decaying wood may add another ~0.2–1 kg N·ha⁻¹·yr⁻¹ (Matzek and Vitousek 2003).

In contrast, Heath et al. (1999) estimated that forests near the 300-year-old site receive substantial atmospheric N in the form of cloud deposition of thermally fixed N from nearby volcanic activity (Huebert et al. 1999; Carrillo et al. 2002). While there are reasonable questions about the quantity of volcanically fixed N that might be included in their analysis, Heath and Huebert (1999) projected ~4–9 kg N·ha⁻¹·yr⁻¹ background deposition (leaving out volcanic episodes, and mainly deposited as clouds). Volcanic thermal fixation is thought to add at least 5 kg N·ha⁻¹·yr⁻¹ more to the 300-year (and probably 2100 year) sites (Carrillo et al. 2002, J. H. Carrillo, *personal communication*). If the high background rates of N deposition reported by Carrillo et al. (2002) apply to all forests across our gradient, and adding fixation, then inputs of fixed N are roughly large enough (4.5–9.5 kg N·ha⁻¹·yr⁻¹) to explain N outputs from all sites older than 20 000 years.

The second point—ecosystem N retention—certainly applies to the youngest forest of the age gradient. Based on Crews et al. (1995), ~30 kg N·ha⁻¹·yr⁻¹ has accumulated in the 300-year history of the youngest

site; this accumulation rate is greater than the current estimate of total (volcanic and background) N deposition at this site (Carrillo et al. 2002). Moreover, since plant production is limited by N in this site (Vitousek and Farrington 1997), we would expect strong retention of biotically available forms of N. Indeed, nutrient accumulation is often high early in primary succession, but decreases rapidly as plant and soil nutrient pools equilibrate over time (Crocker and Dickinson 1957, Walker and Syers 1976, Bockheim 1980, Bormann and Sidle 1990, Bormann et al. 1993, Schlesinger et al. 1998).

However, it is difficult to explain why total N losses remained low (<1.5 kg N·ha⁻¹·yr⁻¹; Fig. 3A and C, Fig. 7B, Table 4) for at least as long as 2100 years (and no longer than 20 000 years) of forest development. Assuming a maximum plant and soil pool of 18 000 kg N/ha (Crews et al. 1995) and atmospheric deposition equal to N accumulation in the youngest site (30 kg N·ha⁻¹·yr⁻¹), it would take only an additional 270 years for the 300-year-old forest to reach equilibrium with respect to N inputs. It would take 550 years if atmospheric inputs were 15 kg N·ha⁻¹·yr⁻¹ in these young sites (representing mean estimates of background and volcanic inputs), still substantially shorter than the observed period of >2100 years. These differences are large enough to suggest either that N inputs drop substantially below those estimated by Carrillo et al. (2002) after the first 300 years of development, that the age of the 2100-year-old site is overstated, and/or that there exists an additional N sink over at least the first 2100 years of forest development.

The third point—significant DON losses—is most clearly seen in the youngest site, where plant growth is strongly N-limited (Vitousek et al. 1993) and where DON constituted >80% of total N losses (dissolved and gaseous; Figs. 3A and 7B). We asked if these DON losses were large enough to explain the slow development of N sufficiency (i.e., N supply in excess of biotic demands) across the age gradient. If external N inputs remained as large as 15 kg·ha⁻¹·yr⁻¹ we calculate

that the total N loss from our youngest sites (1.5 kg-ha⁻¹·yr⁻¹; Table 4) could delay the predicted onset of N sufficiency from 840 to 910 years—a difference of only 70 years. If, however, N inputs decreased to 5 kg N-ha⁻¹·yr⁻¹ after 300 years, the delay in N sufficiency would be as large as 700 years, from 1900 to 2600 years. We conclude that losses of unavailable N forms can offer a mechanism to delay the onset of N sufficiency at sub-millennial scales in these Hawaiian forests. The exact impact of this mechanism will likely differ among ecosystems, however, depending on strengths of DON losses relative to external N inputs by atmospheric deposition or biotic fixation (Perakis and Hedin 2002).

*Implications of available vs. unavailable
N and P losses*

One of our central motivations for measuring N and P losses across this forest age gradient was to test the “leak” hypothesis that in the long-term, nutrient accumulation could be constrained (and nutrient limitation thus sustained) by losses of unavailable forms of DON and DOP—even when the growth of plants and microbes is limited by N or P (Hedin et al. 1995, Vitousek et al. 1998). Our results support the idea that losses of both DON and DOP are not subject to traditional mechanisms of biotic retention, in that their fluxes were relatively independent of forest N or P status. In contrast, losses of NO₃⁻, N trace gases, and PO₄³⁻ all varied depending on N and P availability; we consider these to be controllable because losses for a given nutrient were very low when the nutrient was in short supply within the ecosystem.

Losses of DON were not large enough (relative to N inputs) to constrain the buildup of N in plant and soil pools indefinitely, as is thought to occur in unpolluted and N-poor South American forests (Hedin et al. 1995, Perakis and Hedin 2002). Forests 20 000 years and older displayed sharply higher losses of dissolved NO₃⁻, increased pools of soil exchangeable NO₃⁻, higher rates of N mineralization and nitrification, and higher emissions of NO/N₂O (Figs. 3A–C and 4A). Where N is not limiting to biotic processes, and where N inputs continue, we would expect outputs of N through availability-dependent pathways to increase to match inputs. Our results are consistent with the following events: (1) increased internal N supply due to the progressive buildup of ecosystem N pools (Fig. 4A); (2) increased production and storage of NO₃⁻ in soils due to relaxed competition for NH₄⁺ by plants and nitrifying bacteria (Figs. 4A and C); (3) increased N₂O/NO losses due to increased N mineralization and/or increased supply of NO₃⁻ to denitrifying bacteria (Fig. 8B); and (4) increased ecosystem NO₃⁻ export due to relaxed net biotic demand for N (Fig. 2A).

Losses of both NO₃⁻ and NO/N₂O scaled positively against N fertility, while DON and NH₄⁺ losses did not display a clear relationship (Fig. 8). Since NO₃-N losses

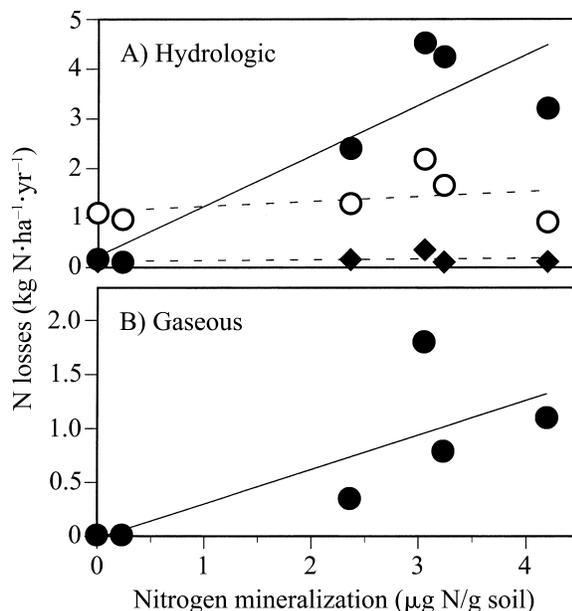


FIG. 8. Changes in vectors of N loss as a function of variations in N mineralization across our Hawaiian forest study sites: (A) hydrologic fluxes of NO₃⁻ (closed circles), DON (open circles), and NH₄⁺ (closed triangles); (B) gaseous fluxes of N trace gases (sum of NO and N₂O; closed circles). Solid lines indicate statistically significant linear-regression relationships at $P < 0.10$; dashed lines indicate nonsignificant linear-regression fits. Losses of NO₃⁻-N scale most strongly against variations in N mineralization (slope = 1.0, $r^2 = 0.80$, $P < 0.02$), followed by N trace gases (slope = 0.3, $r^2 = 0.61$, $P < 0.07$).

were both larger and increased more steeply with N fertility than trace-gas emissions, we conclude that NO₃⁻ leaching exercised the primary (negative) feedback control on N accumulation in these Hawaiian forests. DON losses could in theory limit N accumulation despite the lack of steep increase against N fertility, but only if N inputs do not exceed ecosystem outputs via DON; this could be the case in wetter forests with high DON output relative to N inputs (Hedin et al. 1995, Perakis and Hedin 2002). Indeed, wetter forests (>4000 mm/yr) within the Hawaiian Islands have substantially lower tissue-N levels than the mesic forests studied here (Vitousek and Turner 1995, Schuur and Matson 2001), and increasing dominance of DON over NO₃⁻ losses (B. Z. Houlton and L. O. Hedin, unpublished data).

While DON became a less important path of N loss over the course of forest development, contributions of DOP increased from <20% of all P losses in the youngest forests, to ~50% in forests 20 000 years and older, primarily as a function of declining inorganic P losses. DOP therefore had its largest effect on ecosystem P balances in developmentally old forests, which were characterized by very low P inputs from weathering and atmospheric dust (Chadwick et al. 1999), and by

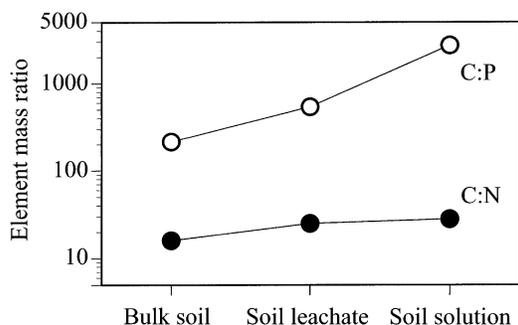


FIG. 9. Ratios of C:P and C:N in bulk soil organic matter (Crews et al. 1995), in organic matter leached from surface soil horizons during short-term laboratory incubations (Neff et al. 2000), and in soil water below the active rooting zone collected by lysimeters in this study. C:P ratios are from the strongly P-limited 4 100 000-year-old site at Kokee. C:N ratios are from the strongly N-limited 300-year-old site at Thurston. Standard errors are too small to be distinguished from the symbols. Note the logarithmic y-axis scale.

persistent P limitation to plant growth (Herbert and Fownes 1995, Vitousek and Farrington 1997).

We interpret this DOP export from P-limited forests as evidence that DOP provided a path of P loss that was (at least partially) independent of biotic demand. However, analysis of element ratios suggested that much of the DOP produced within the forests was retained and recycled relative to organic C and N (Fig. 9). In the oldest site, ratios of C:P were substantially lower in bulk soil organic matter (C: organic P \sim 215, Crews et al. 1995) than in soil water below the active rooting zone (DOC:DOP \sim 2700). Organic matter leached from surface soil horizons during short-term laboratory incubations had intermediate values (DOC: DOP \sim 540, Neff et al. 2000). These ratios suggest that P was retained relative to C along the pathway from dissolution of soil organic matter to the movement of water through the soil profile (cf. Neff et al. 2000). We found no evidence for such strong retention of DON; C:N ratios in the N-limited 300-year-old site differed much less between bulk soil (C:N = 16), soil water below the active rooting zone (DOC:DON = 28), and leached organic matter (DOC:DON = 25, Neff et al. 2000) (Fig. 9).

These differences in DON vs. DOP retention might be caused by biochemical differences between P and N in organic matter. While N forms complex and biotically resistant associations with organic C in soils, most P is linked to C by ester bonds (C-O-P) that are accessible to extracellular phosphatases in soil environments (McGill and Cole 1981, Olander and Vitousek 2000). The liberation of P by phosphatases ("biochemical mineralization") can thus cause P to be recycled more efficiently than N. This mechanism is further supported by Neff et al.'s (2000) finding that soil and water-extract C:P ratios differed most strongly in the oldest (and most P-poor) site.

Despite this evidence for P retention, some DOP escaped biochemical mineralization and was lost to soil water below the active rooting zone. Moreover, while PO_4^{3-} losses declined substantially from young to older sites, small but significant losses persisted in all older sites. These low losses of DOP and PO_4^{3-} may represent concentrations below which neither biotic uptake nor adsorption can act as effective retention mechanisms—a sort of ecosystem-level R^* (i.e., minimum concentration for biotic retention of PO_4^{3-} or DOP; sensu Tilman 1987) below which even the most limiting nutrient can be lost. These losses are availability independent in the sense that they constitute ecosystem-level P outputs that cannot be retained, even in the most P-poor of Hawaiian forests.

Our calculations suggest that these losses, while small, were large enough to constrain P accumulation and sustain P limitation in the most P-poor forests. Atmospheric inputs of dust aerosols from Asia provide the largest vector of P input to the oldest and most highly weathered forests of this Hawaiian age gradient (Chadwick et al. 1999). Long-term inputs of P due to mineral dust average \sim 0.02 kg P \cdot ha $^{-1}\cdot$ yr $^{-1}$, virtually indistinguishable from our lysimeter-based loss estimates of 0.02–0.03 kg P \cdot ha $^{-1}\cdot$ yr $^{-1}$ in forests older than 20 000 years (Table 4). Considerable emphasis has been placed on the accumulation of P in "occluded" pools (insoluble and physically protected forms) as a mechanism for maintenance of P limitation in old tropical soils. However, hydrologic P losses were more than two orders of magnitude greater than any plausible net change in soil "occluded P" (Crews et al. 1995) between our two oldest forests. These losses offset the very low inputs of P in dust, at a point where internal P pools cannot accumulate to bring the ecosystem to P sufficiency. In contrast to Walker and Syers's model, this suggests that "unavailable" hydrologic P losses can constrain P accumulation in P-limited soils, similar to the role proposed for DON in humid and N-poor temperate forests (Hedin et al. 1995, Perakis and Hedin 2002).

Stoichiometric paradox of N and P losses

The dramatic shift in dissolved N and P loss ratios from <10 in young sites, to >300 in older sites (Fig. 10) offers an interesting yet unresolved paradox. The emergence of high N:P loss ratios at the ecosystem level means that, over the long term, substantial rates of N loss (\sim 7–9 kg N \cdot ha $^{-1}\cdot$ yr $^{-1}$) must be balanced by external N inputs of the same magnitude. Such high N throughputs are at odds with expectations of N inputs via biological N fixation and/or atmospheric N deposition. Physiological models predict that N fixation should remain low or negligible in N-rich and P-poor environments (Hartwig 1998); this expectation is further supported by empirical measures across our Hawaiian age gradient (Crews et al. 2001, Pearson and Vitousek 2002, Matzek and Vitousek 2003). In addi-

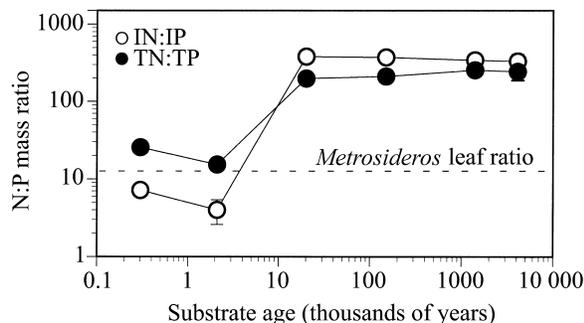


FIG. 10. Changes in dissolved N:P ratios in soil waters below the active rooting zone across the age gradient of study sites. Each value is the long-term arithmetic mean based on 10–22 monthly sample efforts, from 6–12 lysimeters at the different sites (see Appendix B). Error bars identify 1 SE of the mean; the absence of error bars indicates that errors were too small to be differentiated from individual symbols. Open circles indicate the ratio of inorganic N (sum of NO_3^- and NH_4^+) to inorganic P (PO_4^{3-}). Solid circles indicate the ratio of total N (sum of NO_3^- , NH_4^+ , and DON) to total P (sum of PO_4^{3-} and DOP). The dashed line signifies the average tissue N:P ratio in leaves of *Metrosideros polymorpha*, across the sample sites (Vitousek and Turner 1995). Note the logarithmic scales, both axis.

tion, atmospheric models suggest that N deposition should be low in unpolluted regions ($<2 \text{ kg N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$; Holland et al. 1999, Galloway and Cowling 2002); this expectation is supported by Carrillo et al.'s (2002) observation of only $0.2 \text{ kg N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ wet deposition to forests at our oldest site on Kauai. For our oldest forests, that are not affected by local volcanism, we are therefore left with an unresolved stoichiometric paradox: that despite expected low N inputs, these forests develop and sustain N richness and strong P limitation (Figs. 3 and 7), high ratios of dissolved N:P losses (Fig. 10), and substantial losses of N in gaseous and dissolved forms (Table 4).

Conclusions

Our findings show that nutrient losses from Hawaiian forests have been shaped by long-term interactions among geochemical, atmospheric, and biological processes over four million years of landscape development. Weathering was the major source of P (thereby controlling ecosystem N and P interactions), the major influence on losses of base cations and Si (thereby controlling stability of secondary minerals), and controlled the acid–base and Al status of soils and soil water.

Mechanisms affecting long-term interactions of N and P cycles were more complex than expected by previous models (e.g., Walker and Syers 1976), however, and were influenced by losses of forms of N and P that were unavailable to immediate biotic uptake. These forests developed N sufficiency and P limitation only when external P inputs by weathering and atmospheric dust decreased below critical loss rates of DOP and PO_4^{3-} from the rooting zone, and when N

retention and DON losses were overcome by N inputs. We conclude that DOP contributes an important mechanism for maintaining P limitation in forests that are subject to low P inputs, similar to the role proposed for DON in forests subject to low N inputs (Hedin et al. 1995, Perakis and Hedin 2002).

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APPENDIX A

Concentrations of selected nutrients and elements in small streams that drained near four of our six sample sites across the Hawaiian age gradient; data are the arithmetic mean \pm 1 SE of *n* samples from each stream and, in parentheses, the range (min.-max.) from each stream.

Nutrient/ element	Laupahoehoe, 20 000 yr		Kohala, 150 000 yr		Kolekole, 1 400 000 yr		Kokee, 4 100 000 yr	
	Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>
Cl ⁻ (mg/L)	1.6 \pm 0.08 (1.3–2.6)	15	5.9 \pm 0.5 (4.0–9.2)	10	9.7 \pm 1.0 (8.0–12)	3	8.0 \pm 0.10 (7.7–8.6)	10
Na ⁺ (mg/L)	1.0 \pm 0.09 (0.6–2.1)	15	3.3 \pm 0.17 (2.6–4.5)	10	5.7 \pm 0.87 (4.4–7.4)	3	4.4 \pm 0.11 (3.9–4.5)	10
SO ₄ ²⁻ (mg/L)	0.95 \pm 0.09 (0.61–2.1)	15	1.0 \pm 0.08 (0.84–1.6)	9	1.2 \pm 0.19 (0.96–1.6)	3	0.70 \pm 0.02 (0.62–0.81)	10
Mg ²⁺ (mg/L)	0.63 \pm 0.04 (0.45–0.95)	15	0.56 \pm 0.04 (0.42–0.88)	10	0.59 \pm 0.039 (0.52–0.65)	3	0.83 \pm 0.06 (0.59–1.1)	10
H ₂ SiO ₄ -Si (mg/L)	1.18 \pm 0.08 (0.52–1.6)	15	0.75 \pm 0.03 (0.56–0.85)	10	1.0 \pm 0.06 (0.90–1.1)	3	2.0 \pm 0.2 (1.1–2.9)	10
pH	5.2 (5.17–5.24)	15	5.3 (5.2–5.3)	10	5.3 (5.31–5.35)	3	6.4 (5.9–6.8)	8
Ca ²⁺ (mg/L)	0.65 \pm 0.04 (0.46–0.99)	15	0.52 \pm 0.04 (0.36–0.93)	10	0.26 \pm 0.03 (0.21–0.34)	3	0.63 \pm 0.04 (0.46–0.84)	10
PO ₄ ³⁻ -P (μ g/L)	1.6 \pm 0.2 (0.3–4.4)	15	7 \pm 1.1 (2.8–17)	10	4.4 \pm 0.9 (2.6–6.1)	3	1.7 \pm 0.3 (0.6–3.1)	8
NO ₃ ⁻ -N (μ g/L)	121 \pm 26 (2.5–473)	15	5.6 \pm 3.3 (0.0–36)	10	74 \pm 79 (0.0–160)	3	85 \pm 27 (12–117)	10

Notes: Samples from streams were taken less frequently than from lysimeters, and flow paths between lysimeters and streams were not known. Values are based on three small local streams for Kokee, all with similar chemistry. Streams were not present at the 300- and 2100-year-old sites.

APPENDIX B

Concentrations of nutrients and elements in soil solutions sampled by lysimeters across the six sites of our Hawaiian tropical-forest age gradient.

Nutrient/ element	Thurston, 300 yr		Ola'a, 2100 yr		Laupahoehoe, 20 000 yr	
	Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>
NH ₄ ⁺ -N (μ g/L)	6.8 \pm 0.7 (1.8–14) [0.4–6.1]	20	5.8 \pm 1.4 (1.3–19) [0.4–11]	15	6.5 \pm 1.0 (0.6–21) [0.1–6.5]	22
NO ₃ ⁻ -N (μ g/L)	9.7 \pm 1.7 (0.6–28) [0.4–22]	20	6.2 \pm 2.5 (0.02–34) [0.0–34]	15	184 \pm 17 (48–333) [17–311]	22
DON (μ g/L)	64 \pm 6 (31–132) [5–43]	20	56 \pm 3 (44–93) [4–16]	15	53 \pm 6 (7–127) [2–44]	22
PO ₄ ³⁻ -P (μ g/L)	2.9 \pm 0.4 (1.3–8.0) [0.0–1.0]	20	4.1 \pm 0.7 (1.4–11) [0.0–1.5]	14	0.6 \pm 0.1 (0.3–2.4) [0.0–0.9]	22
DOP (μ g/L)	0.7 \pm 0.1 (0.5–1.3) [0.0–0.5]	20	0.8 \pm 0.2 (0.5–3.6) [0.0–1.2]	13	0.8 \pm 0.2 (0.5–4.3) [0.0–0.9]	20
DOC (mg/L)	1.8 \pm 0.1 (1.1–3.0) [0.1–1.3]	20	2.3 \pm 0.3 (1.5–6.0) [0.09–1.6]	15	0.9 \pm 0.1 (0.5–2.1) [0.03–1.1]	20
Ca ²⁺ (mg/L)	5.9 \pm 0.31 (3.9–8.5) [0.4–2.0]	20	6.4 \pm 0.16 (4.9–7.4) [0.1–1.4]	15	0.074 \pm 0.004 (0.037–0.11) [0.005–0.02]	21
Mg ²⁺ (mg/L)	2.6 \pm 0.14 (1.6–3.8) [0.2–1.0]	19	5.2 \pm 0.22 (3.5–6.3) [0.3–1.2]	15	0.25 \pm 0.013 (0.14–0.42) [0.04–0.2]	21
K ⁺ (mg/L)	0.068 \pm 0.008 (0.030–0.17) [0.01–0.08]	20	0.77 \pm 0.043 (0.38–0.97) [0.1–0.2]	12	0.016 \pm 0.002 (0.0025–0.034) [0.0–0.01]	20
Na ⁺ (mg/L)	1.9 \pm 0.13 (1.0–3.8) [0.2–0.7]	20	2.3 \pm 0.056 (1.9–2.7) [0.2–1.0]	15	0.92 \pm 0.040 (0.60–1.2) [0.08–0.4]	20
Cl ⁻ (mg/L)	2.0 \pm 0.24 (0.40–4.5) [0.1–1.2]	20	1.7 \pm 0.21 (0.61–3.0) [0.2–1.6]	15	1.9 \pm 0.12 (1.2–3.0) [0.2–0.6]	21
SO ₄ ²⁻ (mg/L)	16.1 \pm 1.95 (4.8–41) [1–10]	20	7.9 \pm 1.1 (2.0–14.6) [0.1–7]	15	0.79 \pm 0.018 (0.51–0.98) [0.02–0.2]	21
Al _{total} (mg/L)	0.02 \pm 0.007	5 [†]	0.001 \pm 0.0003	2 [†]	0.202 \pm 0.06	5 [†]
H ₂ SiO ₄ -Si (mg/L)	13.6 \pm 0.27 (11.0–15.6) [1.2–3.5]	21	15.3 \pm 0.28 (12.5–16.4) [1.0–2.8]	15	0.91 \pm 0.018 (0.65–1.1) [0.08–0.3]	21
pH	6.7 (6.3–7.4)	19	7.2 (6.9–8.0)	15	5.0 (4.6–5.6)	20

Notes: Values give the arithmetic mean \pm 1 SE of *n* monthly mean concentrations from between 6 and 12 replicated lysimeters within each location (see Table 1). Values in parentheses give the range (min.–max.) in monthly mean concentrations at each location. Values in brackets give the range (min.–max.) in monthly standard errors among lysimeters at each location; this range indicates the degree of within-site variability in lysimeter chemistry. Values for Al³⁺ are based on fewer samples and replicates: see [†] and [‡].

[†] At each effort, 1–3 lysimeters were sampled.

[‡] The mean and SE derive from a single sample effort of *n* lysimeters.

APPENDIX B. Extended.

Kohala, 150 000 yr		Kolekole, 1 400 000 yr		Kokee, 4 100 000 yr	
Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>
9.1 \pm 1.3 (3.5–21) [0.5–6.6]	14	6.3 \pm 0.4 (4.4–8.9) [0.4–3.2]	10	20.6 \pm 4.3 (7.2–58.3) [2.0–24]	12
140 \pm 6 (101–190) [50–135]	14	250 \pm 75 (80–816) [21–178]	9	267 \pm 27 (63–413) [39–338]	16
75 \pm 6 (39–110) [7–37]	14	97 \pm 8 (76–157) [8–24]	10	127 \pm 20 (53–338) [5–56]	14
0.6 \pm 0.1 (0.3–1.8) [0.0–2.7]	14	0.7 \pm 0.1 (0.3–1.9) [0.0–0.2]	10	1.0 \pm 0.1 (0.4–2.3) [0.1–1.1]	14
0.6 \pm 0.1 (0.5–1.4) [0.0–0.6]	14	0.6 \pm 0.05 (0.5–0.9) [0.0–0.2]	10	0.7 \pm 0.1 (0.5–1.7) [0.0–0.9]	15
1.2 \pm 0.1 (0.7–1.8) [0.06–0.9]	14	2.8 \pm 0.1 (2.1–3.3) [0.3–0.6]	10	1.9 \pm 0.3 (0.7–4.3) [0.1–1.1]	14
0.072 \pm 0.006 (0.042–0.11) [0.003–0.02]	14	0.059 \pm 0.005 (0.027–0.078) [0.004–0.02]	10	0.12 \pm 0.009 (0.083–0.19) [0.009–0.04]	12
0.42 \pm 0.019 (0.29–0.52) [0.03–0.09]	13	0.51 \pm 0.051 (0.28–0.84) [0.02–0.08]	10	0.53 \pm 0.021 (0.39–0.71) [0.04–0.2]	14
0.043 \pm 0.0037 (0.026–0.071) [0.005–0.04]	13	0.040 \pm 0.004 (0.025–0.063) [0.003–0.03]	10	0.11 \pm 0.005 (0.082–0.14) [0.01–0.06]	12
3.9 \pm 0.17 (3.0–4.9) [0.3–0.8]	13	5.4 \pm 0.34 (3.9–7.1) [0.09–0.4]	9	5.2 \pm 0.30 (3.9–6.6) [0.21–1.2]	12
7.6 \pm 0.32 (5.9–9.5) [0.3–1.0]	14	9.2 \pm 0.62 (5.3–12.4) [0.07–0.7]	10	9.4 \pm 0.43 (6.5–11.7) [0.6–2.8]	16
0.98 \pm 0.029 (0.84–1.2) [0.05–0.3]	14	1.1 \pm 0.073 (0.66–1.5) [0.04–0.1]	10	1.2 \pm 0.062 (0.90–1.7) [0.2–0.4]	15
0.297 \pm 0.05	3‡	0.247 \pm 0.03	3‡	0.089 \pm 0.05	4†
0.74 \pm 0.012 (0.63–0.82) [0.06–0.2]	14	1.1 \pm 0.043 (0.89–1.3) [0.03–0.1]	10	0.68 \pm 0.025 (0.55–0.77) [0.1–0.2]	10
4.7 (4.3–5.0)	14	4.6 (4.1–5.0)	10	4.6 (3.9–5.3)	15

APPENDIX C

Trace-gas N fluxes, soil N pools, net mineralization (Net min.), and net nitrification (Net nit.) across the Hawaiian age gradient; data are the arithmetic mean \pm 1 SE of n means from n sampling times within each location.

Flux/pool	Thurston, 300 yr		Ola'a, 2100 yr		Laupahoehoe, 20 000 yr	
	Mean \pm 1 SE	n	Mean \pm 1 SE	n	Mean \pm 1 SE	n
N ₂ O-N (ng·cm ⁻² ·hr ⁻¹)	0.010 \pm 0.007 (-0.056-0.082) [0.000-0.056]	26	0.013 \pm 0.007 (0.000-0.027) [0.000-0.062]	4	0.959 \pm 0.415 (0.069-6.106) [0.032-4.919]	15
NO-N (ng·cm ⁻² ·hr ⁻¹)	0.006 \pm 0.003 (-0.008-0.061) [0.000-0.022]	23	-0.014 \pm 0.019 (-0.069-0.013) [0.005-0.069]	4	0.420 \pm 0.088 (0.000-1.048) [0.008-0.823]	15
Moisture (%)						
Organic layer	NA	...	NA	...	73.9 \pm 2.1 (60.2-78.6) [0.7-2.1]	8
Mineral layer	64.2 \pm 0.8 (54.1-69.6) [0.4-3.7]	24	69.2 \pm 1.5 (66.3-73.4) [0.4-3.9]	4	68.1 \pm 1.1 (61.0-71.0) [0.9-3.0]	8
NH ₄ ⁺ -N (μ g/g)						
Organic layer	NA	...	NA	...	32.45 \pm 3.44 (16.80-41.98) [2.25-11.57]	7
Mineral layer	5.65 \pm 0.29 (2.98-8.94) [0.30-2.86]	24	8.49 \pm 1.51 (4.63-11.27) [0.71-2.11]	4	10.39 \pm 1.02 (6.67-14.18) [0.99-3.35]	7
NO ₃ ⁻ -N (μ g/g)						
Organic layer	NA	...	NA	...	5.91 \pm 1.18 (2.47-12.23) [0.64-3.39]	7
Mineral layer	0.63 \pm 0.18 (0.0-3.84) [0.0-0.62]	24	0.60 \pm 0.35 (0.0-1.38) [0.0-0.25]	4	12.78 \pm 2.18 (7.06-22.37) [1.09-3.98]	7
Net min. (μ g/g)						
Organic layer	NA	...	NA	...	11.19 \pm 1.51 (5.54-16.21) [1.33-5.90]	7
Mineral layer	-0.003 \pm 0.07 (-0.60-0.71) [0.01-0.64]	22	0.23 \pm 0.09 (-0.03-0.34) [0.03-0.39]	4	4.19 \pm 0.39 (2.85-5.46) [0.25-1.07]	7
Net nit. (μ g/g)						
Organic layer	NA	...	NA	...	4.49 \pm 0.90 (2.28-8.47) [0.33-2.20]	7
Mineral layer	-0.02 \pm 0.04 (-0.54-0.38) [0.0-0.19]	22	0.03 \pm 0.08 (-0.10-0.28) [0.01-0.10]	4	4.57 \pm 0.23 (3.78-5.28) [0.17-1.32]	7

Notes: Values in parentheses give the range in means at each location. Values in brackets give the range in standard errors of the means at each location; this range indicates the degree of within-site variability; n = number of times each site was sampled. NA indicates that no layer was present.

APPENDIX C. Extended.

Kohala, 150 000 yr		Kolekole, 1 400 000 yr		Kokee, 4 100 000 yr	
Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>	Mean \pm 1 SE	<i>n</i>
0.095 \pm 0.051 (0.000–0.236) [0.000–0.282]	4	0.866 \pm 0.391 (0.206–1.987) [0.070–0.818]	4	0.491 \pm 0.055 (0.128–1.122) [0.000–0.537]	20
0.320 \pm 0.173 (0.075–0.813) [0.052–0.825]	4	0.006 \pm 0.012 (–0.016–0.040) [0.000–0.037]	4	1.699 \pm 0.209 (0.316–3.700) [0.040–2.563]	18
68.6 \pm 3.2 (63.8–74.6) [1.2–2.8]	3	79.8 \pm 1.0 (76.7–81.2) [0.5–1.0]	4	NA	...
61.9 \pm 1.7 (58.8 \pm 64.7) [2.4–2.8]	3	60.2 \pm 4.5 (54.4–73.5) [1.8–2.6]	4	57.7 \pm 1.3 (46.8–74.3) [1.1–8.0]	20
16.78 \pm 1.61 (14.4–19.8) [0.59–4.52]	3	16.98 \pm 3.90 (5.66–23.44) [1.72–5.31]	4	NA	...
9.72 \pm 2.12 (5.54–12.45) [1.04–3.46]	3	6.86 \pm 2.04 (3.24–12.70) [0.37–1.39]	4	6.74 \pm 0.47 (3.19–11.60) [0.29–2.45]	20
1.14 \pm 0.32 (0.57–1.66) [0.33–1.03]	3	1.80 \pm 0.62 (0.92–3.60) [0.28–0.55]	4	NA	...
6.92 \pm 3.44 (3.21–13.79) [0.62–8.86]	3	3.12 \pm 0.67 (2.03–4.96) [0.23–0.60]	4	6.33 \pm 0.51 (2.86–10.37) [0.37–3.23]	20
1.13 \pm 0.47 (0.55–2.07) [0.22–2.31]	3	1.64 \pm 0.49 (0.67–2.18) [0.35–0.76]	3	NA	...
2.36 \pm 1.50 (0.19–5.23) [0.41–0.80]	3	1.59 \pm 0.41 (0.94–2.80) [0.17–0.56]	4	3.05 \pm 0.32 (1.00–5.81) [0.38–3.35]	19
0.03 \pm 0.12 (–0.17–0.23) [0.09–0.22]	3	0.03 \pm 0.10 (–0.09–0.24) [0.02–0.08]	3	NA	...
2.76 \pm 1.20 (1.31–5.15) [0.48–0.58]	3	1.65 \pm 0.32 (1.17–2.57) [0.19–0.57]	4	2.34 \pm 0.21 (0.92–4.45) [0.31–1.32]	19