

CONSEQUENCES OF NITROGEN ADDITIONS FOR SOIL PROCESSES AND SOLUTION LOSSES FROM WET TROPICAL FORESTS

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Abstract. Wet tropical forests growing on highly weathered soil, depleted in rock-derived nutrients, yet rich in nitrogen (N), may respond quite differently to anthropogenic N inputs than those growing on younger soils low in N. We evaluated the effects of first-time and long-term N additions on the pattern and regulation of hydrologic N losses from wet tropical forests located at the extreme ends of a soil age and fertility gradient in the Hawaiian Islands. In contrast to our expectations that a N-limited forest on 300-year-old soils would initially retain N inputs, both forests, regardless of soil age or fertility, responded to first-time N additions with immediate and significantly elevated nitrate (NO_3^-) solution losses. However, patterns of NO_3^- loss differed markedly between sites and largely reflected differences in hydrological processes due to soil age. In the N-limited forest on young soils, N additions to previously unfertilized soils resulted in significant microbial immobilization of ammonium (NH_4^+) and small losses as NH_4^+ , whereas N added as NO_3^- appeared to be free to move in solution. Nitrogen additions to long-term N-fertilized forests (13 years) on young soils significantly increased rates of nitrification, and losses were similar to the total N added during that time period. Poor soil development, and therefore low hydraulic resistance, was a critical factor determining the low NO_3^- -retention capacity in the young soils. In contrast, first-time N inputs to a N-rich forest on 4.1-million-year-old soils resulted in significantly elevated rates of nitrification, but NO_3^- losses were more delayed and lower than those from the young soils. The old, highly developed soils offered greater hydraulic resistance to leaching losses as nitrate than the young soils. High anion exchange capacity (AEC) in the subsurface clay horizon of the old soils also appeared to delay NO_3^- losses.

Our findings suggest that responses to N additions in the tropics will vary as a function of soil age, nutrient status, and the form of N added, and that chemical and physical mechanisms may be more important than biological ones in controlling losses. While retention of added N will be determined by the strength of biotic demand (and the ability of plants and microbes to retain these inputs) and the relative strength of other pathways of retention (cation and anion exchange) and loss (denitrification), hydrological properties and flow paths may be the dominant controls determining the residence time and routing of water and nutrients. Nitrate adsorption on anion exchange sites may also serve as an important abiotic mechanism delaying the onset of large NO_3^- losses from tropical forests receiving elevated anthropogenic N inputs.

Key words: biogeochemistry; Hawaii; hydrologic losses; hydrology; leaching; N additions; tropical forests.

INTRODUCTION

Anthropogenically enhanced nitrogen (N) deposition is shifting from a temperate-zone concern to a global issue with dramatic increases projected in the subtropics and tropics in the next several decades (Galloway et al. 1995, Galloway and Cowling 2002). In some tropical regions, N emissions and subsequent deposition may increase as much as 500% by the year 2020 due rapid industrial and agricultural intensification (Galloway et al. 1994). Despite these large forecasted

changes, little information is available on how anthropogenic N inputs are processed in tropical ecosystems and the consequences of these inputs for aqueous losses. Because tropical rainforests cover 17% of the earth's land surface and make up 40% of the global net primary production (NPP), even small alterations in major biogeochemical cycles will likely have global significance.

In the temperate zone, anthropogenic N inputs have resulted in a cascade of environmental consequences (Vitousek et al. 1997a, Aber et al. 1998, Fenn et al. 1998, Galloway and Cowling 2002). Of particular concern have been enhanced hydrologic losses of N, primarily as nitrate (NO_3^-), to downstream ecosystems. Increased NO_3^- losses affect groundwater drinking supplies and drive acidification, eutrophication, and alter-

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ation of biodiversity in downstream freshwater and marine ecosystems (Howarth 1988, Schindler 1994, Nixon 1995, Howarth et al. 1996, Likens et al. 1996, Rabalais 2002). Studies have also shown that increased NO_3^- solution losses from forests experiencing elevated N inputs lead to base cation depletion, increased aluminum mobility, and long-term soil acidification (Johnson et al. 1982, Likens et al. 1996, Fenn et al. 1998).

The timing and magnitude of N losses are thought to depend largely on the nutrient status of the ecosystem or how close it is to N saturation (Grennfelt and Hultberg 1986, Henriksen and Brakke 1988, Aber et al. 1989, Melillo et al. 1989, Aber 1992). Studies have shown that many temperate forests, often limited by N, respond with increased rates of nitrification (microbial conversion of NH_4^+ to NO_3^-) and NO_3^- leaching losses only after years of N additions or decades of chronic N deposition (Bowden et al. 1991, Aber et al. 1993, 1998, McNulty and Aber 1993, Aber et al. 1995, Wright et al. 1995, Peterjohn et al. 1996, Magill et al. 2000). Until then, retention of N in vegetation and soil appears to delay these responses (Fenn et al. 1998, Goodale et al. 2002). One cardinal sign of N saturation is nitrate leaching that occurs at a significantly higher rate than "background" levels, after N additions without a significant temporal lag period, or aseasonally in a seasonal ecosystem (Peterjohn et al. 1996).

While the N saturation model has been extensively evaluated in the temperate zone, little attention has been focused on its potential application to the tropics, despite projections of enhanced anthropogenic N inputs in this region (Matson et al. 1999, 2002). Will tropical ecosystems respond similarly to anthropogenic N inputs as temperate ecosystems? Will nutrient status be the dominant factor controlling the timing and magnitude of losses or will other factors need consideration? We suggest that many tropical forests may function quite differently from temperate forests, and consequently, the effects of anthropogenic N inputs on tropical ecosystem processes may also differ.

Many tropical forests grow on old, highly weathered soils such as Oxisols and Ultisols (Richter and Babbar 1991), although a smaller proportion grows on relatively young, depositional surfaces. Decades of research have shown that as ecosystems and soils develop with time, rock-derived nutrients such as phosphorus (P) are lost due to weathering, whereas N tends to accumulate in soil primarily due to biological N fixation (Jenny 1941, Vitousek et al. 1997b, Birkeland 1999). Thus, many tropical forests, especially those on old, highly developed soils, are likely to be limited by the supply of P or another rock-derived nutrient (Vitousek 1984, Vitousek and Sanford 1986). Conversely, many tropical forests are likely to have N in excess supply (Martinelli et al. 1999); tropical forests tend to cycle more N through litterfall (Vitousek and Sanford 1986), have higher relative nitrification rates and N trace gas fluxes (Matson and Vitousek 1987, Vitousek

and Matson 1988), and have higher background hydrologic N losses than most temperate forests (Lewis et al. 1999). Unlike N-limited ecosystems that often experience lags in hydrologic NO_3^- losses due to biotic demand for N inputs, ecosystems in which N is already in excess may respond to N inputs with elevated rates of nitrification and immediate and large NO_3^- losses (Matson et al. 1999, 2002).

Edaphic factors such as soil texture, structure, and charge also vary as a function of soil age and may be important determinants of NO_3^- transport and retention processes. Differences in soil texture may influence hydrological transport rates and affect the ability of biotic and chemical processes to retain N. Differences in structure may route water and NO_3^- along differential flow paths during storm events and drainage periods. Tropical soils with substantial quantities of variable charge minerals and, subsequently, high anion exchange capacity (AEC) can adsorb NO_3^- (Singh and Kanehiro 1969, Kinjo and Pratt 1971) and may potentially alter its mobility (Sollins et al. 1988). These hydrological and chemical controls on N cycling and losses may be important in understanding and predicting losses from wet tropical forests receiving elevated N inputs.

Wet tropical rainforests located at the extreme ends of a soil chronosequence in the Hawaiian Islands offer a unique opportunity to explore the responses of tropical forests of different soil age to short- and long-term N additions. Long-term fertilization studies at these sites have demonstrated that N limits aboveground net primary productivity (ANPP) at the youngest, 300-year-old soil site (Vitousek et al. 1993), and P limits productivity at the oldest, 4.1-Myr-old soil site (Herbert and Fownes 1995). Studies across this chronosequence have shown that background rates of nitrification and losses as N trace gases and NO_3^- in soil solution are higher at the oldest site compared to the younger sites, suggesting that N may already be a nutrient in excess at the oldest site (Crews et al. 1995, Riley and Vitousek 1995, Hedin et al. 2003). In one of the few studies looking at the biogeochemical responses of tropical forests to anthropogenic N inputs, Hall and Matson (1999) found that fertilizer-induced N trace gas fluxes from the oldest soil site were higher after a single N fertilizer addition than were those from plots at the youngest soil site that had received 12 years of chronic N fertilization. Their work suggested that biological processes were less important for N retention at the oldest soil site than at the youngest soil site (Hall and Matson 1999, 2003). In these experiments, N trace gas losses represented <5% of the N added as fertilizer; the fate of the remaining N was not followed.

Here, we evaluate the effects of first-time and long-term, repeated N additions on hydrologic nutrient losses from these wet tropical forests. We asked the following general questions: What are the patterns of soil solution NO_3^- losses from tropical forests of different

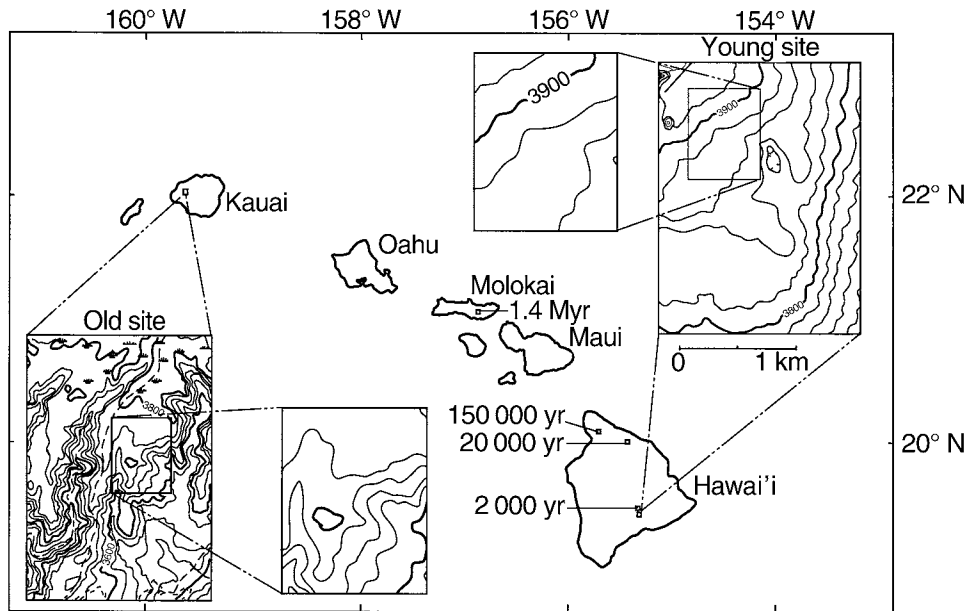


FIG. 1. Location of the young (300-yr-old) soil site on the Big Island of Hawai'i and the old (4.1-Myr-old) soil site on Kauai in the Hawaiian Islands. Boxes indicate locations of six sites along the chronosequence. The double inset boxes show approximate study site locations.

soil age following first-time and long-term N additions? What are the processes controlling these losses? In this paper, we compared background solution N losses between sites, examined in detail NO_3 losses following first-time and long-term N inputs, and explored the biogeochemical and hydrological processes regulating these losses.

METHODS

Study sites

The study sites are a part of a well-characterized soil chronosequence in the Hawaiian Islands (Fig. 1; Crews et al. 1995, Vitousek et al. 1997b). This chronosequence consists of six sites that range in soil age from 300 years to 4.1 million years and span early to late-weathering stages as Andisols, Ultisols, and Oxisols (Crews et al. 1995). While soil age varies across these sites, other state factors (Jenny 1941) including biota, parent material, slope, and climate are held relatively constant. The sites support native, intact wet tropical rainforest forest dominated by *Metrosideros polymorpha* (80–90% of the basal area of species within plots at each site) (Kitayama and Mueller-Dombois 1995). None is known to have been cleared by humans, but as acknowledged by Crews et al. (1995), the possibility of human and natural disturbances cannot be totally dismissed. Soils are derived primarily from basaltic volcanic tephra overlying lava or a lava-ash mixture (Torn et al. 1997). The sites are relatively level with slopes under 6% (Crews et al. 1995). Finally, climate conditions are similar at the sites; modern mean annual temperature and precipitation are 16°C and 2500 mm,

respectively. An island-wide analysis by Juvik and Juvik (1998) has indicated slight seasonality in precipitation, with a majority of the rainfall occurring from November to April. We tested for seasonality at our study sites with 7–12 years of site-specific rainfall data (1987–1999). While we found slightly higher rainfall during winter (November–April) compared to summer rainfall (May–October), these differences were not significant at both sites (ANOVA, $P = 0.1$ – 0.2). Over longer geologic periods, however, climate and vegetation have varied at the older sites due to Pleistocene climate change and subsidence (Hotchkiss and Juvik 1999, Hotchkiss et al. 2000). More detailed descriptions of the soil age gradient and NPP-limitation studies can be found in Crews et al. (1995) and Vitousek (2004).

The two sites used in this study represent the extremes in soil and ecosystem development: a N-limited forest on a poorly developed, 300-year-old soil and a P-limited forest on a highly developed, 4.1-Myr-old soil (Fig. 1). Differences between the sites in forest composition and stature (Kitayama and Mueller-Dombois 1995), productivity and resource use efficiencies (Crews et al. 1995, Harrington et al. 2001), and foliar nutrient concentrations (Vitousek 2004) reflect the effects of soil age and fertility. We refer to these two sites as the young and the old site hereafter. The young site is located on a relatively flat shield surface at an elevation of 1190 m near Hawaii Volcanoes National Park on the Island of Hawai'i (19°25' N, 155°15' W). The young soil, classified as a Lithic Hapludand (Andisol), consists of 200–400 year old tephra deposits

composed of volcanic glass and short-range order minerals (Chorover et al. 1999). An organic matter (O) horizon of 10-cm thickness overlies a 10-cm mineral (A) horizon consisting of cinder with a gravel content of 59% (Soil Survey Staff 2004). Below this layer, a buried soil horizon (Bwb) is in contact with unweathered basalt at 34 cm. The old soil site is situated on a relatively flat ridge top on the remnant shield surface at 1134 m elevation in the Na Pali-Kona State Forest Reserve on the Island of Kauai (22°08' N, 159°37' W). Determination of whether the soils were derived from tephra or lava at this site has been difficult because of the weathered condition of the substrate, but the parent material is estimated to be 4.1 million years old. It is currently thought that the old site may have developed primarily on late-stage caps of post-shield alkalic rocks (Kurtz et al. 2001). The old soil is classified as a Plinthic Kandiodox (Oxisol) and composed primarily of secondary crystalline minerals including halloysite, kaolinite, and crystalline Fe and Al (hydr)oxides (Chorover et al. 1999). An O horizon overlies a weak, often absent, mineral (A) horizon to ~10-cm depth. Below this layer, a Bc horizon, composed of plinthite or indurated peds with a strong medium subangular blocky structure (40% gravel content), overlies a reduced sandy-clay-loam oxic horizon (Bo1) at 20 cm depth (Soil Survey Staff 2004). This horizon extends down into more oxidized silty-clay-loam Bo horizons (Bo2–5). Gleying at the Bo1 horizon contact was indicative of a fluctuating or perched water table and prompted us to examine hydrological as well as biogeochemical controls on nutrient losses.

Experimental design

At both sites, we examined the pattern and regulation of N soil solution losses for six months following each of two fertilization events. Our experimental design included three treatments: unfertilized controls (C), first-time N fertilizer (FTN), and long-term N fertilizer treatments (LTN). The unfertilized controls and long-term N fertilizer treatments at each site were part of an existing complete factorial fertilization experiment ($N \times P \times$ complete nutrients) with four replicates (20×20 m plot). Nitrogen fertilizer, half as urea and half as ammonium nitrate (NH_4NO_3), was initially applied at $100 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ in 1985 at the young site and in 1991 at the old site, and then applied twice yearly at 50 kg N/ha per application thereafter. At the start of this study, these fertilization plots had already received 13 and 7 years of N additions at the young and old site, respectively, and are referred to as the “long-term” N addition plots hereafter. At the old site, one long-term plot at the north end of the site was eliminated from the experimental design due to evidence of erosional activity and soil property differences (P. Vitousek, *personal communication*). Within the vicinity of the established control and long-term plots, we also established four 10×10 m never-before-fertilized

plots that received N additions for the first-time, referred to as the “first-time” N addition plots hereafter.

We maintained a pre-existing, offset fertilization schedule at the two sites, applying N for the first time in late July 1998 at the young site and November 1998 at the old site at the same rate and fertilizer combination as the long-term N addition plots. The first-time and long-term fertilized plots received another N application at 50 kg N/ha in late February and May 1999 at the young and old site, respectively. Prior studies by Hall and Matson (1999) used a similar experimental design (with an offset fertilization schedule) at these two forest sites to evaluate N trace gas responses to experimental N inputs and showed no seasonal variation in trace gas fluxes following fertilization. A recent study by Hedin et al. (2003) also showed no seasonal differences in background N cycling and gaseous and aqueous loss pathways at these two sites over a three-year period, again suggesting that seasonal variation in nutrient-cycling processes are not typical at these sites. The lack of seasonality in rainfall and nutrient cycling justified the offset sampling schedule, but logistical constraints would have necessitated some offset regardless. Although the rate of N application to the first-time and long-term plots was too large and pulsed to mimic anthropogenic N deposition, the experimental design (which was originally chosen to identify nutrient limitation) allowed us to evaluate the response of tropical ecosystems of different soil age to substantial changes in available N.

Lysimeter installations.—Six months prior to these experiments, we established two Prenart tension lysimeters (Prenart Equipment, Frederiksberg, Denmark) in each of the four replicate plots of the unfertilized control, first-time, and long-term treatments at each site (24 lysimeters total at the young site and 22 total at the old site). Following protocols described by Hedin et al. (2003), we installed lysimeters below the majority of the rooting zone (Ostertag 2001); the average depths of the lysimeters were 28 ± 2 cm at the young site and 47 ± 9 cm at the old site. We located the access holes and vacuum containers downslope of the lysimeters to minimize possible installation flow path effects. Previous experience with these lysimeters showed that fine clay particles at the old site clogged the quartz gel pores over time. To eliminate this problem, treat both sites similarly, and improve capillary contact, we installed all lysimeters in slurries of clean and well-rinsed silica flour (Sibelco, M.O.K., Vordingborg, Denmark). Prior to installation, lysimeters, sample tubes, and collection containers were thoroughly rinsed with deionized water and tested for chemical contamination. All cations and anion concentrations were $<0.05 \mu\text{g/L}$. After installation, lysimeters were tested for suction on a regular basis and soil solution flushed.

Hydrological instrumentation.—Along with the lysimeter installations, we established a set of nested hydrological instruments in each of the never-before

fertilized plots to determine the rate and direction of solute transport ($n = 4$ nested sets). This nested design consisted of two tensiometers and one piezometer, one well, and one time domain reflectometry (TDR) probe installed at three different depths representing distinct soil genetic horizons ($n = 24$ tensiometers, 12 piezometers, 12 TDR probes, and 4 wells per site). Tensiometers and piezometers were located along a transect parallel to the low surface gradient with TDR probes of similar depth positioned 0.5 m away. TDR probes were installed vertically to minimize disturbance to the experimental plots. At the young site, tensiometers and piezometers were installed at an average depth of 10 cm (O horizon), 20 cm (A horizon), and 30 cm depth (Bw horizon), and TDR probes were installed vertically to 20 cm and 30 cm depth. At the old site, tensiometers and piezometers were installed at an average depth of 10 cm (O horizon), 20 cm (Bc horizon), and 50 cm (Bo horizon), and TDR probes were installed vertically to 20 cm, 30 cm, and 50 cm depth. Tensiometers were surveyed to account for within-plot elevational differences (z) using a Leica TC-1100 total station surveyor (Leica Geosystems, Heerbrugg, Switzerland). More detailed descriptions of the design, custom-made construction, and installation of tensiometers and piezometers are given by Lohse (2002).

Environmental conditions

We monitored climatic conditions at both sites using existing micrometeorological stations located <2 km from the main experimental plots. Precipitation was measured hourly using an automated tipping bucket rain gauge (0.254 mm per tip). Hourly relative humidity, temperature, global radiation, net radiation (old site), wind speed, and photosynthetically active radiation (PAR) were also obtained. Net radiation (R_n) at 2 m above the canopy was measured with a net radiometer (Q7: Radiation and Energy Balance Systems, Seattle, Washington, USA). The manufacturers have shown that the Q7 underestimates R_n . To improve accuracy, we multiplied R_n data by a correction factor of 1.159 in accordance with manufacturer instructions as described by Bigelow (2001).

We manually monitored soil water content and energy status at the time of lysimeter sampling described below (see *Soil solutions losses*). We used commercially made three-channel TDR wave guides from Dynamax (Dynamax, Houston, Texas, USA) connected to a Tektronix 1502B metallic cable tester (Tektronix, Wilsonville, Oregon, USA) to measure volumetric soil water content (θ_v), the water volume per volume of dry soil (Tindall et al. 1999). We collected and interpreted data using Dynamax TACQ software with algorithms by Topp et al. (1980) and automated wave-form interpretation by Baker and Allmaras (1990). TDR measured θ_v at different soil depths (and therefore different textures) agreed very well with θ_v measurements derived from the product of gravimetric soil water content

(θ_g) and soil bulk density ($r^2 = 0.95$) (Lohse 2002). To monitor the soil energy status in unsaturated soil conditions, we used a digital read-out pressure transducer with short response time of ~ 5 s (see Marthaler et al. 1983) to measure soil water pressure head (h) in units of length (cm) in the tensiometers. Measurement accuracy was within 1 cm. During and after large rainfall events, we monitored piezometers and wells with a solid tape measure for hydraulic head (H), pressure head (h) plus gravitational head (z), and water table boundary conditions.

Soil solution losses

Lysimeter sampling design.—At both sites, we collected lysimeter samples once a week in the month prior to N additions to determine background or pre-fertilization soil solution concentrations. To evaluate the response to fertilizer additions in the first-time and long-term N input treatments, we continuously collected soil solution for the first month immediately after N fertilization and then weekly thereafter. Following the second N application, we sampled lysimeters once a week due to overlapping and conflicting fertilization schedules on the different islands.

Soil solution was collected over a 2–3 day period by applying a 32-cm Hg vacuum to the lysimeter collection containers. We used a clean high-density polyethylene (HDPE) syringe to withdraw sample solution through a small-diameter Teflon access tube and collected duplicate samples in HDPE Nalgene bottles that were washed and pre-leached in deionized (DI) water (18.0–18.2 m Ω). Prior to solution sample collection, each bottle was rinsed three times with 5–10 mL of sample liquid through a pre-leached disposable Gelman acrodisc filter (<1 μ m normal pore size). Samples were kept on ice until they were removed from the field and expressed mailed to Stanford University for analysis. No preservative was added because prior research showed no significant differences between with- and without-chloroform samples (Hedin et al. 2003). One set of soil solution samples was stored at 4–7°C and typically analyzed for NO₃⁻ the day after collection or within a week of collection. The other set of samples was frozen for later analyses.

Soil solution analytical methods.—Soil solution samples were analyzed for NO₃⁻-N by Alpkem continuous-flow colorimetry (OI Analytical, College Station, Texas, USA) using a NO₃⁻ reduction method with cadmium metal (Alpkem 1992b). Method detection limit (MDL) was 1 μ g/L for NO₃⁻-N in water. A subset of samples was analyzed for ammonium (NH₄⁺) and dissolved organic nitrogen (DON). Ammonium was analyzed following the phenol seawater NH₄⁺ method (Alpkem 1992a). The MDL for NH₄⁺-N was <1 μ g/L. Total nitrogen (TN) was measured by NO₃⁻ colorimetric analyses following high-temperature (120°C) persulfate combustion of all N forms to NO₃⁻ (D'Elia et al. 1977, McDowell et al. 1987). Laboratory-made

glycine standards were obtained from laboratories also analyzing for DON at these same study sites (Hedin et al. 2003). NIST standards of NO_3^- and NH_4^+ were digested to test glycine standards and the digestion efficiency. Results from these tests showed 8–9% loss in TN recovery above 3 mg NO_3^- -N/L, so that samples were diluted below this value to obtain total recovery of N. The MDL for TN was 8 $\mu\text{g/L}$ as NO_3^- -N. Dissolved organic nitrogen was calculated as the difference between total nitrogen (TN) and dissolved inorganic N (DIN), $\text{NH}_4^+ + \text{NO}_3^-$. Standard error for DON was estimated by Gaussian error propagation (Taylor 1982, Morgan and Henrion 1990).

Estimating vertical and horizontal water fluxes.—We estimated vertical water fluxes by the following two methods: (1) measurement of total hydraulic head gradient below the rooting zone and the determination of unsaturated hydraulic conductivity (referred to the tensiometry approach hereafter) and (2) solution of a simple water balance equation for water drainage. Both methods are limited in their estimation of soil water drainage (Cooper 1980, Russell and Ewel 1985, Brugge 1988, Bruijnzeel 1991), but a comparison of these estimates allowed evaluation of the individual methods. Detailed descriptions of both methods are provided in Appendix A.

We estimated horizontal water fluxes by tensiometry at different time points and depths to determine the presence and possible importance of lateral flow under varying rainfall conditions. Because the tensiometer design was optimized for measurement of vertical water flux, no attempts were made to estimate cumulative horizontal water fluxes.

Calculated nitrate solution losses below the majority of the rooting zone.—We estimated daily NO_3^- loss with the water balance method described in the previous subsection because it provided a continuous record of drainage and captured all storm events and water movement associated with them. Lysimeter NO_3^- concentrations from the two lysimeters were averaged within each plot and then daily NO_3^- concentrations were linearly interpolated over missing time periods. Daily NO_3^- loss was calculated from the product of the plot-averaged NO_3^- concentration ($c_{x(t)}$) and daily water fluxes (Q_t). We estimated cumulative NO_3^- losses over a three-month and six-month period following N inputs.

Soil mineral N pools and net transformations

To evaluate the effects of first-time and long-term N additions on biogeochemical processes controlling N losses, we determined soil exchangeable mineral N pools and transformation rates weekly in the month prior to and immediately following N fertilization events. In each control, first-time, and long-term plot, five soil cores (0–10 cm depth) were randomly collected, combined, and then processed immediately upon returning from the field. Exchangeable mineral N

concentrations and rates of net mineralization and nitrification were measured following KCl extraction and aerobic laboratory incubation methods described by Hall and Matson (2003). Samples were analyzed for NO_3^- -N by the nitrate method (Alpkem 1992b). Ammonium (NH_4^+ -N) was analyzed using a modified total Kjeldahl N method (Alpkem 1992c). Due to overlapping fertilization cycles at the two sites, we only collected soil samples during the first fertilization period.

We also collected deep soil cores three weeks after N additions to evaluate the effects of first-time and long-term N additions on mineral N pools and transformation rates with soil depth. In each plot, one to two cores were collected down slope and at least 5 m away from the lysimeters to ~30 cm and 50 cm depth at the young and old site, respectively, stratified by soil genetic horizon, and then processed for determination of soil N pools and transformation rates.

Soil pH and cation and anion exchange capacity

Because soils high in anion exchange capacity (AEC) can adsorb NO_3^- and potentially alter its mobility, we also characterized differences in soil pH, cation exchange capacity (CEC), and anion exchange capacity (AEC) between sites and depths on the deep control soils. Soil pH was measured in deionized (DI) water and 0.01 M CaCl_2 suspensions using a combination electrode (Thomas 1996). We determined AEC and CEC using an unbuffered salt extraction method with NH_4Cl and KNO_3 described by Sumner and Miller (1996). Extraction solutions were adjusted to the field pH of the unfertilized soils at each site. We calculated the nitrate retention capacity (NRC) of these horizons as the potential amount of NO_3^- -N that exchange sites could retain assuming no competing anions.

Statistical analyses

Statistical analyses were focused on within-site rather than between-site post-fertilization responses. The effects of N addition treatments were compared separately for the two sites using one of the two approaches, repeated-measures ANOVAs or simple ANOVAs. Repeated-measures analysis of variance (RMANOVA) was performed to test for effects of treatment, time, and treatment \times time interactions on soil and lysimeter solute N concentrations within sites. Statistical tests between sites were performed where hypotheses were explicitly identified; otherwise, differences are reported in terms of magnitude. In many cases, data were cube-root transformed to improve normality and homoscedasticity. Where appropriate, standard errors were estimated by Gaussian or first-order error propagation (Taylor 1982, Morgan and Henrion 1990). Results were considered significant at the $P \leq 0.05$ level. Post hoc Tukey-Kramer honestly significant difference (hsd) tests and Dunnett tests were performed for comparison of all means or treatments relative to control, respectively. Comparison circles were used for mean

TABLE 1. Comparison of total rainfall and cumulative drainage (ΣQ ; mean \pm SE) over three- and six-month periods following fertilization at the young (300-yr-old) and old (4.1-Myr-old) soil sites.

Site and fertilization event [†]	Study period (mo)	Rainfall (mm)	Cumulative drainage (mm)	
			Water balance	Tensiometry
Young soil site				
First	3	546	329.0 \pm 30	362 \pm 38.7
	6	1831	1477.2 \pm 100	1076.2 \pm 45.8
Second	6	1166	821.8 \pm 60	760.6 \pm 34.6 [‡]
Old soil site				
First	3	550	320.7 \pm 30	370.3 \pm 41.2
	6	782	331.0 \pm 40	521.9 \pm 49.3
Second	6	558 [§]	138.9 \pm 20	379.7 \pm 39.8

Note: Water losses (cumulative drainage) were calculated by tensiometry and water balance.

[†] The first fertilization occurred on 31 July 1997 (young site) and 18 November 1997 (old site). The second fertilization took place on 26 February 1998 (young site) and 26 May 1998 (old site). During the one month prior to the second fertilization, 24 January–25 February 1997, 912 mm of rain fell at the young site. This period was not included in the six-month post-fertilization rainfall and water flux estimates.

[‡] Tensiometry data were available for three months.

[§] The micrometeorological station was down for repairs during 14 May–7 June 1998 at the old site.

comparisons with unbalanced data. For post hoc comparison of repeated measures, we adjusted for experiment-wise error using the Bonferroni method (Sokal and Rohlf 1981). Statistical calculations were carried out with JMP software (SAS Institute 1999).

RESULTS

Environmental conditions

Although the two sites were selected because they receive the same mean annual precipitation, they experienced differing amounts of rainfall during the two six-month study periods (Table 1). During the three months following the first N fertilization, however, the sites received similar amounts of rainfall, 546 mm at the young site and 550 mm at the old site. Thereafter, the young site received above normal rainfall, and the old site received below normal rainfall (Fig. 2a, d). In the analyses and discussion that follow, we focus our between-site comparisons on this three-month period, when rainfall conditions were similar, and evaluate the within-site responses to N additions over the six-month fertilization cycles.

At the young site, rainfall amounts were higher than normal for most of the study period. One month prior to and after the first fertilization, however, conditions were drier than normal due to an El Niño episode reflected by more negative soil pressure heads and lower θ_v (Fig. 2b, c). Thereafter, soil water potential and θ_v varied with rainfall events. In December 1998, the site started to experience enhanced rainfall due to strong La Niña episodes, and these conditions persisted through most of the second fertilization cycle.

In contrast to the young site that received above normal rainfall, the old site received below normal rainfall for most of the study period and experienced more

dramatic wetting and drying cycles. One month before the first fertilization, the old site went through a major drying event indicated by very negative water potential and low θ_v (Fig. 2e, f). Fertilization took place in mid-November after a major storm event wetted the entire soil profile, and for the two months following fertilization, rainstorm events were relatively frequent. On numerous occasions during this period, the soil profile neared soil water saturation (Fig. 2f, inset); pressure head neared zero and even positive pressures were observed in the tensiometers in the subsurface Bo horizon. A perched water table at the contact between the Bc and Bo1 horizon was also observed during and after these storm events (Fig. 2f, inset); 20–25 cm water collected in all four wells, but not piezometers, indicating that water was draining rapidly through the surface layer, ponding at the clay contact, collecting in the wells, and slowly draining through the clay horizon. Drought conditions commenced in March and persisted through the second N application cycle.

Nitrate solution losses following first-time and long-term fertilization

Prior to N additions, DON was the dominant form of soil solution N at the young site, whereas NO_3^- was at the old site (Fig. 3a, b). Background soil solution NH_4^+ and DON concentrations did not vary between sites, while concentrations of NO_3^- were two orders of magnitude higher at the old site than the young site, 0.442 ± 0.0125 compared to 0.002 ± 0.0002 mg NO_3^- -N/L (mean \pm SE; $n = 27$). Following fertilizer additions to the first-time and long-term N addition treatments, NO_3^- was the dominant N form in soil solution at both sites (Fig. 3c–f). Soil solution NH_4^+ and DON concentrations were similar in the first-time and long-term N treatments.

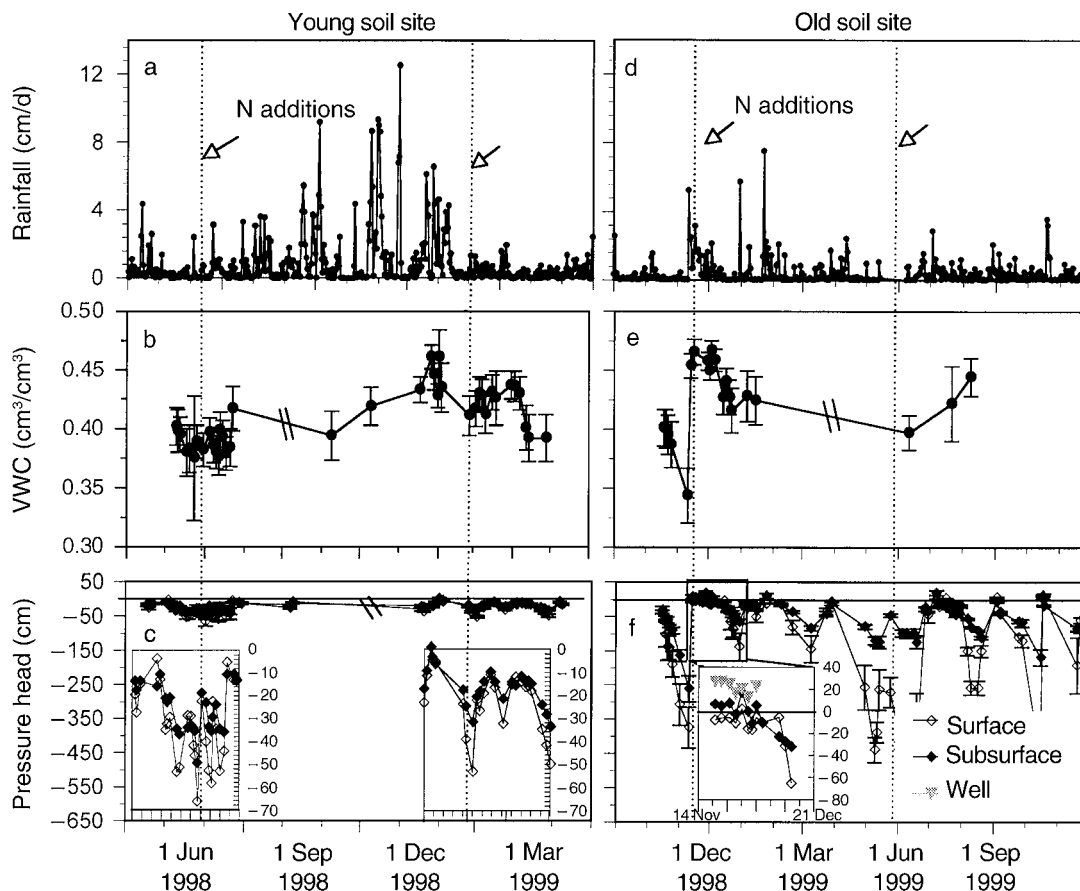


FIG. 2. Daily rainfall, volumetric water content (VWC; \pm SE), and pressure head (\pm SE) at (a–c) the young (300-yr-old) soil site from 1 June 1998 to 1 June 1999 and (d–f) the old (4.1-Myr-old) soil site from 1 September 1998 to 1 December 1999. Dotted lines indicate timing of fertilization. Soil energy status as pressure head is shown in the surface soils (at 10 cm depth; open diamonds) and subsurface soils (30 cm depth [young site] or 50 cm depth [old site]; solid diamonds) ($n = 4$). The inset in (f) shows the water level in wells (gray triangles) at the old site.

In contrast to our expectations that the young, N-limited forest would initially retain N inputs, both forests responded immediately to first-time N additions with significantly elevated soil solution NO_3^- concentrations (Fig. 4; RMANOVA, $P < 0.0005$). Long-term fertilized forests responded to N additions with even higher concentrations. Patterns of NO_3^- in solution differed markedly between sites and appeared to reflect differences in rate and quantity of soil-water flow.

At the young site, we observed a significant increase in soil solution NO_3^- concentrations approximately one month after fertilization in the first-time and long-term N plots (Fig. 4c) that coincided with first major rainfall event and high instantaneous vertical water fluxes (J_{wv}) as measured by tensiometry (Fig. 4e). Concentrations in the first-time fertilized forests declined thereafter, but concentrations continued to increase in the long-term N-fertilized forests and peaked two months after N additions, again coinciding with another storm event and relatively high water fluxes. Concentrations returned to background levels four months after fertil-

ization. Responses following the second fertilizations showed similar patterns of immediate and significant, albeit much smaller, NO_3^- losses (RMANOVA, $P < 0.05$).

At the old site, N inputs to first-time and long-term fertilized forests resulted in immediate and significant increases in lysimeter NO_3^- concentrations, but concentrations were lower and more extended than those at the young site (Fig. 4d). As seen in Fig. 4f, concentrations followed the temporal pattern of slow soil water drainage as measured by tensiometry, consistent with low saturated hydraulic conductivity (K_s) measures found in the subsurface Bo horizon (0.08 cm/h) (Lohse 2002; Lohse and Dietrich, *in press*). In contrast to the young site, where concentrations returned to pre-fertilization levels, lysimeter concentrations at the old site remained elevated even five months after N additions. The patterns of NO_3^- in solution following the second application of N were similar to the first, but slightly more variable due to the behavior of one aberrant lysimeter (RMANOVA, $P < 0.05$).

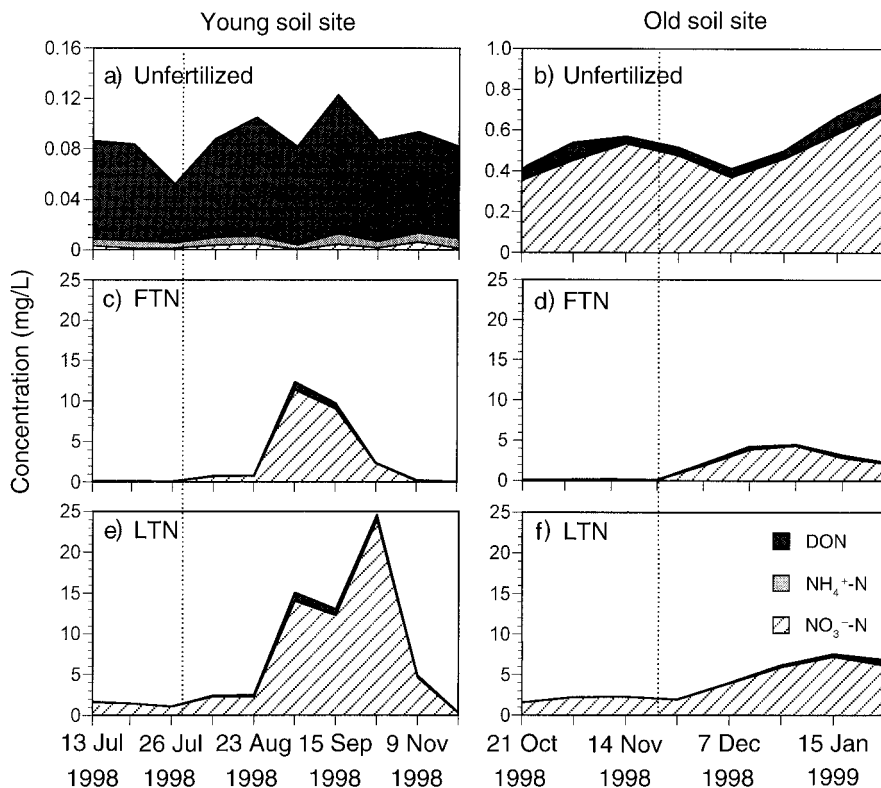


FIG. 3. Background soil solution $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and dissolved organic nitrogen (DON) at the (a) young (300-yr-old) soil site and (b) old (4.1-Myr-old) soil site, and (c-f) soil solution concentrations following first-time (FTN) and long-term (LTN) N additions.

Horizontal flux analyses by tensiometry showed that horizontal fluxes (J_{wh}) of water and likely NO_3^- occurred at both sites, but the relative importance appeared to differ between sites. A comparison of Fig. 4e and g shows that under almost all rainfall conditions, vertical fluxes of water and NO_3^- dominated at the young site. However, under extremely high intensity and duration rainfall (maximum 12.5 cm/h intensity, 101 cm total monthly rainfall), water and, potentially nitrate, appeared to move laterally as well as vertically. At the old site, solute transport was downward moving under low rainfall conditions. When rainfall intensities exceeded the soil water drainage rate of the subsurface clay layer (0.08 cm/h), lateral movement of water and NO_3^- appeared to be equal or slightly higher than vertical solute transport (Fig. 4f, h).

Estimated daily vertical water fluxes.—Methods for estimating daily vertical water loss (Q) showed variation in timing and magnitude of Q (Fig. 4i, j) but yielded reasonable cumulative water losses (Table 1). In general, the water balance approach reflected the timing and magnitude of soil water fluxes associated with storm events better than the tensiometry method. The water balance method also provided a continuous record of soil water drainage compared to the tensiometry method, in which interpolation between large

time gaps was required to estimate cumulative fluxes. Finally, this method illuminated that we were unable to sample our tensiometers and lysimeters during several large rainfall events. In particular, we missed two storm events early after the second addition of N at the young site that delivered 330 mm total rainfall, compared to the initial rainfall event of 118 mm that resulted in large NO_3^- solution losses following the first application of N (Fig. 4i). These findings suggest that we missed large pulses of NO_3^- associated with these storms and therefore underestimated fluxes of water by tensiometry and nitrate in solution by lysimetry during these events. Given the limitations of the tensiometry method, we display mean daily NO_3^- fluxes and report cumulative N losses by the water balance method.

Cumulative nitrate solution losses.—In the three months following the first application of N, when rainfall conditions were similar between sites, total NO_3^- leaching losses from first-time and long-term fertilized forests were significantly elevated relative to control at both sites (ANOVA, $P < 0.0001$; Fig. 4k, l). Nitrate losses from the first-time N-fertilized forests at the young site were larger than those from forests receiving first time N inputs at the old site (Table 2). Nitrate losses from long-term fertilized forests at the young site were significantly greater than losses from forests

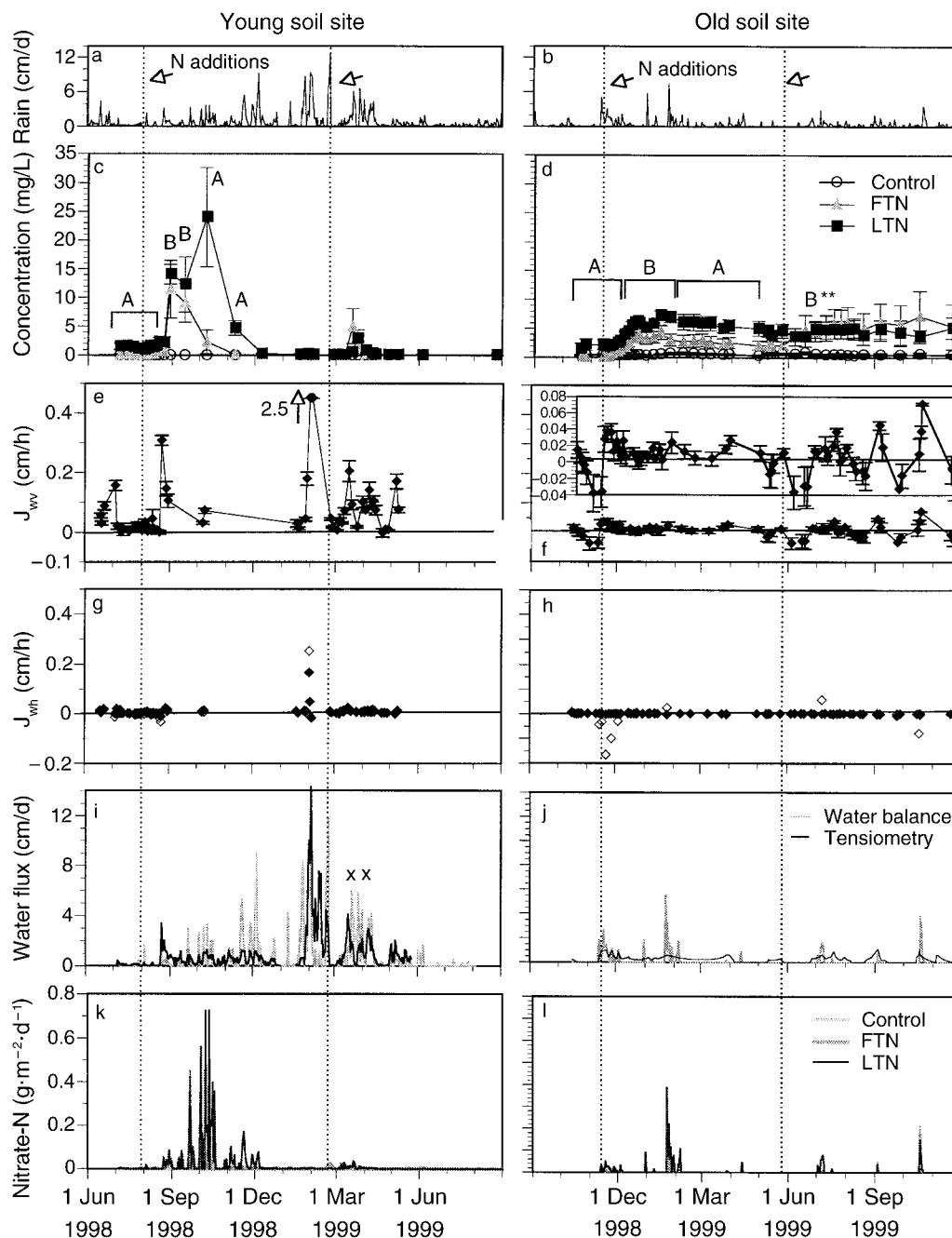


FIG. 4. Fertilizer effects of first-time and long-term N additions on NO_3^- solution losses from the young (300-yr-old) and old (4.1-Myr-old) site. (a, b) Daily rainfall at the two sites. (c, d) Mean (\pm SE) NO_3^- -N concentrations for control (open circles), first-time (FTN; gray triangles), and long-term (LTN; solid squares) N fertilizer treatment ($n = 4$, except at the old site, where LTN $n = 3$). Dotted lines indicate timing of first and second fertilizations. Nitrate concentrations were cube-root transformed prior to RMANOVA and post hoc analyses. Uppercase letters indicate the following: A, LTN > control; and B, both FTN and LTN > control. Post hoc results are considered significant if $P < 0.01$ prior to N additions and $P < 0.003$ after N additions, except after the second fertilization at the old site, where results were considered slightly significant as indicated by B** if $P < 0.01$. (e, f) Measured mean vertical fluxes (J_{wv} ; by tensiometry approach) below the rooting zone (20–30 cm at the young site and 20–50 cm at the old site; solid diamonds). (g, h) Mean horizontal water fluxes (J_{wh}) at the following soil depths: 10–20 cm (open diamonds) and 20–30 cm at the young site and 20–50 cm at the old site (solid diamonds). (i, j) Estimated mean daily vertical water flux (Q) by the tensiometry (black line) and water balance (gray line) methods. Lowercase x's indicate the times when two major rainstorms were missed at the young site. (k, l) Mean daily nitrate fluxes below the majority of the rooting zone for the young and old sites.

TABLE 2. Fertilizer lost as nitrate leaching losses at the young (300-yr-old) and old (4.1-Myr-old) soil sites during the three and six months following N additions.

Site and treatment	NO ₃ ⁻ -N leaching losses (kg/ha)	
	3 months	6 months†
Young soil site		
Control	0.009 ^a ± 0.001	0.041 ± 0.01
FTN	11.83 ^b ± 5.32	12.57 ± 5.92
LTN	53.11 ^c ± 16.41	66.25 ± 19.55
Old soil site		
Control	1.83 ^a ± 0.48	1.88 ± 0.49
FTN	6.57 ^b ± 1.83	6.81 ± 1.89
LTN	15.51 ^b ± 1.56	16.04 ± 1.68

Notes: Treatment abbreviations are: FTN, first-time N fertilized; LTN, long-term N fertilized. Lowercase letters indicate significant differences within columns (ANOVA, $P < 0.05$). All fluxes were cube-root transformed prior to ANOVA and post hoc Tukey tests.

† Between-site ANOVA tests were only performed for the three-month period when rainfall conditions were similar.

receiving first-time N inputs at both sites (Tukey, $P < 0.05$). Horizontal flux data during this time period indicated that lateral losses would have been minimal at the young site, whereas total NO₃⁻ losses via lateral movement from the old site would have been potentially significant.

Six months after N additions, total fertilization-induced losses from the first-time and long-term N treatments were similar to those after three months (Table 2), although total losses from the long-term N treatment plots at the old site were now significantly elevated relative to the first-time N addition treatment and control plots (Tukey, $P < 0.05$). While leaching losses as NO₃⁻ were lower and more variable following the second application of N, they were still significantly elevated (ANOVA, $P < 0.05$). At the young site, NO₃⁻ losses were 1.26 ± 0.90 and 3.11 ± 1.3 kg N/ha in response to fertilization in the second-time and long-term N plots, respectively. Sampling error most likely explained the smaller observed losses. At the old site, six-month cumulative losses in the second time and long-term N treatments were 6.98 ± 3.66 kg N/ha and 6.49 ± 1.69 kg N/ha, respectively. We expect that losses would have been much higher under normal rainfall conditions at this site (Table 1).

Soil inorganic N pools and transformation rates

Prior to N additions, NH₄⁺ pool sizes in unfertilized control soils were not substantially different between sites (Fig. 5). In contrast, soil NO₃⁻ pools at all soil depths were two orders of magnitude higher at the old site compared to the young site (Fig. 5, Appendix B). Rates of net mineralization and nitrification in surface soil horizon at the old site were also one to two orders of magnitude higher than the young site and initially declined with depth (Appendix B).

At both sites, N additions to previously unfertilized and long-term N-fertilized forests significantly in-

creased soil mineral N pools relative to controls, and these pools varied significantly over time (RMANOVA, $P < 0.05$; Fig. 5). At the young site, N additions significantly increased soil NO₃⁻ pool sizes relative to NH₄⁺ pools (Fig. 5a, b), whereas they significantly increased NH₄⁺ but did not alter NO₃⁻ pools at the old site (Fig. 5e, f). At both sites, soil mineral N pools in long-term fertilized forests were significantly elevated immediately after N inputs and even five months after the last fertilization (Fig. 5).

Consistent with our expectations, rates of net mineralization and nitrification differed dramatically between sites after first-time and long-term N inputs and varied significantly with time at the young site (RMANOVA, $P < 0.05$). Significant microbial immobilization of N took place immediately after first-time N additions in the N-limited forest at the young site (Fig. 5c). In contrast, N additions to the long-term fertilized forests at this site significantly increased rates of net mineralization and nitrification (Fig. 5c, d). At the old site, N additions to previously unfertilized and long-term fertilized forests did not alter rates of net mineralization (Fig. 5g), but significantly increased already high rates of net nitrification relative to control (Fig. 5h).

Three weeks after N additions, soil mineral N pools and process rates were still significantly elevated at depth (Appendix B). At the old site, soil NO₃⁻ pools were significantly elevated in the subsurface horizons of the long-term fertilized forests. While immobilization of N was no longer significantly elevated in the surface soil horizons at the young site, significant N immobilization was still taking place in the subsurface soil horizons. In the long-term fertilized forests, rates of net nitrification were significantly elevated with soil depth. At the old site, rates of net nitrification remained significantly elevated at depth in the first-time and long-term fertilized forests.

Soil pH and cation and anion exchange capacity

Soil pH, CEC, and AEC varied significantly with soil depth and between sites (ANOVA, $P < 0.05$; Table 3). Soil pH in DI-water suspensions were generally below 5 at the young site and below 4 at the old site in all soil horizons. Soil pH suspensions in CaCl₂ were even lower. In many cases, CEC was lower than AEC, indicating a slightly positive net charge. AEC was the highest in the subsurface Bo horizon at the old site. Potential NO₃⁻ retention capacity (NRC) was extremely high in the subsurface soil horizon at the old site.

Mass balance of different forms of N added

A synthesis of our results is presented as budgets for the different forms of N added to the first-time and long-term fertilized forests (Table 4). We report the amounts of different forms of N that were measured as exchangeable N immediately after N additions as the observed N pools (which also included any background

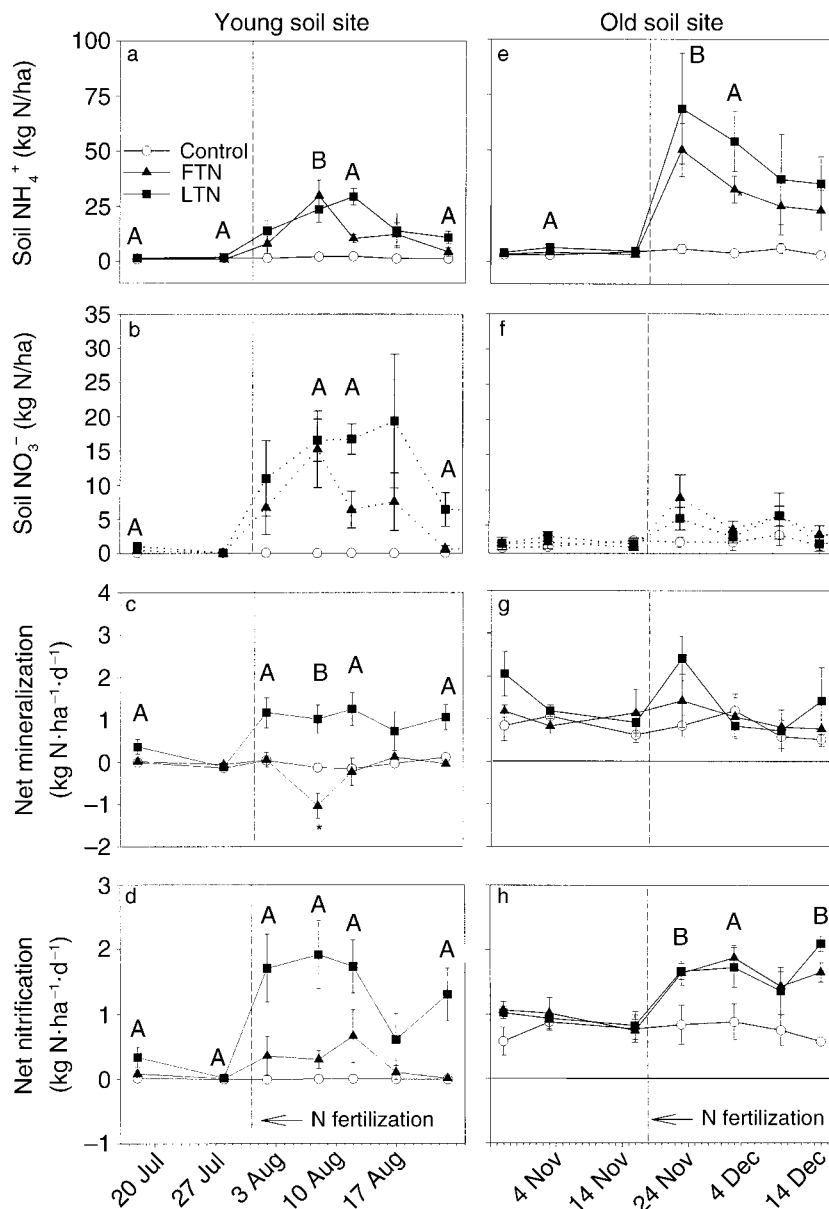


FIG. 5. Fertilizer effect of N additions on soil NH_4^+ and NO_3^- concentrations, net mineralization, and net nitrification rates in the first month after N additions at the (a–d) young (300-yr-old) and (e–h) old (4.1-Myr-old) soil sites (August and November 1998). Mean (\pm SE) values are shown for the unfertilized control (open circles), first-time (FTN; solid triangles) and long-term (LTN; solid squares) N fertilizer treatments ($n = 4$, except at the old site, where, for LTN, $n = 3$). Dashed lines indicate timing of N fertilization. All pools and fluxes were cube-root transformed prior to RMANOVA and post hoc analyses. Uppercase letters indicate the following: A, LTN > control; B, both FTN and LTN > control. Post hoc results are considered significant when $P < 0.01$.

N and residual fertilizer N from long-term fertilization), atmospheric N inputs estimated from Carrillo et al. (2002), the cumulative nitrate produced via nitrification and microbial N uptake as net immobilization in the first month following N additions, and cumulative N solution losses over a six-month period. The budgets showed striking differences in the patterns of N cycling and losses between sites and forms of N

(Table 4; data for the second fertilization are not shown).

At the young site, rates of net nitrification were quite low in response to first-time additions at the young N-limited site, yet we estimated that net nitrification produced an additional 7.75 ± 4.70 kg N/ha as NO_3^- during the month immediately following N additions before returning to pre-fertilization levels (Fig. 5). Nitrate

TABLE 3. Mean (and SE) soil pH in deionized (DI) water and 0.01 mol/L CaCl₂ suspensions, cation exchange capacity (CEC), anion exchange capacity (AEC), and NO₃⁻-N retention capacity (NRC) at the young (300-yr-old) and old (4.1-Myr-old) soil sites.

Site and soil depth (cm)	pH		CEC (cmol _c /kg)	AEC (cmol _c /kg)	NRC (kg N/ha)
	DI	CaCl ₂			
Young soil					
0–10	4.09 ^b (0.06)	3.84 ^b (0.09)	2.13 ^b (0.51)	3.03 ^{ab} (0.23)	118.04 (19.00)
10–20	4.82 ^a (0.08)	4.48 ^a (0.06)	0.59 ^c (0.27)	0.93 ^d (0.06)	53.35 (8.29)
20–50	5.07 ^a (0.07)	4.77 ^a (0.08)	1.87 ^{bc} (0.19)	1.92 ^c (0.17)	265.05 (44.13)
Old soil					
0–10	3.72 ^c (0.08)	3.41 ^b (0.16)	4.47 ^a (0.44)	3.43 ^a (0.13)	112.14 (16.42)
10–20	3.75 ^c (0.06)	3.43 ^b (0.12)	1.31 ^{bc} (0.09)	2.47 ^{bc} (0.06)	139.45 (20.03)
20–50	3.85 ^{bc} (0.08)	3.51 ^b (0.16)	1.57 ^{bc} (0.05)	3.44 ^a (0.06)	1159.83 (165.33)

Notes: Control and FTN treatments were not different, and samples were pooled ($n = 8$). Lowercase superscript letters indicate significant differences within columns at $P \leq 0.05$. Effects of site, depth, and site \times depth effect are as follows for soil pH: site, $F_{1,18} = 326.11$, $P \leq 0.0001$; depth, $F_{2,18} = 74.16$, $P \leq 0.0001$; site \times depth, $F_{2,18} = 15.36$, $P \leq 0.0001$. For CEC the effects were: site, $F_{1,18} = 12.79$, $P = 0.0009$; depth, $F_{2,18} = 28.84$, $P \leq 0.0001$; site \times depth, $F_{2,18} = 9.44$, $P = 0.0004$. For AEC, the effects were: site, $F_{1,18} = 98.39$, $P \leq 0.0001$; depth, $F_{2,18} = 57.21$, $P \leq 0.0001$; site \times depth, $F_{2,18} = 10.92$, $P = 0.0002$.

losses were in approximate balance with the NO₃⁻ added as fertilizer and produced via nitrification. In contrast, losses of NH₄⁺ in solution over the same six-month period were negligible, suggesting that much of the NH₄⁺ fertilizer that was not nitrified to NO₃⁻ was retained. Nitrogen additions to long-term fertilized forests at young site resulted in NO₃⁻ losses that were commensurate with NO₃⁻ sources as fertilizer and nitrification.

At the old site, N additions to previously unfertilized forests resulted in immediately high rates of nitrification. During the first month following N inputs, high rates of nitrification converted almost all of the added NH₄⁺ to nitrate. Solution NO₃⁻ losses, however, were not equivalent to these sources of NO₃⁻. Vertical losses from long-term fertilized forests at the old site were larger than losses from previously unfertilized forests, but they could only account for 32% of the NO₃⁻ added

TABLE 4. Nitrogen budgets (mean, with SE in parentheses; all values are kg N/ha) for different forms of N in unfertilized, first-time N-fertilized (FTN), and long-term N-fertilized (LTN) forests at the young (300-yr-old) and old (4.1-Myr-old) soil sites.

Site and measures	Unfertilized			FTN			LTN		
	NH ₄ ⁺	DON	NO ₃ ⁻	NH ₄ ⁺	DON	NO ₃ ⁻	NH ₄ ⁺	DON	NO ₃ ⁻
Young soil site									
Inputs									
Atmospheric [†]	2.53 (1.00)	1.33 (1.00)	2.25 (1.00)	2.53 (1.00)	1.33 (1.00)	2.25 (1.00)	2.53 (1.00)	1.33 (1.00)	2.25 (1.00)
N pools [‡]	2.00 (0.52)		0.007 (0.004)	29.7 (7.0)		15.2 (5.9)	23.5 (5.6)		16.6 (3.1)
Uptake/production [§]	-2.50 (0.98)		-0.41 (0.28)	-6.02 (2.90)		7.75 (4.70)	35.81 (6.89)		42.89 (19.28)
Losses	0.07 (0.02)	0.99 (0.37)	0.04 ^a (0.01)	0.05 (0.02)	2.5 (3.9)	12.57 ^b (5.92)	0.07 (0.01)	4.2 (13.9)	66.26 ^c (19.55)
Old soil site									
Inputs									
Atmospheric [†]	0.50 (0.50)	0.57 (0.50)	0.60 (0.50)	0.50 (0.50)	0.57 (0.50)	0.60 (0.50)	0.50 (0.50)	0.57 (0.50)	0.60 (0.50)
N pools [‡]	5.60 (2.1)		2.57 (0.76)	50.1 (11.9)		8.9 (3.3)	68.8 (25.0)		5.9 (1.6)
Uptake/production [§]	31.32 (4.58)		33.93 (13.62)	46.07 (7.60)		62.34 (25.43)	53.18 (8.22)		67.96 (27.60)
Losses	0.03 (0.02)	0.31 (0.15)	1.88 ^a (0.49)	0.65 (0.55)	1.8 (0.9)	6.81 ^b (1.89)	0.2 (0.1)	3.1 (1.7)	16.04 ^c (1.68)

Notes: Fifty kg N/ha as half urea and half NH₄NO₃ was added (equivalent to 37 kg NH₄⁺-N/ha and 12.5 kg NO₃⁻-N/ha added). Lowercase superscript letters indicate significant differences among treatments within site (ANOVA, $P < 0.05$).

[†] Six-month atmospheric inputs are estimated from Carillo et al. (2002).

[‡] Reported N pools are the measured NH₄⁺ and NO₃⁻ pools immediately after N fertilization.

[§] Production of NH₄⁺ and NO₃⁻ refers to the cumulative organic N (including urea) mineralized to NH₄⁺ and nitrified to NO₃⁻ over the month after N inputs, respectively. Negative values indicate uptake of NH₄⁺ and NO₃⁻ by microbes. Solution losses are during the six-month period following N fertilization.

and produced via nitrification. Significant amounts of soil exchangeable NO_3^- were found at 20–50 cm depth (29.57 ± 12.92 kg N/ha; Appendix B).

DISCUSSION

Wet tropical forests located at the extreme ends of a well-characterized soil age and fertility gradient across the Hawaiian Islands provided an opportunity to examine how N additions as NH_4^+ and NO_3^- are processed in tropical forests of different soil age and nutrient status. Our findings lend insights into how soil and ecosystem properties that vary as a function of soil age control the timing and magnitude of these losses.

Responses of tropical forests to N additions

Many of the observed responses of terrestrial systems to N deposition can be understood within the context of the conceptual model of N saturation (Agren and Bosatta 1988, Aber et al. 1989, Aber 1992). In general, the N saturation model predicts that N-limited systems initially retain anthropogenic N due to use in plant and microbial growth as well as accumulation in biomass and soil organic matter. At some point, however, inputs of N begin to exceed the biotic (and perhaps abiotic) demands for N within the ecosystem, and the system is predicted to lose its N retention capacity. As the capacity to retain N is exceeded, excess N is available to be lost from the system via solution losses and gas fluxes.

These generalizations stem largely from studies in several well-characterized regions of the temperate zone. We asked if the N saturation model can be applied to the tropical forests where many ecosystems grow on highly weathered soils that are often depleted in rock-derived nutrients and rich in the supply of N. We hypothesized that, unlike many N-limited ecosystems that experience delays in losses following N additions, non-N limited ecosystems would not retain initial inputs of N and would respond with large and immediate increases in nitrification and NO_3^- solution losses. Alternatively, we predicted that soil chemical and physical properties that vary with soil age would strongly influence NO_3^- transport and retention processes.

Our study documents that, regardless of nutrient status or soil age, two wet tropical forests responded to first-time N inputs with immediate and substantial NO_3^- losses. In the three months immediately following N additions, when rainfall conditions were similar, NO_3^- losses were larger from the N-limited tropical forest at the young site than the P-limited forest at the old site. Over the six-month study period, NO_3^- losses were substantial from both forests, representing 25% of the 50 kg N/ha added at the young site and 14% at the old site. At both sites, losses as NH_4^+ and DON after N additions were small relative to NO_3^- losses. While differences in precipitation amounts helped to explain differences in total N losses between sites during the six-month post-fertilization periods, our results

suggest that biogeochemical and hydrological processes that vary with soil development controlled the timing and magnitude of losses.

Biogeochemical controls

Differences in biogeochemical processes due to soil age were important in explaining retention of different forms of N added and losses between sites. Findings from our study showed that biotic processes were important in explaining retention of initial inputs of NH_4^+ at the young N-limited site. Consistent with earlier findings by Hall and Matson (1999), we found rapid immobilization of NH_4^+ immediately following first-time N inputs to the young N-limited forest (Fig. 5c). We estimated that this immobilization of N could account for 36% (range = 28–65%) of the added NH_4^+ (Table 4). In a 24-h ^{15}N tracer study under static, laboratory conditions, Hall and Matson (1999) showed that most of the NH_4^+ added to previously unfertilized forest soils at the young site was retained in microbial biomass and soil organic matter (92.5%). Our study showed very small NH_4^+ losses under highly transient water flow conditions and over a longer six-month period (Table 4), suggesting that much of the NH_4^+ remained stabilized on soil organic matter and in microbial biomass. Abiotic processes such as high CEC (Table 3) and NH_4^+ fixation (Tamimi 1964), as well as plant uptake (Harrington et al. 2001), could also explain this high retention. Recent estimates suggest that 30–35 $\text{kg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ of N is taken up by plants in both sites (Vitousek 2004).

In contrast to NH_4^+ inputs that were largely retained, we found that anthropogenic NO_3^- additions, as well as NO_3^- produced via nitrification, was apparently free to move in solution (Table 4). Although AEC was relatively high throughout the soil profile (Table 3), we did not find that it influenced the mobility of NO_3^- in the short- and long-term. High SO_4^{2-} loading due to emissions from Kilauea Volcano, located 6 km from this site (McGee and Gerlach 1998), resulted in high concentrations of SO_4^{2-} in soil solution at this site (16.1 ± 1.9 mg/L; Hedin et al. 2003); preferential absorption of this SO_4^{2-} on anion exchange sites may help to explain lack of selectivity for NO_3^- . These results suggest that the interaction of NO_3^- and SO_4^{2-} may be important to consider as the tropical regions undergo industrialization and may have a large impact on the responses of tropical systems to anthropogenic inputs and the processes delaying losses.

At the old site, biotic processes appeared to play a small role in retaining added N. Consistent with other studies conducted at this site (Hedin et al. 2003), we found that background rates of nitrification and solution losses as NO_3^- were two orders of magnitude higher at the old site than at the young site. We also observed that first-time N additions to the old site significantly increased already high rates of net nitrification in the surface soils, consistent with our hypotheses and find-

ings by Hall and Matson (1999, 2003). Hall and Matson (1999) showed that significantly elevated N trace gas losses were associated with these high N cycling rates. In this study, we observed immediate NO_3^- solution losses following first time additions of N (Fig. 4) and significantly elevated losses relative to control over the six-month period despite low rainfall conditions. These symptoms together lend support to the suggestion that this forest is already naturally N saturated (Hall and Matson 2003).

Despite substantial losses from this site, however, they were not equivalent to the NO_3^- added as fertilizer and produced via nitrification (Table 4), suggesting that other processes were important in delaying losses. Besides low rainfall, findings from our study suggest that NO_3^- adsorption in the subsurface Bo horizon may be a factor contributing to delayed losses. In the temperate zone, NO_3^- adsorption has not been found to be an important process in retaining nitrate, except in some southeastern U.S. soils (Gillman and Sumner 1987, Eick et al. 1999), but it can be substantial in variable-charged soils in the tropics, especially those high in kaolinite or derived from volcanic ash deposits (Kinjo and Pratt 1971, Uehara and Gillman 1981). Results from our laboratory study showed relatively high AEC and nitrate retention capacity (NRC) in the subsurface Bo horizon (Table 3). In the field, we found high retention of NO_3^- in this subsurface horizon one month after N additions (and relatively high rainfall; Appendix B). We also found greater amounts of total N in these soils relative to control, suggesting that some of the NO_3^- may be more irreversibly adsorbed or retained in this horizon by other mechanisms (Lohse 2002).

Previous research in the tropics has suggested that nitrate adsorption can be important in delaying NO_3^- losses, but all of these studies have been focused on disturbed or agricultural soils. In Costa Rica, Matson et al. (1987) showed that NO_3^- adsorption was an important process in delaying losses following felling and burning of tropical forests on volcanic soils. Another study in coffee plantations in Costa Rica found substantial NO_3^- adsorption of fertilizer additions due to high AEC (Ryans et al. 2001). Across a wide range of tropical agricultural soils, Wong (1990) demonstrated that delayed NO_3^- leaching losses in soil columns were in good agreement with those predicted from soil variable charge. In aggregate, our results and these limited data sets suggest that NO_3^- adsorption may serve as an important abiotic mechanism delaying losses of anthropogenic N inputs across a wide range of tropical soils. This capacity to retain nitrate will likely depend on soil pH, the presence of interacting anions, and the amount of variable charge.

Hydrological controls

In our study, differences in hydrological properties due to soil age were the dominant controls determining the timing and magnitude of NO_3^- solution losses be-

tween sites. At the young site, large NO_3^- losses immediately after N additions were associated with large storm events and high soil water fluxes (Fig. 4). Rather than indicating N saturation, these large losses appeared to reflect the short contact time of NO_3^- with the coarse-textured soils under high rainfall conditions. Detailed hydrological studies conducted concomitantly with this study support this assertion and showed that both upper and subsurface soil horizons drained rapidly under unsaturated and field saturated conditions (Lohse 2002; Lohse and Dietrich, *in press*). Several studies in the temperate zone have shown similar strong hydrological controls on NO_3^- losses in N-limited forests growing on coarse-textured soils (Lathja et al. 1995, Seely and Lajtha 1997), on more structured soils (Creed et al. 1996), and in some seasonally dry ecosystems (Riggan et al. 1985, Fenn and Poth 1999, Williams and Tonnessen 2000, Brenner et al. 2001). Similar to our study, NO_3^- was flushed or bypassed from the ecosystems immediately following precipitation events, and losses appeared to reflect the short contact time between soil and drainage water that prevented microbes and plants from retaining the added N.

Past research has suggested that N losses such as DON loss that are out of the control of the plant community may result in the persistence of N limitation (Hedin et al. 1995, Vitousek and Field 1999). Sickman et al. (2003) have further suggested that asynchronies between seasonal N availability and hydrologic losses may limit plant growth in seasonal ecosystems. In our study, we found that 11 years of N additions at the young site appeared to relieve N limitation to microbes and significantly increase rates of nitrification such that most of the added N was also nitrified to NO_3^- (Table 4). Despite this increased N availability, tree growth in the young site remained weakly limited by N (Harrington et al. 2001). Our results indicate that the NO_3^- that was produced via nitrification was lost as solution loss (Table 4). Placed in the context of the soil age gradient, findings from our study suggest that rapid drainage and, therefore, poor contact time in young soils, may ultimately control the ability of N-limited systems to retain and accumulate exogenous N inputs and thus may influence nutrient limitation to tree growth.

At the old site, we found that NO_3^- losses were significantly elevated immediately following first-time N additions, but were lower and more delayed than that measured at the young site. In the three months following N additions, rainfall was similar between sites (Table 1); thus, the lower losses observed at this site during this time period were not confounded by this factor. Rather, the delay reflected the slow downward movement of solution through the impeding subsurface Bo horizon (Fig. 4); hydrological characterization showed that saturated water flow in this horizon was more than two orders of magnitude lower than the upper soil horizons (0.08 compared to 36 cm/h; Lohse

2002, Lohse and Dietrich, *in press*). In physical terms, the older soils with lower saturated hydraulic conductivity (K_s) with depth and greater soil thickness offered greater hydraulic resistance (R) to NO_3^- losses than the young soils, where R is defined as d/K_s , d_j is the thickness of a soil horizon (cm) and K_j is the hydraulic conductivity of this horizon (Tindall et al. 1999). Based on K_s alone, we estimate that one molecule of water spends 166 times longer in the soil profile at the old site than the young site, and therefore, NO_3^- has longer time to react with the soil and biota.

Findings from our study also suggest that rapid subsurface lateral flow during large storm events may have short-circuited the long residence time of water and nutrients through the subsurface clay horizon. Instantaneous measurements of horizontal fluxes by tensiometry (J_{wh}) showed lateral fluxes of water at the old site along the Bo1 horizon contact when rainfall intensity exceeded the drainage rate of this horizon (Fig. 4). Positive pore pressures in tensiometers at depth (50 cm) and a perched water table across the ridge top flat substantiated these measures (Fig. 2). Analysis of long-term rainfall data showed that the probability of a rainfall event exceeding the drainage rate of the subsurface horizon was relatively high (37%), suggesting that losses along this lateral pathway may frequently occur (Lohse 2002; Lohse and Dietrich, *in press*). Thus, discrepancies between vertical NO_3^- losses and sources that we observed at this site may be explained in part by this loss pathway (Table 4).

A quantitative estimate of N loss via lateral flow and the fate of this N were well beyond the scope of this study and experimental design. Based on our current hydrological understanding of this site and knowledge of rooting distribution, we suggest that much of the NO_3^- that is transported to this subsurface horizon is already beyond the majority of the rooting zone. Nitrate then has the following possible fates: (1) it can drain vertically and losses delayed by the subsurface horizon, (2) it can be lost immediately to downstream ecosystems along rapid lateral flow paths, and/or (3) it can be lost along preferential flow paths such as cracks that may not have been detected with this experimental design. All possible fates suggest that this NO_3^- is effectively lost from the ecosystem, but the implication for downstream ecosystems is quite different; the first delays the onset of large NO_3^- losses, at least in the period after onset of additions, and the later two result in immediate and episodic losses that are coupled to storm events.

While limited in number, a review of available studies show that impeded drainage in tropical forests on highly weathered soils is relatively common across a broad range of geographic settings (Lohse 2002). In particular, impeded drainage appears to be important in older soils derived from silica-poor and chemically unstable metamorphic rock that tend to weather into clay-rich soils (Bonell and Balek 1993). The few wa-

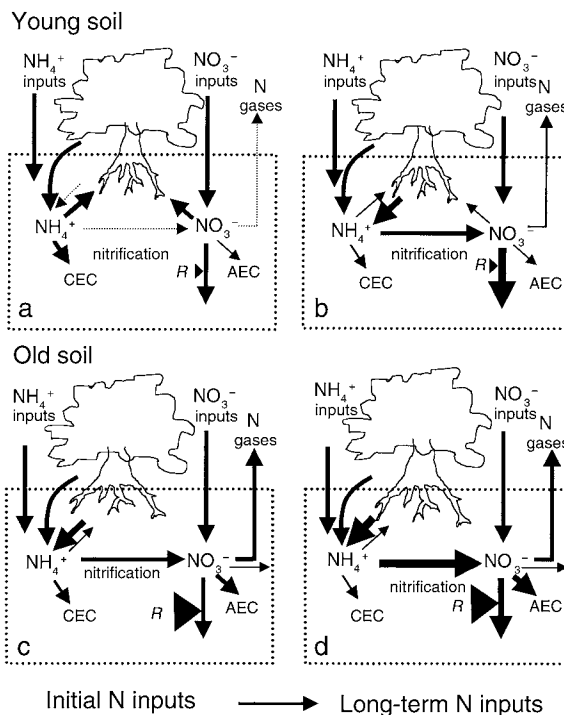


FIG. 6. Conceptual model of the relationship of soil solution losses to soil properties and processes that vary as a function of age. Abbreviations are: hydraulic resistance (R), cation exchange capacity (CEC), and anion exchange capacity (AEC).

tershed studies conducted in pristine tropical rainforests on highly weathered soils also clearly demonstrate episodic changes in stormflow chemistry due to changes in hydrologic flow paths (Lesack 1993, Elsenbeer et al. 1994, Elsenbeer and Lack 1996a, b, Markewitz et al. 2001). In future studies, preferential flow as a loss pathway will need consideration (Sollins and Radulovich 1988, Bonell and Balek 1993, Elsenbeer 2001). Our study and these limited data sets suggest that determining the storm size/intensity frequency and the runoff mechanisms associated with tropical soils, particularly those with impeding subsurface horizons, will be critically important in predicting the timing and loss pathways of anthropogenic N.

Implications for ecosystem responses to N deposition

In this study, we took a step towards understanding how tropical forests of different soil age and, consequently, nutrient status respond to first-time and long-term N inputs. We demonstrated that the responses of tropical forests to anthropogenic N inputs varied clearly with soil age and nutrient status (Fig. 6). Besides rainfall, differences in soil physical, biological, and chemical processes due to soil age explained differences in N losses and retention in the contrasting forests. Hydrological properties due to soil age emerged as the dominant controls regulating the differences in timing

and magnitude of nitrate losses. Retention of the remaining added N was determined by the strength of biotic demand, the level of nitrification, and abiotic mechanisms that modulated the mobility of the different forms of N.

At the young site, rapid drainage through the coarse-textured soils appeared to constrain the ability of biotic processes to retain NO_3^- whereas NH_4^+ appeared to be retained in the short term by CEC and biological demand for N (Fig. 6a). With long-term N additions, microbial demand for N decreased, and NO_3^- added as fertilizer and produced via high rates of nitrification was free to move in solution (Fig. 6b). The old site, depleted in P, but high in N supply, appeared to be already naturally N saturated with most of the added N nitrified to NO_3^- and free to move in solution (Fig. 6c). However, subsurface mechanisms in the old soil served to route water and NO_3^- along differential flow paths during storm and drainage events. During drainage events, subsurface horizons offered high hydraulic resistance (R) to vertical losses and AEC served to delay NO_3^- losses in the short and long term (Fig. 6d). During storm events, this high hydraulic resistance resulted in subsurface lateral flow that potentially bypassed these physical and chemical retention mechanisms.

Based on our findings, we suggest that, unlike many temperate ecosystems that experience a lag between the initiation of N inputs and losses, many tropical forests, particularly those growing on older soils, may respond without temporal delay between initiation of anthropogenic N inputs and N losses. In tropical forests rich in N, biotic demand for N may be low. Soil chemical and physical properties that vary with soil development over time may be more important than biotic processes in controlling the timing and magnitude of NO_3^- losses from these tropical forests.

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APPENDIX A

Descriptions of soil water flux methods are available in ESA's Electronic Data Archive: *Ecological Archives* A015-048-A1.

APPENDIX B

A table showing the effects of first-time and long-term N additions on soil dynamics with depth at the 300-year-old and 4.1-Myr-old soil sites is available in ESA's Electronic Data Archive: *Ecological Archives* A015-048-A2.