Organic forms dominate hydrologic nitrogen export from a lowland tropical watershed

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Abstract. Observations of high dissolved inorganic nitrogen (DIN) concentrations in stream water have reinforced the notion that primary tropical rain forests cycle nitrogen (N) in relative excess compared to phosphorus. Here we test this notion by evaluating hydrologic N export from a small watershed on the Osa Peninsula, Costa Rica, where prior research has shown multiple indicators of conservative N cycling throughout the ecosystem. We repeatedly measured a host of factors known to influence N export for one year, including stream water chemistry and upslope litterfall, soil N availability and net N processing rates, and soil solution chemistry at the surface, 15- and 50-cm depths. Contrary to prevailing assumptions about the lowland N cycle, we find that dissolved organic nitrogen (DON) averaged 85% of dissolved N export for 48 of 52 consecutive weeks. For most of the year stream water nitrate (NO_3^-) export was very low, which reflected minimal net N processing and DIN leaching from upslope soils. Yet, for one month in the dry season, NO_3^- was the major component of N export due to a combination of low flows and upslope nitrification that concentrated NO_3^- in stream water. Particulate organic N (PON) export was much larger than dissolved forms at 14.6 kg N·ha^{-1}·yr^{-1}, driven by soil erosion during storms. At this rate, PON export was slightly greater than estimated inputs from free-living N fixation and atmospheric N deposition, which suggests that erosion-driven PON export could constrain ecosystem level N stocks over longer timescales. This phenomenon is complimentary to the "DON leak" hypothesis, which postulates that the long-term accumulation of ecosystem N in unpolluted ecosystems is constrained by the export of organic N independently of biological N demand. Using an established global sediment generation model, we illustrate that PON erosion may be an important vector for N loss in tropical landscapes that are geomorphically active. This study supports an emerging view that landscape geomorphology influences nutrient biogeochemistry and limitation, though more research is needed to understand the mechanisms and spatial significance of erosional N loss from terrestrial ecosystems.

Key words: biogeochemistry; Costa Rica; ecosystem ecology; nutrient cycling; nutrient limitation; Osa Peninsula; tropical rain forest; watershed hydrology.

INTRODUCTION

A widely held conceptual model in ecosystem ecology holds that tropical forests growing on highly weathered soils exhibit phosphorus (P) limitation and cycle nitrogen (N) in excess of biological demand (e.g., Vitousek 1986, Hedin et al. 2009). Multiple forms of evidence from plants, soils, and streams have been used to support this paradigm. These include: high rates of net N mineralization and nitrification (e.g., Vitousek and Matson 1988, Davidson et al. 2000), processes that could elevate soil NO_3^- pools (e.g., Davidson 2007,

Sotta et al. 2008), relatively high foliar N:P ratios (McGroddy et al. 2004, Townsend et al. 2007, Fyllas et al. 2009), and relatively low foliar N resorption efficiency (Vitousek 1984). Furthermore, comparatively high natural abundance ^{15}N in foliage and soil of lowland forests imply high rates of N transformation via fractionating pathways (Martinelli et al. 1999, Amundson et al. 2003, Bai and Houlton 2009), all of which would be consistent with high concentrations of DIN reported in some tropical streams (Bruijnzeel 1991, McDowell and Asbury 1994, Newbold et al. 1995, Dechert et al. 2005, Schrumpf et al. 2006, Brookshire et al. 2012*a*).

These observations, which generally point to high relative N abundance, have shaped general paradigms of tropical forest organization, function, and nutrient

limitation (Davidson 2007, Hedin et al. 2009, Cleveland et al. 2011, Brookshire et al. 2012b, Menge et al. 2012, Quesada et al. 2012). However, the majority of past studies in lowland forests have been conducted in portions of the tropical forest biome that feature stable landscapes in which weathering-driven depletion of P will be greatest (e.g., Neill et al. 2001, Anaya et al. 2007). At the same time, in topographically diverse tropical landscapes, geomorphic forces rejuvenate soils with bedrock nutrients through uplift, erosion, and disturbance (Porder et al. 2007, Vitousek et al. 2010). In these regions, such as the Andean arc of the Amazon, much of Southeast Asia, localities throughout Central America and the Antilles, and many tropical islands, the patterns and mechanisms of nutrient limitation are unresolved and under-studied relative to their proportion of the forested tropical biome (Asner et al. 2014).

This legacy has motivated research in a primary rain forest on the Osa Peninsula, Costa Rica, where a picture of conservative tropical N cycling has been emerging over the past decade, one that may operate more broadly across many wetter, lowland forests (Nardoto et al. 2008, Posada and Schuur 2011). Indicators of "conservative" N cycling (sensu Davidson 2007) exist throughout this forest. Despite moderately high inputs of N from deposition (Hofhansl et al. 2011) and biological fixation (Reed et al. 2007) in the region, KCl-extractable DIN concentrations in soils from this region are often at or below detection limits (Wanek et al. 2008, Wieder et al. 2013). The soil N cycle is a classic example of a small available N pool, fast-turnover system (Davidson et al. 1992, Stark and Hart 1997, Perakis et al. 2005); the entire surface soil nitrate pool has been shown to turn over on extremely short (i.e., ~2 h) timescales (Wieder et al. 2013), and net N mineralization rates may be three orders of magnitude lower than the gross N flux. The natural abundance ^{15}N of surface mineral soils averages 2.4‰ (Wieder et al. 2013), which is on the low end of measurements for tropical forests (Martinelli et al. 1999, Craine et al. 2009). Low natural abundance ^{15}N implies limited accumulation of N in excess of demand (Martinelli et al. 1999); i.e., limited biological fractionation of N. Supporting this notion, soil NO_3^- concentrations are much lower than NH_4^+, unlike that observed in studies from drier, more weathered regions (Davidson 2007). The low availability of NO_3^- is reflected in the very low gaseous flux of N as N_2O, averaging <1 kg N·ha^{-1}·yr^{-1} across the year (Wieder et al. 2011). Overall, these metrics suggest that N availability may constrain biological metabolism, which is supported by the response of soil respiration and root biomass to N fertilization (Cleveland and Townsend 2006).

These indicators of the N cycle also suggest that the export of biologically available N via nitrate leaching should be low in the Osa forest study region, which opposes traditional notions of tropical N cycling. Rather, the conditions are more like those found in pristine temperate rain forests (Hedin et al. 1995, Perakis and Hedin 2002), which are characterized by high export of dissolved organic vs. inorganic N. Such observations in Chilean ecosystems unpolluted with anthropogenic N led to the "DON leak" hypothesis, which states that despite high biological demand for N, organic forms of N can bypass biological uptake at rates to maintain ecosystem N limitation over long timescales (Hedin et al. 2003). In such ecosystems, observations of a strong correlation between DON and dissolved organic C (DOC) suggest that DON export is associated with the leaching of soil organic matter that is recalcitrant to microbial decomposition (Hedin et al. 1995). This relationship often deteriorates in nitrogen-rich ecosystems, such as those impacted by anthropogenic N inputs, and DON concentrations tend to correlate more strongly with inorganic N availability (McDowell et al. 2004, Brookshire et al. 2007, Fang et al. 2009).

Undissolved forms of C and N are also exported together as particulate organic C (POC) and N (PON) in organic matter. The erosion of rocks and soil from mountainous tropical regions is an important source of POC to rivers and oceans (McDowell and Asbury 1994, Aufdenkampe et al. 2007, Townsend-Small et al. 2008, Brunskill 2010, Hilton et al. 2011, Lloret et al. 2011, 2013, Alongi et al. 2013, Clark et al. 2013). However, little is known about the magnitude and mechanisms of PON export in tropical landscapes (McDowell and Asbury 1994), particularly when compared to our understanding of dissolved N.

Hydrologic regime can strongly influence the forms, timing, and magnitude of PON export by altering the linkages between terrestrial and aquatic systems (Kinner and Stallard 2004, Boy et al. 2008, Shanley et al. 2011). Intense storm events are known to generate episodes of soil erosion that transport terrestrial organic matter to downstream systems (Hilton et al. 2008a, b, 2011, 2013, Townsend-Small et al. 2008, Clark et al. 2013, Lloret et al. 2013). For example, on the island of Oahu in the Hawaiian archipelago, storm-driven particulate organic N (PON) loss exceeds dissolved N export rates in steep watersheds (Hoover and Mackenzie 2009). Erosional forces are also strong across the Osa Peninsula. The region experiences a combination of high rainfall, which ranges from 3.5 to 7 m/yr, and fast geologic uplift at rates between 2.5–6.5 m/kyr (Gardner et al. 1992). These factors give rise to a topographically dissected landscape where watershed soils have relatively short residence times and forest hillslopes are prone to erode into incising river channels. Under these conditions, erosion could be an important vector for both POC and PON loss from forests to downstream ecosystems.

In this study we address these knowledge gaps by measuring dissolved and particulate organic N export from a 9.5-ha watershed on the Osa Peninsula, Costa Rica for one year. We evaluated controls on stream water N export by quantifying seasonal shifts in climate

and potential upslope sources of C and N, including litterfall, soil organic matter content, N net processing and availability, and soil solution chemistry at surface, 15-cm, and 50-cm depths. Storm events were sampled with an autosampler to investigate the terrestrial loss of POC and PON during high flow events. We expected that DON export would be closely linked to DOC export and dominate over DIN because of the strong biotic retention of inorganic N in upslope soils. We also expected that high rates of PON export would be driven by storm events that cause episodic soil erosion. Lastly, we examined the importance of dissolved and particulate N export within an ecosystem N budget, and used a spatially explicit sediment model to explore the significance of PON export as vector for terrestrial N loss pantropically.

Methods

Study site

The field site is located in the Golfo Dulce Forest Reserve in southwest Costa Rica on the Osa Peninsula (8°43′ N, 83°37′ W). The forest is a highly diverse, mature forest with no known history of substantial human disturbance, at least in modern times. Mean annual rainfall is ~5000 mm and mean annual temperature is 26.5°C (Wieder et al. 2009). The region typically experiences a pronounced dry season between December and February, when monthly rainfall averages <100 mm/month. Rainfall begins to increase roughly in March and intensifies in September through November. This research was focused on a 9.35-ha watershed drained by Quebrada Mariposa, which is located near the village of Progresso.

The Osa Peninsula is at the convergent margin between Central America and the subducting Cocos Plate, which originated at the Galapagos paleo hotspot, and is currently moving northwest at a rate of 90 mm/yr (Trenkamp et al. 2002). The Osa Peninsula proper is composed of two main lithological units: the Osa Igenous Complex to the north, and the Osa Melange in the central and southern portions. The Quebrada Mariposa watershed is located within the Osa Igneous Complex, which is broadly divided between many subunits composed mainly of basalt arising from accredited seamounts and oceanic plateaus originating during the middle Eocene to middle Paleocene (Buchs et al. 2009). Soils are predominantly Ultisols with areas of Inceptisols on the steep slopes and Entisols in the alluvial areas. There has been no recent volcanic activity in the region, and the nature of landscape evolution restricts inter-basin water transfer. Therefore, we assumed closed basin water dynamics, and examined the mass balance of the ecosystem N cycle from a hydrologic perspective.

Water budget

Precipitation was measured using a HOBO tipping bucket (Microdaq, Contoocook, New Hampshire, USA)

positioned in a clearing adjacent to the watershed. Discharge (Q) was measured 38 times during the one-year study using a salt slug injection (Moore 2005), with 11 of these measurements done during high-flow events ($Q > 7$ L/s). Generally, stream water levels were too low to conduct cross-sectional measurements of Q. A time-series of discharge at one-hour intervals was derived using a rating curve, which was developed by relating discharge to stage height. Stage height was measured using a pressure transducer (Solinst, Georgetown, Ontario, Canada) placed in a gauging well. The well was dug by hand and never dried during the course of monitoring.

Sample collection, chemical analyses, and calculations

Precipitation samples for chemistry measurements were collected in acid-washed HDPE bottles connected to a telescopic funnel elevated 2 m from ground level. Stream water was sampled for chemistry using an ISCO 6200 autosampler (Teledyne-ISCO, Lincoln, Nebraska, USA) for 52 consecutive weeks. Every week, the ISCO autosampler ran for a three-day period, and sampled stream water at a regular four-hour interval to capture both baseflow and storm flow conditions. A total of 18 individual samples were collected per week. Samples were not preserved during collection, but were retrieved from the ISCO autosampler at 36 and 72 hours during each collection period to minimize biological C and N transformations in the collection bottle during the collection period. All samples were filtered through an ashed, pre-weighed Whatman GFF 0.7-μm filter (Whatman, Florham Park, New Jersey, USA). Particulate organic matter (POM) samples were immediately filtered, then frozen along with the filtrate that was used for dissolved C and N analysis.

At the University of Colorado, filters were dried at 60°C, then pulverized with a mortar and pestle and analyzed on CHN analyzer (Carlo Erba, Lakewood, New Jersey, USA). Particulate organic carbon (POC) and nitrogen (PON) concentrations were calculated as the percentage of C or N of total suspended sediments (SS) per unit volume. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were analyzed on a Shimadzu TOC/TN (Shimadzu TOCvcpn, Kyoto, Japan). NO_3^- was analyzed colorimeterically as $NO_3^- + NO_2^-$ on an Alpkem flow injection analyzer (OI Analytical, College Station, Texas, USA). NH_4^+ was analyzed on a microplater reader (Seal Analytical Incorporated, Mequon, Wisconsin, USA). Detection limits for NO_3^- and NH_4^+ were 3.10 μg N/L and 2.21 μg N/L, respectively. DON was calculated as the difference between TDN and DIN.

Precipitation inputs of N were calculated as volume-weighted mean concentrations of N in rainfall samples. For stream water export, we randomly selected four weekly samples to characterize dissolved and particulate C and N under baseflow conditions, which were used to calculate weekly flow-weighted mean concentration and export. We analyzed all samples when Q exceeded 7 L/s

to maximize the characterization of stream water chemistry during storm flow conditions. Export fluxes were calculated using flow-weighted mean concentrations. For POM, which scaled strongly with flow (see *Results: Suspended sediment, POC, and PON concentration and export*), concentrations used in export calculations were derived from a log–log concentration–discharge relationship (McDowell and Asbury 1994, Lloret et al. 2013).

In addition to C and N input–output measurements, we analyzed several biogeochemical parameters in upslope soils known to influence hydrologic N export, including litterfall, net nitrogen processing, and soil solution chemistry. We established 10, 5 × 5 m monitoring plots throughout the watershed. Litterfall was measured bi-weekly in 0.25-m² litterfall traps. Litter was air-dried at the field station, and subsequently dried offsite at 60°C for moisture correction. We measured net N mineralization and nitrification using a short-term soil incubation in the field, similar to Ross et al. (2009). First, we sampled and homogenized four soil cores (0–10 cm depth) into a composite sample for each of the 10 field plots. Initial soil N concentrations were extracted within one hour of harvest using 2mol/L KCl at a 1:10 mass:volume ratio. The remainder of the soil was placed in a polyethylene bag in situ and removed five days later for the extraction of final concentrations of N. Soil samples were frozen immediately after each field extraction. Net N transformation rates were calculated as final minus initial N concentrations expressed as micrograms of N per gram of soil per day and were assessed every four weeks for one year.

Mineral soil and soil solution chemistry was analyzed in samples collected in 10 monitoring plots. Mineral soil C and N concentrations were measured once at the beginning of the study at surface, 15-, and 50-cm depth in all 10 plots. In the laboratory, soils were hand homogenized, then a small subsample was ground to a fine powder and oven dried (105°C for 48 h) to determine total soil C and N content using a CHN analyzer (Carlo Erba, Lakewood, New Jersey, USA). Each plot was instrumented with a zero-tension surface lysimeter placed immediately below the leaf litter layer (described in Wieder et al. 2009), and tension lysimeters placed at 15- and 50-cm depth. Tension lysimeters were installed using an auger to hand-dig holes, placed within a silica slurry to improve soil–lysimeter connectivity, and given two months to equilibrate within the soil matrix. Soil water was pulled at 0.3 MPa, collected every two weeks, and analyzed for the same constituents as surface water using the same analytical methods. Soil solution C and N concentrations were analyzed using the laboratory methods and instruments discussed previously.

Global modeling of PON export from tropical watersheds

We conducted a modeling exercise to explore the role of PON export in humid tropical forests globally. The WBMsed model (Cohen et al. 2013) is a spatially explicit global-scale riverine sediment flux model developed within the Community Surface Dynamics Modeling System (Syvitski et al. 2005, Kettner et al. 2010).[6] First, we conducted a meta-analysis of field data for PON and suspended sediment (SS) to constrain the relationship between N content and sediment yield in tropical headwater streams and rivers. Then, we generated a PON export map by multiplying average modeled SS fluxes between 2000 and 2005 by the mean percentage of PON observed in small tropical watersheds. We limited our modeling analysis to relatively undisturbed regions using a boundary constraint of humid tropical forests generated from remote sensing of land use (Hansen et al. 2008). This exercise is meant to provide a first-look illustrative analysis of areas where PON loss from tropical watersheds might play a significant role in ecosystem N budgets. Notably, the spatial resolution of the WBMsed is 0.1° (~11 × 11 km pixel size at the equator), which is larger than the small watersheds considered here. Because elemental yields and runoff are strongly inversely proportional to watershed area (Milliman and Syvitski 1992), the modeling results are inherently conservative, and actual PON yields are likely much higher. Accurate intrabasin downscaling is limited by the paucity of data to calibrate erosion processes in small headwaters (Kettner et al. 2010).

Results

Hydrology

Over the 52 weeks of the study it rained 3220 mm, which was substantially lower than the long-term average of ~5000 mm (Wieder et al. 2009). Runoff during the same period was 1111 mm, suggesting that evapotranspiration was ~2109 mm (assuming no change in ecosystem water storage). N inputs totaled 8.0 kg $N·ha^{-1}·yr^{-1}$, which was very similar to a nearby study site (Hofhansl et al. 2011) and an intermediate value for pristine rain forests (Wilcke et al. 2001, Umana and Wanek 2010). Rainfall increased and storms intensified with the progression of the wet season (Fig. 1A). Base flow varied from <0.5 to >7 L/s across the year, and was punctuated by episodes of high flow coincident with large rainfall events (Fig. 1B).

Terrestrial processes and soil solution chemistry

Total litterfall in the watershed during the study period was 11.6 Mg $DM·ha^{-1}·yr^{-1}$, and showed strong seasonal variability. Litterfall rates were highest in the dry season and early wet season, and then declined throughout the remainder of the rainy portions of the year (Fig. 1C). Across all bi-weekly (every two weeks) data, net mineralization and nitrification averaged 0.30 ± 0.81 and 0.20 ± 0.25 $\mu g·[g \, soil]^{-1}·d^{-1}$ (mean ± SE),
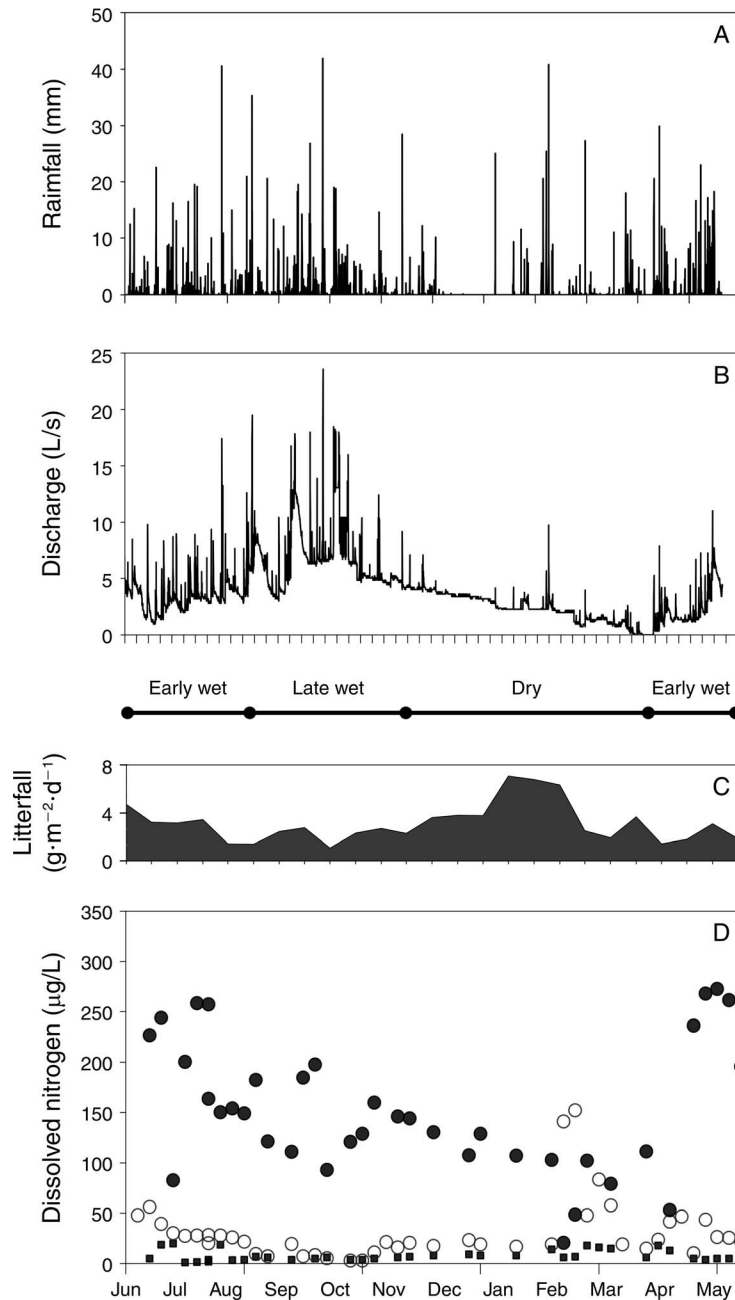
FIG. 1.   At Quebrada Mariposa on the Osa Peninsula, Costa Rica, a 52-week time series of (A) rainfall and (B) discharge (15-minute intervals), (C) litterfall, and (D) flow-weighted mean dissolved nitrogen concentrations in hydrologic export: DON (solid circles); NO_3^- (open circles); NH_4^+ (solid squares). Also shown are delineations between wet and dry seasons, as referred to in *Methods* and throughout the text.

respectively, whereas NO_3^- and NH_4^+ concentrations averaged 0.85 ± 1.25 and 1.48 ± 1.83 µg N/g soil, respectively. Soil solution chemistry also varied seasonally (Appendix: Table A1). DOC collected beneath leaf litter in zero tension lysimeters was highest after the onset of rainfall when leaf litter standing stocks were greatest, and declined to a low during the dry season (Appendix: Table A1). This seasonal pattern was paralleled in soil solution collected in tension lysimeters;

however DOC concentrations declined on average by 93% between 0 and 15 cm depth and 98% between 0 and 50 cm depth (Appendix: Table A1), a pattern that was mirrored by DON (Appendix: Table A1). Soil C and N content decreased strongly with increasing soil depth: C and N averaged 4.85% and 0.44% from 0 to 15 cm, declined to 2.31% and 0.20% from 15 to 50 cm, and declined further to 0.81% and 0.08% from 50 to 100 cm, respectively.
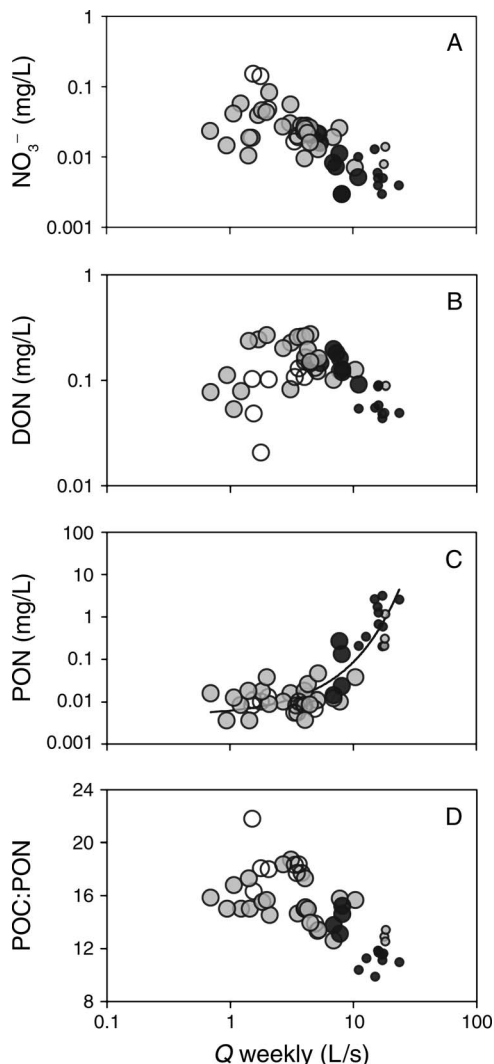
FIG. 2. Concentration–discharge relations for (A) NO_3^-; (B) DON; (C) PON; and (D) POC:PON. (C) The exponential equation $y = 0.00564\exp(X \times 0.3511)$ was used to calculate flow-weighted mean PON concentrations. The large circles represent samples collected during baseflow (weekly mean) and the small circles represent samples collected during storm flow (event mean). Note the logarithmic spacing of x-axis values in graphs A–C. Symbol shading refers to the season of sample collection: white circles, dry season; gray circles, early wet season; black circles, late wet season, as shown in Fig. 1.

Dissolved carbon and nitrogen concentration and export

Organic N dominated dissolved N export (Fig. 1D), averaging 85% of TDN across the year. Concentrations of DON and DOC were tightly correlated ($R^2 = 0.68$, $P < 0.001$; Appendix: Fig. A1) and DOC:DON ratios showed little variation through the year (7.94 ± 3.36). Hydrology exerted strong control on DON and NO_3^- concentration (Fig. 2), both of which displayed a "boomerang" shaped response to rising flow, which was more weakly exhibited by NO_3^- (Fig. 2A). Antecedent litterfall rate was a moderately strong

predictor of stream water DOC ($R^2 = 0.56$, $P < 0.001$) and DON ($R^2 = 0.41$, $P = 0.018$) concentrations, as well as the DOC and DON concentrations collected in surface, 15-, and 50-cm depth lysimeters (data not shown). DOC in stream water scaled 1-to-1 with DOC collected at 15 cm depth ($R^2 = 0.46$, $P = 0.003$; Appendix: Fig. A2), whereas DOC concentrations in solutions collected at 50 cm averaged half of stream concentrations ($R^2 = 0.43$, $P = 0.009$; Appendix: Fig. A2). The same was true for DON given their tight correlation.

In stream water, DIN concentrations were low throughout the year, except for a brief period when NO_3^- concentrations spiked during the height of the dry season when flows were very low (Fig. 1D). These NO_3^- concentrations were related to antecedent nitrification measured in surface soils one month prior ($r^2 = 0.40$, $P = 0.028$). Stream water NO_3^- weakly reflected NO_3^- in 15-cm depth lysimeters and displayed no relationship with chemistry at 50-cm depth (Appendix: Fig. A2). However, NO_3^- concentrations were inversely related to DOC concentration in the stream and soil solution (Appendix: Fig. A3). Flow-weighted NH_4^+, NO_3^-, and DON fluxes in stream water were 0.06, 0.26, and 1.37 kg $N \cdot ha^{-1} \cdot yr^{-1}$, respectively. DOC export was 10.96 kg $C \cdot ha^{-1} \cdot yr^{-1}$.

Suspended sediment, POC, and PON concentration and export

Suspended sediment concentrations increased exponentially with discharge, and total export was 1510 kg·$ha^{-1} \cdot yr^{-1}$ (151.0 Mg·$km^{-2} \cdot yr^{-1}$). POC ($r = 0.99$, $P < 0.001$) and PON ($r = 0.97$, $P < 0.001$; Fig. 3A, inset) increased strongly with SS concentration and were strongly correlated ($r = 0.96$, $P < 0.001$; Appendix: Fig. A2). Particulate organic matter C and N contents were higher in the dry and early wet season, averaging 2.5% and 0.16%, respectively, and sharply declined into the wet season at high flows (C, 0.88%; N, 0.07%). The POC:PON ratio varied from 10 to 22, and was lowest at very high flows (Fig. 3D). POC export totaled 177.8 kg $C \cdot ha^{-1} \cdot yr^{-1}$ (17.78 Mg·$km^{-2} \cdot yr^{-1}$), which was roughly 3% of the annual C inputs from litterfall. Annual PON export was higher than dissolved N export at 14.6 kg $N \cdot ha^{-1} \cdot yr^{-1}$ (1.46 Mg·$km^{-2} \cdot yr^{-1}$). Event-driven export of PON overwhelmed base flow export. At flows exceeding 13.5 L/s, which occurred only 0.5% of the year (i.e., 51 hours), the watershed lost a total of 7.6 kg N/ha as PON.

Illustrative map of PON export from tropical watersheds

As in Quebrada Mariposa, tropical stream and river PON concentrations were highly correlated to fine SS concentrations (Fig. 3A; $y = 0.0009X + 0.0753$, $r = 0.97$ [Lewis 1986, Paolini et al. 1995, Lewis et al. 1999, Neill et al. 2001, McDowell et al. 2004, Aufdenkampe et al. 2007, Alin et al. 2008, McClain et al. 2008, Townsend-Small et al. 2008]). Among these field studies, PON
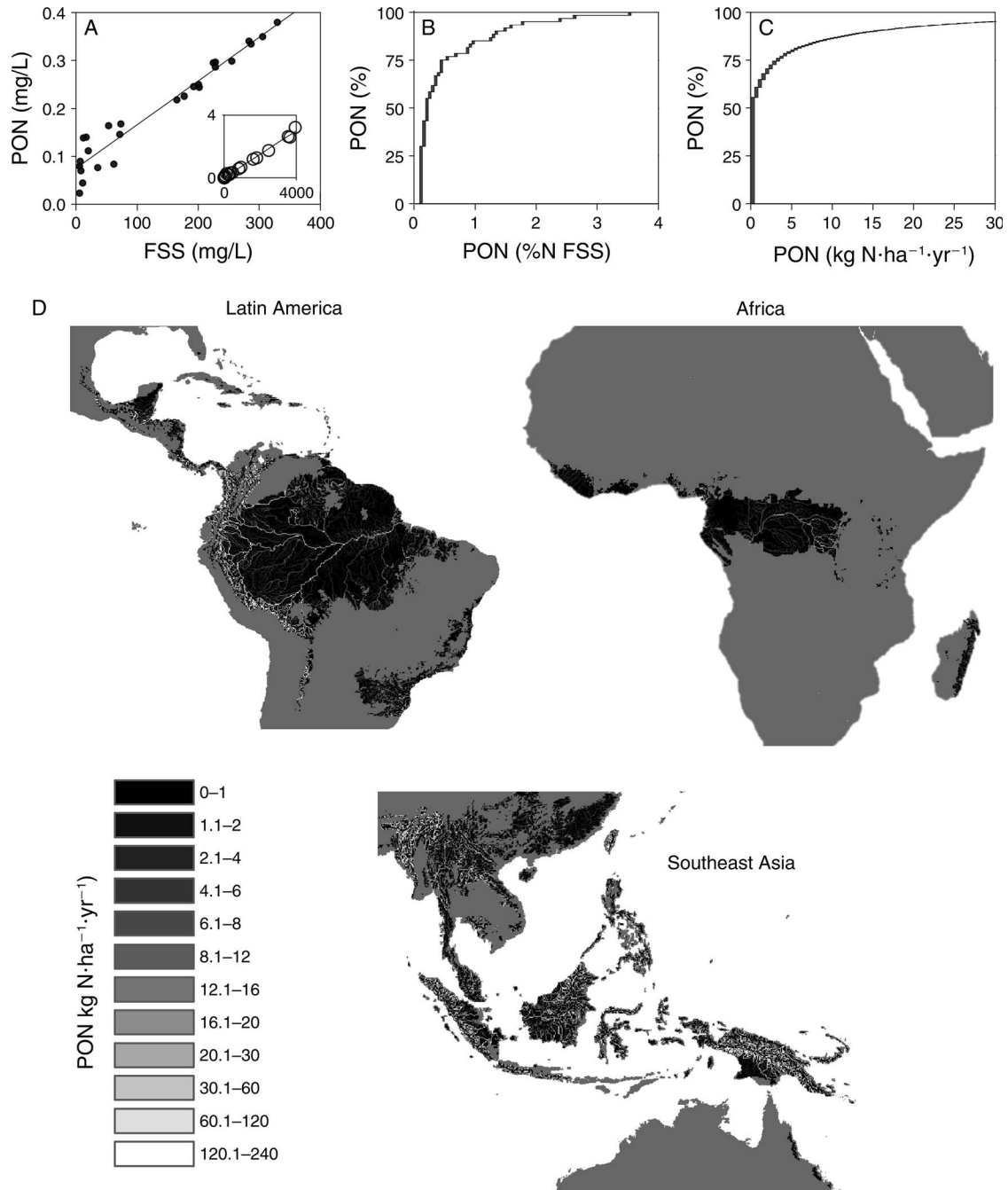
FIG. 3. Particulate organic nitrogen (PON) composition and export in tropical landscapes with mature forests. (A) PON is strongly correlated to fine suspended sediment (FSS) concentrations ($n = 61$; $y = 0.0009[X] + 0.0753$, $r = 0.97$), which is also observed in Quebrada Mariposa (inset; $y = 0.0007[X] + 0.0102228$, $r = 0.99$). (B) A cumulative relative histogram for the empirical measures of stream water PON listed above, showing that fine SS tend to have low N content. (C) A cumulative relative histogram of pixel values of modeled PON export generated with the WBMsed model (Cohen et al. 2013), which is a spatially explicit global-scale riverine sediment flux model developed within the Community Surface Dynamics Modeling System. (D) An illustrative map of modeled PON export from tropical watersheds. The map is constrained to the extent of mature humid tropical forests (Hansen et al. 2008), as we only consider systems with minimal human disturbance to the landscape. See *Methods* for more detailed description.

content averaged 0.52% of SS; however 75% of field samples of SS were below 0.41% N (Fig. 3B). A cumulative relative histogram of modeled PON loss rates (Fig. 3C and D) suggests that 25% of tropical landscapes that contain humid tropical forests export >5 kg N·ha^{-1}·yr^{-1}. The map in Fig. 3D shows that the highest rates of PON export occur in mountainous regions of Latin America and Southeast Asia.

Discussion

Stream water DON dominated the hydrologic export of dissolved N. Stream water DIN export was low and reflected high biotic retention of inorganic N in upslope soils. PON export was driven by high flow events during intense storms in the wet season, and exceeded dissolved N export by an order of magnitude. Here we consider potential mechanisms controlling dissolved and particulate C and N export, and discuss the broader role of PON export in humid tropical forests. Overall, our data reveal a different picture of hydrologic N export and the ecosystem N economy for a lowland tropical forest than the one that is thought to prevail in more topographically uniform regions.

Dissolved N export

Past studies show that inorganic forms of N dominate N hydrologic export from many pristine tropical lowland rain forests (Bruijnzeel 1991, Neill et al. 2001, Schwendenmann and Veldkamp 2005, Brookshire et al. 2012a). The primary mechanism of hydrologic N export is through nitrification of NH_4^+ to NO_3^- (Vitousek and Matson 1988, Hedin et al. 2003, Lohse and Matson 2005, Corre et al. 2010), which is mobile in most soils and can be readily leached to streams when supply exceeds biotic demand (Brookshire et al. 2012a). Early studies of several lowland forests showed one-to-one scaling between net NH_4^+ and NO_3^- production (Vitousek and Matson 1988), and net nitrification in surface soil can predict NO_3^- export (Hedin et al. 2003).

Yet in this watershed, net nitrification rates and soil NO_3^- concentrations were extremely low throughout the year, except for a four-week period during the dry season when stream water NO_3^- briefly spiked. During this time, stream water NO_3^- concentrations were related to antecedent net nitrification rates (one-month offset), suggesting a direct link, and lag, between NO_3^- production in upslope soils and hydrologic transit to the stream. Elevated net nitrification rates have been observed in other rain forest soils during the dry season (Anaya et al. 2007, Vernimmen et al. 2007, Kiese et al. 2008, Sotta et al. 2008, Owen et al. 2010), and have been linked to brief spikes in stream water NO_3^- (Lewis 1986). During this period, a paucity of soluble, bioavailable organic C compounds likely limits heterotrophic microbes, driving increases in soil NH_4^+ concentrations that can stimulate nitrification (Schimel and Bennett 2004, Anaya et al. 2007). Taylor and Townsend (2010) showed that NO_3^- concentrations are low when soluble C levels are high enough to keep heterotrophic microbes in a state of N limitation, which could underlie the nonlinear relationship between NO_3^- and DOC in soil lysimeters and stream water (Appendix: Fig. A3), and is consistent with a pattern that emerges in ecosystems worldwide (Taylor and Townsend 2010).

The dry season was also a time when soil moisture and stream flows were low, factors that could have concentrated surface water NO_3^-. Our data suggest this effect was minor; the less than twofold decline in base flow (Fig. 1B) can only partially explain the concurrent 10-fold increase in stream water NO_3^- concentrations observed during the late dry season (Fig. 1D). Greater runoff can elevate stream water NO_3^- when large precipitation events exceed the infiltration capacity of the underlying mineral soil, and transfer DIN to streams via lateral flow. This is commonly seen in montane ecosystems with organic-rich soil horizons (Bruijnzeel 1991, Goller et al. 2005, 2006, Saunders et al. 2006, Boy et al. 2008). Notably, this mechanism can effectively short-circuit biological N uptake and lead to increases in stream water NO_3^- concentrations, a process that likely operates independent of significant biological control. This flushing effect is partially seen in the discharge–concentration relationships for Quebrada Mariposa. The positive slope of the "boomerang" shape of the discharge–concentration relationship likely represents an initial flush with rising discharge up to intermediate flow, while the downturn indicates dilution during high flows. This same pattern is observed in Puerto Rican watersheds (McDowell and Asbury 1994, Shanley et al. 2011).

Anion exchange capacity can also reduce NO_3^- mobility through nonspecific sorption (Lohse and Matson 2005) in soils with variable charge clays, such as many of the Ultisols and Oxisols that occur throughout the lowland tropics (Sanchez and Buol 1975). In a nearby watershed to Quebrada Mariposa, with parent material of the same origin, soil mineralogy was mainly composed of chlorite, smectite, and kaolinite with only trace levels of iron and aluminum oxide minerals such as gibbsite and goethite (Scheucher et al. 2008). The dominance of early- to intermediate-stage weathering products suggests anion sorption capacity could play a role. However, kaolinite is generally positive at pH levels well below those observed in watershed Mariposa soils (Ma and Eggleton 1999), which average 4.85 (Cleveland et al. 2006), implying a limited role of anionic sorption.

Another potentially important fate for NO_3^- is denitrification to N gas. However, Wieder et al. (2011) found that N_2O fluxes in this ecosystem were low (<1 kg $N·ha^{-1}·yr^{-1}$). It is certainly possible that plentiful rainfall may shift gaseous N species production toward N_2 predominance (Davidson et al. 2000, Holtgrieve et al. 2006, Houlton et al. 2006), and N_2 production cannot be readily quantified directly. However, consistently low extractable nitrate concentrations, high microbial N immobilization rates, and mineralization to nitrification ratios well below 1 (Wieder et al. 2013) all suggest a relatively low potential for significant terrestrial nitrate export by either hydrologic or gaseous pathways.

Biology and hydrology also interact seasonally to control patterns of DON export and underlie the discharge–concentration patterns. Concentrations of DON are highly correlated with DOC throughout the

year, and both vary strongly with antecedent leaf litterfall, a large source of potentially soluble organic matter. Litterfall rates generally decline as the wet season progresses until a dramatic increase in the dry season (Fig. 1C), which is a typical pattern of many tropical forests that experience rainfall seasonality (e.g., Chave et al. 2009). As a result, substantial litter stocks build up on the forest floor, which undergoes physical dissolution (Wieder et al. 2009) and intensive microbial decomposition (Cleveland et al. 2006, Leff et al. 2012) at the onset of the rainy season. Soil solution and stream water DOC:DON ratios were on par with microbial biomass stoichiometry (Wieder et al. 2011), which aligns with previous evidence that chemical signatures of microbial metabolism are abundant in the bulk soil organic matter (Leff et al. 2012). This suggests that soluble DOC and DON could be microbial metabolites, or at least reflect an imprint of microbial processing of organic matter (Grandy and Neff 2008). Nonetheless, the increase in stream water DOM at baseflow in the early wet season reflects the flushing of the forest floor when soluble C fluxes are high (e.g., Bücker et al. 2011, Shanley et al. 2011), with subsequent depletion and dilution as the wet season progresses.

The one-to-one scaling between stream water and 15-cm soil depth suggests hydrologic coupling between surface soils and stream water, whereas DON concentrations at 50-cm depth average half of those found in the stream. Since significant deep sources of DOM are unlikely (e.g., Saunders et al. 2006, Chaves et al. 2009), this pattern suggests that shallow subsurface soil macropore flow may bypass deeper zones of biogeochemical processing. Soil pipes are commonly found along the stream channel of Quebrada Mariposa, are very common in tropical soils (Chappell and Sherlock 2005, Negishi et al. 2007, Chappell 2010), and may route water and dissolved elements to the stream water from surface soil layers.

Particulate organic nitrogen export

Sediment erosion and yield has been extensively studied in the tropics (reviewed in Douglas and Guyot 2005), yet PON composition is rarely measured in tandem, with the exception of a few published studies (McDowell and Asbury 1994, Neill et al. 2001, Townsend-Small et al. 2008, Hoover and Mackenzie 2009, Hilton et al. 2013, Lloret et al. 2013). In Quebrada Mariposa PON remained low for most of the year under baseflow conditions until intense rainfall events (>20 mm/h) generated a multiplicative rise in SS concentration (Fig. 2D). The high nonlinearity in the discharge–PON concentration relationship suggests that pulses of PON export arise from threshold-driven geomorphological changes in the watershed (e.g., Douglas et al. 1999, Shanley et al. 2011). Over half of PON export occurred during 51 separate hours of high flow (0.6% of the year), predominantly in the late wet season) when rainfall intensity exceeded 20 mm/h. This dispropor-

tionate influence of storms on PON export has been observed in other studies (Hilton et al. 2011, Alongi et al. 2013, Lloret et al. 2013). A more detailed study is needed to identify the contribution of potential sources, including overland flow, landslides, slope wash, soil creep, or treethrow (Larsen et al. 2012).

POC and PON were very strongly correlated, and changes in stoichiometry and composition offer some insight into upslope sources. The two end members for particulate organic matter sourcing are fresh leaf litter and mineral soil organic matter; C:N ratios for these end members average 42 and 10, respectively. During the dry and early wet season when discharge was low, the POC:PON ratio averaged ~22, which likely reflects a mix of detritus (possibly originating from litterfall within stream) and mineral soil organic matter. As the wet season progresses with more frequent and intense high flows, the C:N ratio dropped to 10 (Fig. 3D), which reflects the C:N composition of mineral soil. These changes in POC and PON suggest shifts in sediment sourcing from soils between seasons. The carbon content of SS reflects surface soil (0–15 cm) during the dry and early wet season, but dramatically declines and matches deeper mineral soil (50–100 cm) composition in the late wet season. These patterns suggest that heavy, late-season rainfall events trigger landslips into the channel that engage deeper soils in erosion, akin to previous studies (e.g., Douglas et al. 1999, Townsend-Small et al. 2008, Shanley et al. 2011).

N export in a systems perspective

The role of N export from ecosystems over long timescales is best understood in relation to other important N fluxes in the ecosystem. We summarize the ecosystem N budget in the Appendix: Fig. A4 to show that the export of NO_3^- in stream water (0.32 kg·ha^{-1}·yr^{-1}) was very low compared to the turnover of N in surface mineral soils. Gross rates of ammonification and nitrification averaged 1900 and 355 kg N·ha^{-1}·yr^{-1}, respectively (Wieder et al. 2013), indicating that only 0.09% of the NO_3^- generated by nitrification within the top 10 cm of mineral soil leaches below the active plant–soil zone to stream water. Mineral soil solution had low concentrations of NH_4^+ and NO_3^- for the majority of the year. A comparison of surface to shallow soil solution suggests that <2% of NO_3^- production in the litter layer leaches to 15 cm depth. In fact, the low residence time of soil NO_3^- (~2.4 h) in this ecosystem is far less than the two-day average found in likely N-limited systems of Oregon (Stark and Hart 1997) and Chile (Perakis et al. 2005). Strong N demand prevented DIN leaching to stream water where DON dominated dissolved N export for most of the year.

The dominance of DON over DIN in stream water suggests that some soluble N escapes biotic recycling and retention in the terrestrial ecosystem. Yet, unlike temperate systems (Hedin et al. 1995, Perakis and Hedin 2002, Brookshire et al. 2007), the dissolved organic

matter in Quebrada Mariposa had low DOC:DON ratios that were more reflective of microbial processing than the high C:N composition of recalcitrant compounds thought to underpin the "DON leak" concept (Hedin et al. 1995). While this raises the possibility that DON leaks can occur in the face of strong microbial processing, the flux of DON in stream water was small compared to exogenous N inputs. Though measurements over one year represent too short a timeframe to characterize the long-term mass balance of nutrients at the ecosystem scale (Bücker et al. 2011, Shanley et al. 2011), DON export appears to play a minor role in balancing N inputs from deposition and fixation, as found in pristine temperate ecosystems (Hedin et al. 1995, Perakis and Hedin 2002). Stream water DON export was an order of magnitude lower than estimates for inputs from free-living N fixation, and deposition totaled 13 kg·N ha^{-1}·yr^{-1}. In Quebrada Mariposa, only PON export was sufficient to potentially balance N inputs of this magnitude (Appendix: Fig. A4).

The erosional export of PON in stream water occurs independent of biological demand, a phenomenon that is complimentary to the DON leak concept (Hedin et al. 1995). However, PON export is almost exclusively controlled by hydrologic regime, whereas DON export depends on the formation and transport of recalcitrant DON compounds that escape biological demand. That is, the DON leak relies on the fact that the plant–microbial system is unable to retain all soluble DON compounds before delivery to downstream ecosystems (Hedin et al. 1995, Neff et al. 2003). Erosive PON export bypasses N retention regardless of decomposability, though much of the PON appears to have a source in mineral soil derived below the active rooting zone.

Importantly, these patterns suggest that PON export may help explain the metrics of conservative N cycling at our study site. Here we show that PON, just as with DON, can be lost from ecosystems despite high biotic N demand, and at levels large enough to constrain N accumulation at longer timescales. In topographically diverse landscapes the rapid rejuvenation and erosion of soil can limit the natural abundance ^{15}N because physical erosion can remove terrestrial N via non-fractionating pathways. This notion is supported by evidence that natural abundance ^{15}N in soils and plants declines with increasing slope angle (Amundson et al. 2003, Hilton et al. 2013, Weintraub et al. 2015), which implies that terrestrial ecosystems accumulate less and less N in excess of biological demand as the landscape terrain gets steeper (Martinelli et al. 1999, Nardoto et al. 2008). Hilton et al. (2013) developed an elegant isotopically explicit mass-balance model to demonstrate that erosional processes on slopes limit the accumulation of natural abundance ^{15}N in soil by decreasing residence time of soil. In the field, watershed studies in mountainous regions of Taiwan (Hilton et al. 2013), the French West Indies (Lloret et al. 2013), and islands in the Arafura and Timor Seas (Brunskill 2010, Alongi et al.

2013, Suwarno et al. 2013) show that erosional loss of terrestrial PON can range from 10 to 50 kg N·ha^{-1}·yr^{-1}, which is on the same order of magnitude as observed for Quebrada Mariposa on the Osa Peninsula.

These recent studies suggest that the erosion of PON may be meaningful in terrestrial ecosystems beyond the Osa Peninsula. The illustrative map in Fig. 3D provides a preliminary look at regions within the humid tropical forest biome where erosion could be an important vector for terrestrial PON loss. The model indicates that PON export throughout much of Central America, the western arc of the Amazon, nearly all of Southeast Asia, and tropical islands, exceeds 5 kg N·ha^{-1}·yr^{-1}, which is itself a very conservative estimate, given the fact that this model cannot resolve small-scale effects of topography.

Overall, this study supports an emerging view that landscape geomorphology influences patterns of nutrient cycling and limitation (Porder and Hilley 2011, Hilton et al. 2013). Just as erosional processes can rejuvenate tropical soils with bedrock nutrients (Porder et al. 2007, 2009), these same processes might constrain ecosystem N availability. Future research should explore the causes and consequences of erosional PON loss for terrestrial N cycling, with a focus on the role of storms in driving episodic N loss from watersheds, which is rarely studied. Finding answers could help resolve long-term controls on terrestrial ecosystem nutrient limitation. Watershed PON export from mountainous tropical watersheds also subsidizes downstream ecosystems, yet the fate and significance of terrestrial PON is unknown. Resolving the importance of such terrestrial–aquatic interactions in global biogeochemical cycling deserves more attention, and may be particularly important in coastal marine systems, like the Osa Peninsula, Costa Rica.

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SUPPLEMENTAL MATERIAL

Ecological Archives

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