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The biogeochemistry of dissolved nitrogen, phosphorus, and organic carbon along terrestrial-aquatic flowpaths of a montane headwater catchment in the Peruvian Amazon

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Abstract:

Dissolved nitrogen (N), phosphorus (P), and organic carbon (C) were sampled along two transects in a first-order montane tropical (2414 m.a.s.l.) rainforest catchment of the Peruvian Amazon to investigate spatial and temporal controls on nutrient concentrations from uplands to streams. Surface and subsurface waters along transects were sampled during baseflow conditions and following rainfall events from March 2002 to March 2003. During baseflow conditions, we observed strong terrestrial controls on N, P, and dissolved organic carbon (DOC) concentrations in streams. Median NO_3^- concentrations were relatively constant during both dry and wet seasons in stream water (dry, 0·8 μM; wet, 1·7 μM) compared to upland soil water (dry, 15·5 μM; wet, 32·5 μM) despite significant seasonal fluctuations of NO_3^- in the upland, riparian, and hyporheic zones. During the dry season, concentrations of dissolved organic N (DON) also decreased markedly between the upland and the stream. Despite this decrease, DON remained the dominant component of total stream water dissolved N. Dissolved organic P (DOP) and soluble reactive P (SRP) concentrations generally followed a spatial trend inverse to that of N. Low median SRP concentrations were recorded during dry and wet seasons in the upland (dry, 0·11 μM; wet, 0·08 μM) while the highest median SRP concentrations were in stream water (dry, 0·22 μM; wet, 0·20 μM). DOP also dominated total dissolved P concentrations from the upland to the stream. Stoichiometric ratios of dissolved N and P contrasted between the upland (DON : DOP = 734, dissolved inorganic N (DIN) : SRP = 166; dry season) and the stream (DON : DOP = 3, DIN : SRP = 12; dry season), indicating a clear divergence of nutrient composition between terrestrial and aquatic systems. Under baseflow conditions, strong mechanisms in the terrestrial environment and at the terrestrial–aquatic interface controlled the nutrient concentrations in the stream and buffered the seasonal fluctuations occurring in the terrestrial environment. In contrast, storm flowpaths may short-circuit baseflow nutrient controls, thereby exporting a pulse of nutrients to the stream. Understanding the influences of storms in headwater catchments will be a valuable next step in determining the effects of changing precipitation regimes on the nutrient status of montane tropical forests and their receiving waters.

KEY WORDS seasonal variation; nitrate; phosphate; nutrient dynamics; riparian; Andes; stoichiometry; topohydrosequence

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INTRODUCTION

Mountain headwaters are a distinctive component of many of the world's major river basins and often exert a disproportionately large influence on the biogeochemistry of lowland river reaches. This is certainly the case in the Amazon River Basin, where the biogeochemical composition of Andean Amazon rivers generally reflects

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the characteristics of the catchments they drain (Stallard and Edmond, 1983; Guyot *et al.*, 1988; Sobieraj *et al.*, 2002) and where Andean contributions of sediment, major ions, trace metals, and sediment-bound organic matter strongly influence the biogeochemistry of the mainstream river (Seyler and Boaventura, 2003; Gibbs, 1967; Richey *et al.*, 1986; Richey *et al.*, 1990; Hedges *et al.*, 2000; Stallard and Edmond, 1983; Aalto *et al.*, 2003). Despite the recognized influence of Andean processes on the larger river basins, little systematic research has been focused there to date (McClain *et al.*, 1995; Wilcke *et al.*, 2001; Townsend-Small *et al.*, 2005). The vast majority of aquatic biogeochemical research has focused on the lowland Amazon (Junk, 1997; McClain *et al.*, 2001; Sioli, 1984). There is a clear need to improve our understanding of the dynamics of Amazon headwater regions in order to predict the systemic changes resulting from climate and land-use change.

Terrestrial-aquatic linkages are best studied in first- and second-order streams, which commonly account for up to 85% of the total length of river networks (Horton, 1945). Owing to the small ratio of their surface-area to channel-length, small streams are closely connected to adjoining riparian and upland terrestrial systems. Strong terrestrial influences on stream dissolved organic and inorganic nutrient concentrations have been recognized across many environments. For example, near-stream subsurface biogeochemical reactions have been shown to regulate the inorganic nitrogen concentrations in groundwater passing through compositionally and geographically diverse riparian zones (Chestnut and McDowell, 2000; Cooper, 1990; Hill, 1996; Lowrance *et al.*, 1984; Jordan *et al.*, 1993; Konohira *et al.*, 2001; Ostrom *et al.*, 2002). Furthermore, the low ratios of stream-volume to channel-area enhance interactions with the stream bed and promote greater surface–subsurface exchange and inorganic nitrogen retention in streams as compared to higher-order rivers (Findlay, 1995; Alexander *et al.*, 2000; Peterson *et al.*, 2001; Pinay *et al.*, 2002; Sophocleous, 2002).

Perakis and Hedin (2002) found that streams in unpolluted temperate forests of South America were consistently dominated by dissolved organic nitrogen (DON). It is not clear whether a tendency towards organic dominance of N fluxes holds in unpolluted montane rainforests of the tropical South. The high seasonality of rainfall in Amazon catchments may also influence the character of terrestrial–aquatic nutrient concentrations and fluxes. Storms have been shown to significantly alter the dominant flowpaths of terrestrial–aquatic hydrologic transfers and associated geochemical exports within both pristine and anthropogenically altered headwater catchments (Elsenbeer and Lack, 1996; Elsenbeer, 2001; Sidle *et al.*, 2000; Grimaldi *et al.*, 2004; McGlynn and McDonnell, 2003; Schellekens *et al.*, 2004). Recent studies in steeply sloped tropical rainforests of Puerto Rico, French Guiana, and Borneo have also demonstrated the significant contribution of overland flow to storm runoff in rainforest catchments (Dykes and Thornes, 2000; Grimaldi *et al.*, 2004; Schellekens *et al.*, 2004). Despite a growing body of knowledge focused on the hydrological and geochemical processes produced by high rainfall periods in the montane tropics, basic information regarding nutrient dynamics in response to rainfall variability remains to be addressed.

Our research focused on the following questions to address the N and P dynamics in an Andean Amazon montane rainforest headwater stream: (i) What is the spatial distribution of dissolved organic and inorganic N and P across an upland-stream transect under baseflow conditions? (ii) What mechanisms control the distribution of N and P along the transect studied? (iii) Do the spatial distributions of nutrients along the transect change as a function of season? (iv) Does the stream draining the catchment reflect processes occurring in the upland or riparian zone? and (v) How do precipitation-dependent flowpaths affect terrestrial–aquatic nutrient transfers?

SITE DESCRIPTION

The study site was located alongside a first-order headwater stream (Wara) located at 2414 m above sea level (m.a.s.l.) in the montane tropical rainforest (Figure 1) (S 10 32′ 45·9″, W 075 31′ 28·4″) of Yanachaga-Chemillen National Park, Perú. Prior to the establishment of the park in 1986, the sole anthropogenic disturbance near the site was minor selective logging of large and commercially valuable timber species

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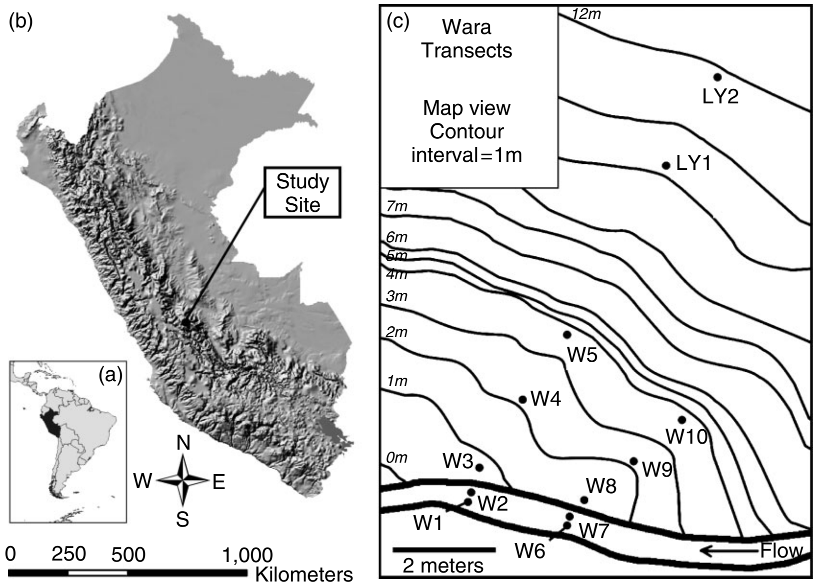

Figure 1. Orientation of (a) Perú in South America, (b) the study site in relation to the relief in Perú (Data Source: ESRI World Shaded Relief, 2000), and (c) a topographic map and sampling locations of the Wara transects; 'W' indicates a piezometer and 'LY' indicates a tension lysimeter

such as *Cedrela lilloi* and *Cedrela montana*. The area receives over 1800 mm of precipitation annually as recorded in Oxapampa (1814 m.a.s.l., 1987–1996 averages) while the montane forests surrounding the study site often receive greater precipitation inputs. Recent measurements (October 2003–September 2004) taken within two hundred metres of the study site recorded an annual rainfall of 2502 mm and an average annual temperature of 13·7 °C (Catchpole, 2004). There are marked wet (October–April) and dry (May–September) seasons and temperatures generally vary between 10 and 19 °C with the highest values occurring during the rainy season and the lowest values coinciding with the dry season.

Hillslopes surrounding the stream are steep (30–80°) and unstable, resulting in frequent landslides, intense erosion, and rapid hydrologic response to precipitation events. Hillslope soils are very heterogeneous due to intense erosion, burial of organic layers by landslides, fallen trees, and occasional outcropping of consolidated regolith and bedrock. The regolith contains weathered granites, breccia, and sedimentary rocks, resulting in a stream bed dominated by sand-size quartz and feldspars. Riparian vegetation covers most of the narrow (0·5–2 m) stream channel. Small gullies originally formed by landslides are common along the stream and concentrate the surface flow from hillslopes during storms. Curvatures of hillslopes bordering the stream alternate between convex and concave, depending on recent landslide activities and erosive gullying.

Vegetation at the study site includes multiple species from the families of Araceae, Araliaceae, Begoniaceae, Chloranthaceae, Cunoniaceae, Cyatheaceae (dominant), Euphorbiaceae, Melastomataceae, Meliaceae, Moraceae, Oxalidaceae, Piperaceae, Rubiaceae, and Sabiaceae (Mendoza, Pers Com). In a one-hectare plot at the study site, Gomez (1999) identified 154 species of trees with diameter at breast height (dbh) >10 cm, a diversity higher than previously reported in any montane tropical rainforest. No N-fixing leguminous species were reported within the plot.

METHODS

The study plot was fitted with instruments to sample upland soil water, riparian and hyporheic groundwater, and stream water under baseflow conditions. Additional samplers were installed to collect throughfall, litter

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leachate, and overland flow during storm events. Two transects of five 2·35 cm inside diameter (ID) PVC piezometers were installed using an iron driving rod at a ∼75° angle to the stream (Figure 1). Stream piezometers were nested and installed up to depths of 50 and 30 cm beneath the stream bed. Two Prenart Super Quartz suction lysimeters (Prenart Equipment) were installed, one each up to 50 and 80 cm below the upland soils (not including the organic horizon). A minimum of 10 casing volumes were purged from all piezometers following installation and lysimeters and piezometers were allowed to equilibrate for over a month before sampling began. Canopy throughfall collectors consisted of a 1·0 m length of 7·6 cm ID PVC pipe cut in half longitudinally and joined to a sampling bottle that, adjusted for a 15-cm vertical offset from end to end, provided approximately 750 cm^2 of collection area. Overland flow collectors (30 cm of 5 cm ID PVC) were also cut lengthwise, screened, and placed flush against the hillside within the riparian zone, collecting from over a 25-cm length of the riparian hillslope. A zero-tension lysimeter was installed to collect leachate from the organic horizon at 20 cm below the top of the organic horizon. A ladder system was constructed alongside each transect to minimize any hillslope disturbance during sampling.

Samples were collected weekly from March 2002 to March 2003. Lysimeter samples were collected using a Prenart portable vacuum pump equipped with a pressostate to provide a constant vacuum (−550 mbar) and a glass sampling bottle. Piezometer samples were taken using a hand pump, PVC tubing, and barbed flask. All sampling equipment was washed between sampling events and triple-rinsed with de-ionized (DI) water between piezometers. Piezometer water levels were measured using an electronic water level detector (precision = 1 mm) prior to sampling. Wells were completely purged and allowed to recharge within 2 h of sampling. Stream samples were taken as grab samples.

The study site was surveyed using a surveying level/tripod and stadia-rod. Hydraulic conductivity (K) was estimated by completely purging each well and monitoring recovery with the water level detector (pump test). The Hvorslev method (Freeze and Cherry, 1979) with a shape factor correction for an unscreened well (Cedergren, 1989) was used to estimate K from the piezometric head recovery data.

All samples were filtered in the field directly following collection, through Gelman A/E (0·7 μm nominal pore-size) glass-fibre filters using a Nalgene filter apparatus, into 60 ml HDPE bottles. It should be noted that what we refer to as 'dissolved' throughout this paper therefore includes all particles less than 0·7 μm. Samples taken for inorganic nitrogen analyses were preserved with 20 μl of concentrated H_2SO_4, bringing the pH to <2, while samples analyzed for total dissolved N and P (TDN and TDP, respectively) and SRP were not treated with acid. Samples for DOC were filtered through pre-combusted 0·7 μm glass-fibre filters using a glass filtration apparatus and stored in pre-combusted 20 ml glass scintillation vials with Teflon seals. Total dissolved N, TDP, and DOC samples were only available for a subset of dry season samples because of constraints of low sample volumes, material, and storage. Conductivity and pH were measured in the raw sample using temperature-corrected electrodes prior to filtration in the case of soil and groundwater and *in situ* for stream samples. Samples were stored on ice in coolers while in the field and were transported within 6 h to the Andean Amazon Research Station and analyzed immediately or kept frozen until further analysis.

Samples were analyzed colorimetrically for inorganic nutrients. Species analyzed included NO_3^-, NH_4^+, and SRP according to the methods of Strickland and Parsons (1972 (NO_3^- and SRP)) and Koroleff (1969 (NH_4^+)). Samples for DOC, TDN, and TDP were frozen and transported to Florida International University in Miami. DOC was analyzed for non-purgeable dissolved organic carbon (DOC) via high temperature combustion (760 °C) using a Shimadzu TOC-V Total Carbon Analyzer, while TN/TP were analyzed simultaneously using the method of Bronk *et al.* (2000) as modified by Valderrama (1981) for the simultaneous analysis of TN and TP. Dissolved organic fractions were calculated by subtracting inorganic concentrations from total dissolved nutrient concentrations.

Data were categorized as 'Wet' (October–April) or 'Dry' (May–September) season. Locations were categorized as 'Upland' (LY1, LY2), 'Riparian' (W3, W4, W8, W9), 'Hyporheic' (W1, W2, W6, W7), and 'Stream'. Differences among seasons and locations were evaluated using MANOVA and multiple-comparisons (Bonferoni correction for family wise error, confidence level = 0·95). Nutrient data were log-transformed prior to MANOVA analyses in order to normalize sample distributions. Percentages presented were calculated using sample medians of the untransformed data.

RESULTS

Piezometric water levels

Seasonal variation in piezometric water level (PWL) was substantial along the Wara transects (Figure 2). The wet season was characterized by marked fluctuations in water table elevation while dry season PWL values remained relatively constant (Figure 3). A steep hydraulic gradient (~40°) existed between riparian piezometers and the stream during both wet and dry seasons. Groundwater below the stream bed rose from W1 towards W2 and demonstrated that the stream gained groundwater inputs at the study site (Figure 3). However, owing to the steep (~35°) longitudinal angle of the stream, groundwater likely migrated within the stream bed, mixing with surface water and creating a hyporheic zone. Hyporheic exchange was especially evident in the dry season, when mean PWL values in W2 were less than the elevation of the stream bed itself (elevation <0). Saturated hydraulic conductivity (K) varied from 10^{-5} to 10^{-3} cm/s across all piezometers and showed no significant spatial trends. The reported K values corresponded to unconsolidated substrates consisting of silt or silty sand according to the range of values given by Freeze and Cherry (1979).

Spatial patterns of solution chemistry

Median upland NO_3^- concentrations during the dry and wet season were significantly higher ($p < 0{\cdot}001$) than riparian, hyporheic, and stream NO_3^- concentrations (Figure 4, Table I, Table II). A large decrease in NO_3^- concentrations between the upland and the stream suggested a large potential for NO_3^- losses of up

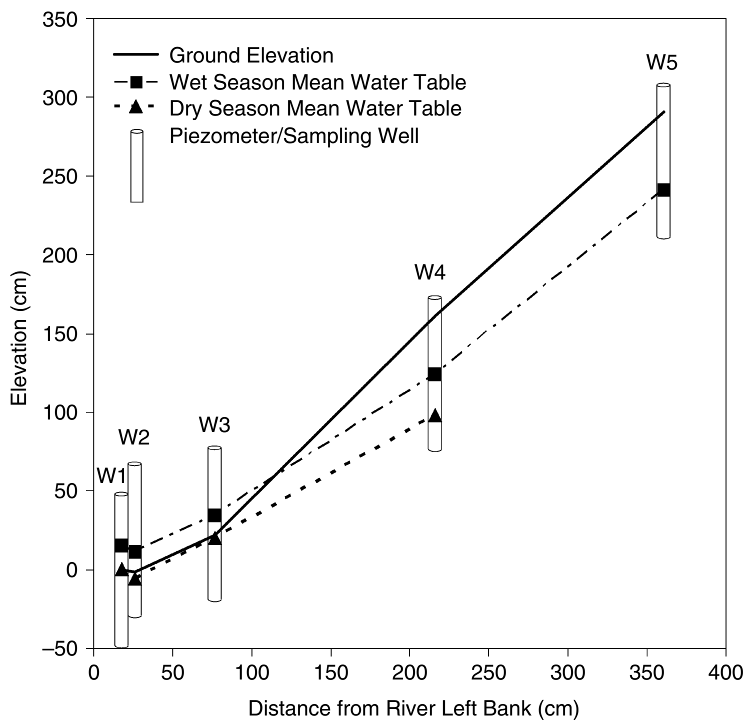

Figure 2. Cross section of W1–W5 and seasonal water table averages

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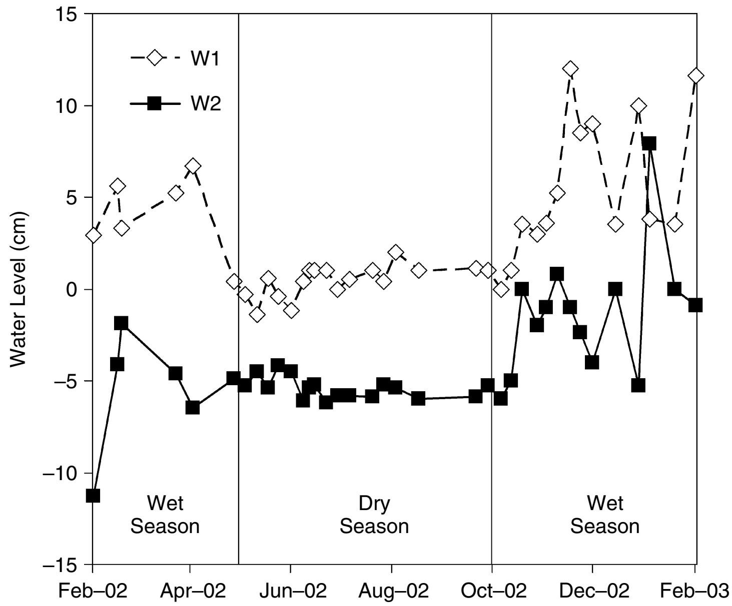

Figure 3. W1 and W2 water level elevations over time, based on a zero water level at the stream bottom

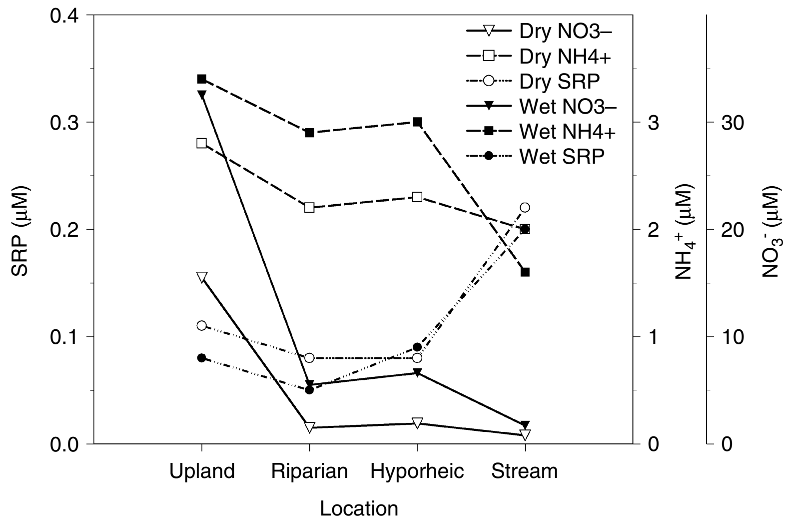

Figure 4. Spatio-temporal variation in median nutrient concentrations by class

to ~95% along hydrologic pathways flowing from the upland to the stream during both seasons. Wet season stream concentrations of NO_3^- were also significantly less than those in both the riparian and hyporheic classes ($p < 0{\cdot}001$; Table II). Soluble reactive P (SRP) concentrations were significantly higher in the stream when compared with riparian and hyporheic classes ($p < 0{\cdot}01$; Figure 4, Table I, Table II). Median total dissolved inorganic N (DIN) (calculated by the addition of median $NO_3^- + NH_4^+$ concentrations) decreased markedly from the upland to the stream during both seasons (Table I, Table II). Total DIN : SRP ratios also decreased greatly along the transect, with median values of 166 and 449 in the upland, compared with values of 12 and 17 in the stream, during the dry and wet season, respectively (Table I, Table II).

Table I. Median dry season baseflow inorganic nutrient concentrations (μM ± (SD)). Superscript letters mark significant spatial or temporal differences ($p < 0{\cdot}05$). W—greater in wet season, D—greater in dry season, U—upland, R—riparian, H—hyporheic, and S—stream. Ratios were rounded to nearest whole number

Location	NO_3^-	n	NH_4^+	n	SRP	n	DIN	DIN : SRP
Throughfall	0·7(1·4)	9	2·9(3·0)	8	1·07(4·25)	7	3·6	3
0-tension	16·7(1·7)	2	7·6(6·6)	2	0.02	1	24·3	1215
Overland	1·6(1·5)	6	2·4(5·6)	6	1·02(7·3)	5	3·0	3
Upland	15·5(19·2)^{W,R,H,S}	25	2·8(2·4)	25	0·11(4·39)	17	18·3	166
Riparian	1·5(3·4)^{W,U}	73	2·2(2·8)^{W}	71	0·08(0·34)^{D,S}	70	3·7	46
Hyporheic	1·9(2·8)^{W,U}	78	2·3(3·7)	74	0·08(0·44)^{S}	75	4·2	60
Stream	0·8(2·4)^{U}	20	2·0(2·6)	19	0·22(6·80)^{R,H}	20	2·8	12

Table II. Median wet season baseflow nutrient concentrations (μM ± (SD)). Superscript letters mark significant spatial or temporal differences ($p < 0{\cdot}05$). W—greater in wet season, D—greater in dry season, U—upland, R—riparian, H—hyporheic, and S—stream. Ratios were rounded to nearest whole number

Location	NO_3^-	n	NH_4^+	n	SRP	n	DIN	DIN : SRP
Throughfall	1·5(2·4)	17	2·4(10·3)	15	1·58(3·80)	15	3·9	3
0-tension	13·7(9·8)	3	1·3(1·3)	3	0·16(0·06)	3	15	94
Overland	2·1(9·9)	21	2·3(1·7)	21	1·05(0·73)	21	4·4	4
Upland	32·5(49·9)^{W,R,H,S}	32	3·4(5·1)	31	0·08(2·56)	26	35·9	449
Riparian	5·5(7·3)^{W,U,S}	104	2·9(4·5)^{W}	100	0·05(0·38)^{D,S}	91	8·4	168
Hyporheic	6·6(6·6)^{W,U,S}	98	3·0(2·9)	95	0·09(0·43)^{S}	90	9·6	107
Stream	1·7(1·4)^{U,R,H}	27	1·6(1·6)	26	0·20(0·38)^{R,H}	26	3·3	17

Table III. Median dry season baseflow DOC, DON, and DOP concentrations (μM ± (SD) unless otherwise indicated). Superscript letters mark significant spatial or temporal differences ($p < 0{\cdot}05$). U—upland, R—riparian, H—hyporheic, and S—stream. Ratios were rounded to nearest whole number

Location	DOC	n	DON	n	DOP	n	DOC: DON	DON: DOP	DOC: DOP	%DON	%DOP
Throughfall	1362·4	1	41·1	1	23·9	1	33	2	57	92	96
0-tension	4478·8	1	608·7	1	33·9	1	7	18	132	96	100
Overland	2404·6(847·3)	3	—	—	—	—	—	—	—	—	—
Upland	409·9(23·1)	3	587·2(57·7)^{R,H,S}	3	0·8(2·5)	3	1	734	512	97	88
Riparian	259·1(253·3)	37	16·3(16·7)^{U}	31	1·8(9·6)^{S}	31	16	9	144	82	96
Hyporheic	230·8(238·8)	43	12·6(18·9)^{U}	39	1·7(6·3)^{S}	39	18	7	136	75	96
Stream	260·2(129·0)	12	8·3(6·0)^{U}	11	2·7(20·7)^{R,H}	11	31	3	96	75	92

Concentrations of DOC and DON decreased from the upland towards the stream; however, DON decreased by two orders of magnitude while DOC decreased by one order of magnitude (Figure 5, Table III). Median DOC concentrations in throughfall (1362 μM) and overland flow (2405 μM) were notably higher than in riparian (259 μM) or stream waters (260 μM). Median DOC : DON ratios were extremely low (∼1) within the upland soil water dissolved organic matter (DOM) and subsequently increased in the downslope positions, reaching 31 in the stream (Table III). During the dry season, DOP was concentrated in throughfall and the zero-tension lysimeter; however, in contrast to both DON and DOC, DOP concentrations were lowest in the upland and subsequently increased toward the stream (Figure 5, Table III). Ratios of DON : DOP and DOC : DOP peaked within the upland soil water and declined markedly at locations closer to the stream (Table III). Organic N and

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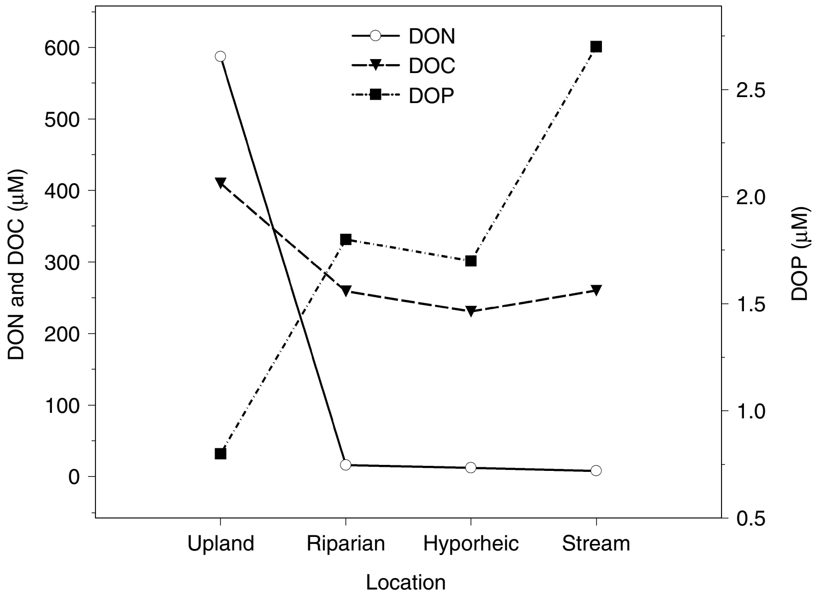

Figure 5. Spatial variation in median dissolved organic concentrations by class

P dominated the total dissolved nutrient concentrations within all classes; eventually resulting in DON and DOP constituting 75% and 92%, respectively, of the median dissolved nutrient concentrations in the stream (Table III).

Median specific conductivity increased from the upland towards the stream and was highest in the riparian and hyporheic classes regardless of season. Median pH values also increased from the upland to the stream, with concentrations that generally ranged from 7·0–8·0 during both seasons (Table IV).

Temporal patterns of solution chemistry

Upland soil water NO_3^- concentrations increased significantly in the wet season compared with the dry season ($p < 0{\cdot}01$; Table II). Nitrate concentrations in riparian and hyporheic classes followed a similar trend and increased by over 300% ($p < 0{\cdot}02$ for both) in the wet season compared with the dry season. Ammonium concentrations increased significantly in the riparian zone during the wet season ($p < 0{\cdot}01$). Despite significant seasonal variations elsewhere, NO_3^-, NH_4^+, and SRP concentrations in the stream did not vary significantly with season (Table I, Table II). Upland nutrient concentrations had the most distinct variability with season and with relative concentrations of NO_3^-, NH_4^+, and SRP. In contrast, stream concentrations remained comparably constant with respect to both relative nutrient concentration and temporal variability (Figure 6). Specific electrical conductivity was highest during the dry season for all classes (Table IV). There was no significant variation in pH between seasons (Table IV).

Table IV. pH and conductivity reported by class and season (SD)

Location	pH (wet)	Conductivity μS (wet)	*n* (wet)	pH (dry)	Conductivity μS (dry)	*n* (dry)
Upland	7·0(1·4)	44(34)	16	7·0(1·9)	96(21)	13
Riparian	7·4(0·4)	85(36)	67	8·0(0·7)	106(33)	59
Hyporheic	7·6(0·4)	106(18)	69	7·9(0·6)	113(28)	67
Stream	7·7(0·4)	53(30)	16	7·9(0·6)	62(26)	17

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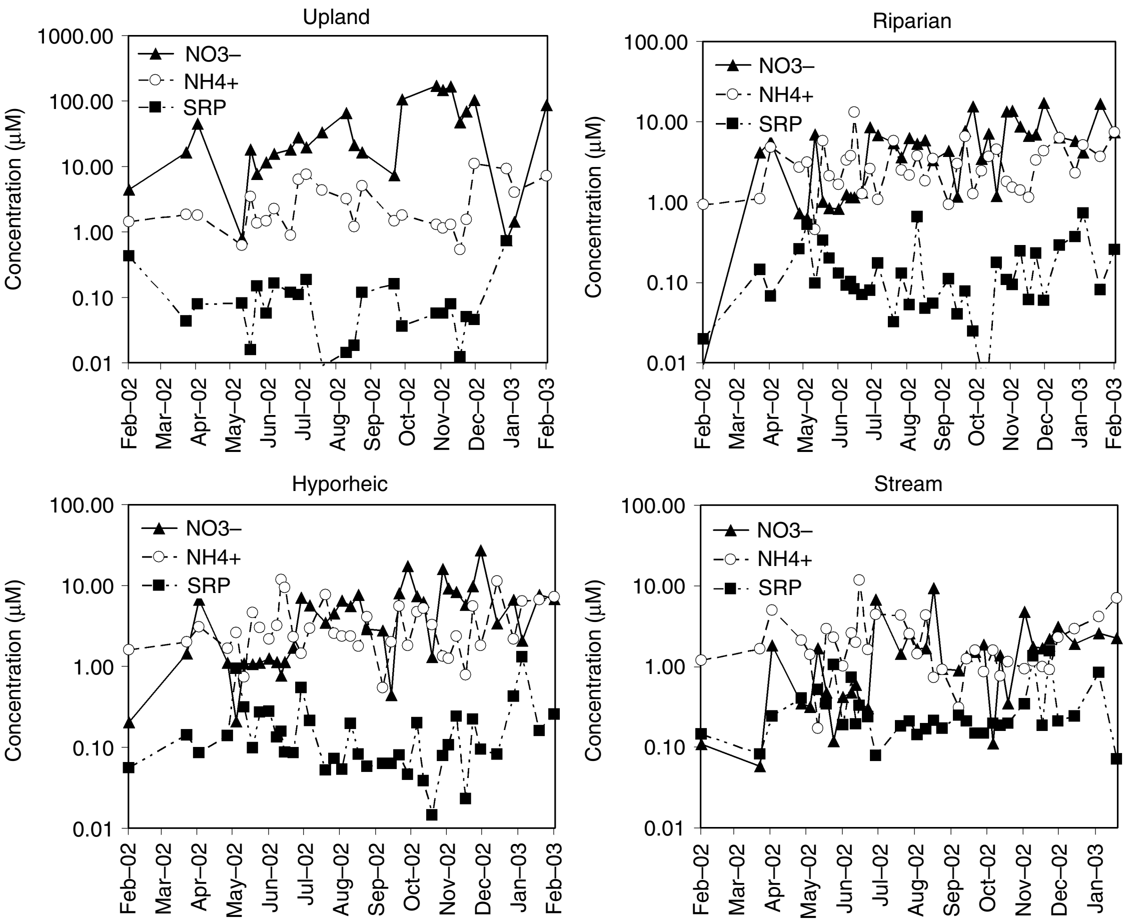

Figure 6. Log_{10} of nutrient concentrations over time for different spatial classes (note the scale difference on Upland *y*-axis)

Precipitation-dependent flowpaths measured during this study included throughfall, overland flow, and storm water infiltration through the upland surface organic horizon up to a depth of 20 cm. Concentrations of SRP were consistently multiple orders of magnitude higher in throughfall and overland flow compared to any other class sampled along the Wara transects (Table I, Table II). Conversely, DIN concentrations were relatively low in throughfall and overland flow and yet became comparatively enriched in the waters infiltrating into the upland soils.

DISCUSSION

Spatial influences on concentrations

The sharp decline in NO_3^- concentrations from upland to riparian zone in Wara indicated that mechanisms operating at or above the upland-riparian boundary were mainly responsible for the low N values observed in the stream under baseflow conditions. In Wara, the soil and vegetation blanketing the steep watershed were subject to frequent landslides, which created buried organic soil horizons (pers. obs). We suggest that this environment promoted the heterogeneous redox conditions favorable for denitrification above the riparian-stream interface. The following factors that are hypothesized to be responsible for the loss of inorganic N across

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tropical terrestrial-aquatic interfaces studied to date may also play a role in the decrease of N concentration in Wara: (i) in-stream losses of DIN resulting in a dilution of infiltrating groundwater, (ii) heterogeneous redox potentials at the upland-riparian and riparian-stream boundaries stimulating nitrification–denitrification reactions, and (iii) plant uptake and immobilization (McDowell *et al*., 1992; McClain *et al*., 1994; Brandes *et al*., 1996; Williams *et al*., 1997; Chestnut and McDowell, 2000; McSwiney *et al*., 2001). Although not directly investigated during any previous field study, the abiotic immobilization of NO_3^- to DON (Davidson *et al*., 2003), if functioning within the catchment, could also play a role in NO_3^- immobilization.

Despite large differences in geographic location, geomorphology, elevation, soils, and vegetation along topohydrosequences of the montane and lowland tropical forests studied to date, mean stream values of NO_3^- at all sites, including Wara, fell within the range of 0–8 μM and mean NH_4^+ concentrations remained below 3 μM (Chestnut and McDowell, 2000; McDowell *et al*., 1992; McClain *et al*., 1994; Brandes *et al*., 1996; Williams *et al*., 1997; McSwiney *et al*., 2001). The low variance observed in baseflow DIN concentrations within geographically and geomorphologically diverse tropical forest streams suggests that hydrologic flowpaths approaching the stream are subject to active biogeochemical processes in the terrestrial environment and/or at the terrestrial–aquatic interface that control baseflow DIN export to adjacent stream waters.

SRP was not reported in many of the investigations cited above and SRP data across upland-stream transects within montane tropical rainforests are currently limited. We found that SRP concentrations were consistently greater in the stream compared to the upland, behaving inversely to NO_3^-. SRP concentrations within soil and groundwater were likely partially controlled by abiotic adsorption to metal oxides (Filippelli, 2002; Martin *et al*., 2002; Mayer and Jarrell, 2000) and precipitation with Fe, Al, or Ca. Low SRP concentrations and high DIN: SRP ratios in subsurface flow samples also suggested a strong biotic demand for available phosphorus. Under baseflow conditions, relatively high SRP concentrations in the stream could have resulted from a combination of OM mineralization, mineral weathering, and decreased sorption/precipitation reactions within the stream channel.

Although limestone was not directly observed within the catchment, the hillslopes of neighboring catchments have distinct outcrops of limestone, and buried limestone was the likely source of increasing pH from the upland to the stream. Increasing specific conductivity of subsurface waters as they approached the stream indicated a greater influence of mineral weathering on dissolved ion concentrations along the transects (Table IV).

While sorption processes along groundwater flowpaths undoubtedly played a significant role in preventing stream losses of both DOC and DON, what remains unclear is the extent to which biological processes influenced the decreasing concentrations of DOC and DON along the transects and the mechanisms that were responsible for an accelerated rate of DON loss relative to DOC. We could not distinguish among competing hypotheses to explain the mechanisms that generated the patterns of DOC and DON concentrations along the transect, which included the following: (i) DON compounds, specifically remaining hydrophobic and basic amino acids, were sorbed along the transects thus causing an increase in the DOC : DON ratio of remaining DOM (Aufdenkampe *et al*., 2001), (ii) preferential enzymatic cleavage of N functional groups present in the DOM resulted in a relative enrichment of DOC in soil water DOM (Qualls and Haines, 1992), (iii) lower in the transects, DOM was largely derived from the breakdown and dissolution of soil organic matter (SOM), which is generally characterized by relatively high recalcitrance, molecular-weight, and C : N ratios (McDowell *et al*., 1998). These hypotheses can be formally tested and expanded in the future. However, regardless of which hypothesis, or combination of hypotheses, is correct, we conclude that under baseflow conditions the soils along the Wara transects appear to be remarkably efficient in preventing significant stream losses of both organic and inorganic forms of N.

A similar distinction between terrestrial soil/groundwater and stream water DOM composition as in the Wara catchment has been documented in the lowland Amazon. McClain *et al*. (1997) found that DOM in groundwater of terra-firme forests (oxisols) was compositionally distinct from DOM sampled from the river corridor, while DOM in waters draining campinara (spodosols) was compositionally similar to that in the

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groundwater of its drainage area. The soils along the Wara transects were more similar to those of lowland terra-firme rainforest soils in their clay content and Fe and Al oxide contents in contrast with the quartz sand-dominated spodosols of the campinara. Higher concentrations of clay, Fe oxides, and Al oxides can adsorb OM and effectively prevent upland-derived DOM from reaching streams under baseflow conditions.

The mean DOC : DON ratio (Table III) at our upland site was lower than the values reported in the literature for DOM in leachates and soil solutions (Cleveland *et al*., 2004) and approaches the DOC : DON ratio expected for pure urea (0·5). This was unexpected, given that our samples were in contact with a heterogeneous mixture of litter types at various stages of decomposition and within a mineral soil horizon. The value reported was the result of four separate measurements (NO_3^-, NH_4^+, TN, DOC) on three different pieces of analytical equipment and there was a potential for compounding error and producing bias in our measurements. The low DOC : DON ratio that we reported at the upland site is best interpreted as a low-value end-member in the clear trend of increasing DOC : DON from the upland to the stream (Table III). We hypothesize that the following mechanisms may have been responsible for elevated DON concentrations at the upland site: (i) preferential leaching of hydrophilic and non-protein amino acids and other N-rich water soluble compounds from the upper litter layer while hydrophobic C-enriched DOM remained sorbed to mineral components (McDowell *et al*., 1998; McDowell and Likens, 1988) and (ii) the abiotic immobilization of NO_3^- to DON, formally presented as the 'ferrous wheel hypothesis' by Davidson *et al*. (2003), the conditions for which occur within the upland, namely, high OM concentrations, heterogeneous oxidation-reduction potentials (as evidenced by co-presence of NO_3^- and NH_4^+), and the presence of Fe.

Spatial trends in nutrient stoichiometry highlighted a clear divergence in the nutrient composition of terrestrial and aquatic hydrologic compartments along the Wara transects. This divergence is illustrated by organic and inorganic stoichiometric ratios that contrast the two extremes found within the upland and stream classes as follows: (i) the highest median DOC : DOP ratio (512) was measured in the upland *versus* the lowest value (96) in the stream, (ii) the highest median DON : DOP ratio (734) was also in the upland, contrasting the lowest ratio (3) in the stream, (iii) the lowest DOC : DON ratio was in the upland (1) while the highest was in the stream (31) and most importantly, (iv) DIN : SRP ratios (449 and 17, upland and stream, respectively) clearly reflected a marked switch in nutrient composition between upland soil water and the stream.

Temporal influences on concentration

In comparison to other tropical topohydrosequences, Wara was the only site where a significant seasonal variation in upland soil water has been reported. The high wet season NO_3^- concentrations observed along the Wara transects could have resulted from elevated air temperatures and moisture promoting increased N mineralization and nitrification. Despite significant seasonal increases of DIN concentrations in the upland, riparian, and hyporheic zones during the wet season, processes facilitating NO_3^- removal appeared to prevent an increase in NO_3^- concentrations in stream. In an agricultural landscape, Dhondt *et al*. (2002) also found that the riparian zone was able to dissipate significant seasonal increases in upland NO_3^- concentrations, thus also maintaining a relatively constant N input to the stream.

The influence of storm events on total nutrient export from headwater catchments in the Andes is not known. Stieglitz *et al*. (2003) emphasize the ability of discrete storm events to connect a river corridor with its hillslopes and stress that the effects of these interactions warrant further research. Elsenbeer and Lack (1996) and Hensel and Elsenbeer (1997) in La Cuenca, a headwater catchment found in the lower (∼300 m. a. s. l.) Pachitea River Basin of Perú, identified surface flow as well as return flow as significant components of total stormflow, sometimes contributing up to 50% of the total event water. Within the Wara catchment, Ramos *et al*. (2003) reported increased stream NO_3^- concentrations during storms, suggesting that throughfall, overland flow, and shallow subsurface storm pathways could rapidly leach NO_3^- from surface organic horizons and flush it towards the stream. Severe events of the type responsible for export of huge quantities of suspended sediments, such as those associated with ENSO events (Aalto *et al*., 2003), likely have significant implications in terms of nutrient export from the Andes and must also be addressed in order to understand the influence of storm events over longer temporal scales.

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CONCLUSIONS

We observed strong spatially related controls on terrestrial-aquatic transfers of organic and inorganic N and P. Under baseflow conditions, organic and inorganic N in upland soil water were either denitrified or immobilized along the Wara transects and were only detected at low concentrations in the stream. Phosphorus had an inversely related concentration distribution to N in both organic and inorganic forms and was concentrated in the stream as compared to the upland. We believe that these trends represent a shift in nutrient status between terrestrial and aquatic systems over extremely short distances. Total dissolved N and P concentrations were dominated by the organic fraction in all of the classes sampled in this pristine catchment.

Significant seasonal changes of all inorganic nutrients were detected at some point along the Wara transects yet NO_3^- fluctuations within the upland class were the most notable. Relatively high temperatures and moisture during the wet season likely promoted increased mineralization and nitrification rates resulting in median wet season NO_3^- concentrations that doubled those of the dry season. Nonetheless, spatially related processes buffered temporally related variation of NO_3^- concentrations in the upland, riparian, and hyporheic zones and held stream NO_3^- concentrations relatively stable. Therefore, spatial controls superseded broad temporal fluctuations, and ultimately determined the baseflow composition and concentration of N and P delivered to the stream. However, in response to storms, NO_3^- concentrations in the stream increased (Ramos *et al.*, 2003) and both SRP and NO_3^- fluxes in throughfall and overland flow increased notably. Therefore, although spatial controls dominated temporal fluctuations, sporadic events such as storms temporarily bypassed spatial controls, delivering a pulse of N and P, sediments, and OM to the stream.

Our research has provided a general characterization of N and P biogeochemistry and the potential spatial and temporal controls that affect nutrient transfers between terrestrial and aquatic systems at the plot scale in a pristine montane catchment of the Peruvian Amazon.

Further work to assess the significance of terrestrial controls on total watershed N and P export in different elevation and vegetation zones and to quantify the significance of storm-related nutrient exports will improve our understanding of terrestrial-aquatic nutrient transfers in the Andean Amazon and their consequences for downstream environments.

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