Biogeochemistry (2006) 81:131–143
DOI 10.1007/s10533-006-9026-6

ORIGINAL PAPER

Soluble reactive phosphorus transport and retention in tropical, rainforest streams draining a volcanic and geothermally active landscape in Costa Rica. : Long-term concentration patterns, pore water environment and response to ENSO events

Frank J. Triska · Catherine M. Pringle · John H. Duff · Ronald J. Avanzino · Alonso Ramirez · Marcelo Ardon · Alan P. Jackman

Received: 21 March 2005 / Accepted: 3 April 2006 / Published online: 3 June 2006

Abstract Soluble reactive phosphorus (SRP) transport/retention was determined at four sites in three rainforest streams draining La Selva Biological Station, Costa Rica. La Selva is located at the base of the last remaining intact rainforest transect from ~30 m above sea level to 3000 m along the entire Caribbean slope of Central America. Steam SRP levels can be naturally high there due to regional, geothermal groundwater discharged at ambient temperature. Monitoring since 1988 has revealed distinctive long-term differences in background SRP and total P (TP) for three streams in close proximity, and identified the impact of ENSO (El Nino Southern Oscillation) events on SRP-enriched reaches. Mean interannual SRP concentrations (± standard deviation) were 89 ± 53μg/l in the Salto (1988–1996), 21 ± 39μg/l in the Pantano (1988–1998), and 26 ± 35μg/l in the Sabalo (1988–1996). After January, 1997 the separate upland-lowland contributions to discharge and SRP load were determined monthly in the Salto. SRP in Upper Salto was low (19 ± 8μg/l, 1997–2002) until enriched at the upland-lowland transition by regional groundwater. Mean SRP concentration in Lower Salto (108 ± 104μg/l) was typically highest February–April, the driest months, and lowest July–September, the wettest. SRP concentration was positively correlated to the inverse of discharge in Lower Salto when ENSO data were omitted (1992 and 1998–1999), but not in the Upper Salto, Pantano, or Sabalo. TP was positively correlated to the inverse of discharge in all three streams when ENSO data were omitted. High SRP springs and seeps along the Lower Salto contributed ~36% of discharge but ~85% of SRP export 1997–2001. Annual SRP flux from the total Salto watershed (1997–2001) averaged 2.9 kg/ha year, but only 0.6 kg/ha year from the Upper Salto. A dye tracer injection showed that pore water environments were distinctly different between Upper and Lower Salto. Upper Salto had high surface water–pore water exchange, high dissolved oxygen, low SRP, and low conductivity similar to

F. J. Triska (✉) · J. H. Duff · R. J. Avanzino
U.S. Geological Survey, 345 Middlefield Rd., MS 439, Menlo Park, CA 94025, USA
e-mail: fjtriska@usgs.gov

C. M. Pringle · M. Ardon
Institute of Ecology, University of Georgia, Athens, GA 30602, USA

A. P. Jackman
Department of Chemical Engineering, University of California, Davis, CA 95616, USA

A. Ramirez
Institute for Tropical System Studies, University of Puerto Rico, San Juan, PR 00936, USA

surface water, and Lower Salto had low surface water–pore water exchange, low dissolved oxygen, high SRP, and high conductivity reflecting geothermal groundwater influence. SRP export from the Salto was controlled by regional groundwater transfer, which in similar volcanic settings could be a significant P source. However, ENSO events modified the SRP concentration in the Salto suggesting that long-term monitoring is required to understand underlying SRP dynamics and P flux to downstream communities.

Keywords Phosphorus · Retention · Sorption · SRP · Streams · Tropical · TP · Transport · Volcanic · ENSO

Introduction

Phosphorus cycling in fluvial environments involves numerous interacting biotic and abiotic reactions that regulate its uptake and transport. Physical factors affecting SRP include pH (Holtan et al. 1988; Kleeberg and Schlungbaum 1993), temperature (Mulholland et al. 1985; Bothwell 1988; Holtan et al. 1988; D'Angelo et al. 1991; Meals et al. 1999), sorption/desorption (Meyer 1979; Hill 1982), interstitial redox conditions (Enell and Lofgren 1988; Holtan et al. 1988; Gonsiorczyk and Koschel 1997), and discharge (Meyer 1979). All control P levels in surface water and depending on concentration, can limit biotic production and decomposition (Elwood et al. 1981; Newbold et al. 1981; Rosemond et al. 2002; Ramirez et al. 2003). P occurs in numerous dissolved and particulate forms in fluvial environments. Dissolved P occurs as either SRP or unreactive P. SRP is the most biologically available and thus the focus of most fluvial studies. Differing SRP results reported in published field studies are likely due to differences in background concentration, geologic setting, magnitude of experimental amendment, channel geomorphology, or study duration. For example, Munn and Meyer (1990) reported rapid SRP uptake in an eastern USA stream draining deeply weathered granitic bedrock, but less uptake in a stream draining volcanic bedrock. Within a similar geologic setting, Hart et al. (1992) reported that P uptake length decreased with decreasing concentration. Mulholland et al. (1997) reported greater SRP retention in Hugh White Creek, NC, USA with larger hyporheic volume compared to Walker Branch TN, USA with smaller hyporheic volume. In contrast Hall et al. (2002) found P uptake unrelated to hyporheic volume at Hubbard Brook, NH, USA, because P uptake there was dominated by abiotic sorption Within years, storm flows can induce high-P pulses to an otherwise P-limited biotic community. Between years, P retained in a dry year can be transported in a subsequent wet year (Meyer and Likens 1979).

Shifts in SRP concentration, exacerbated by land use, are increasingly common especially in large watersheds with combined urban and agricultural use. Land use modifies temporal concentration patterns by shifting SRP sources under variable hydrologic conditions (Devito et al. 1989; Dorioz et al. 1998). For example, SRP retention decreased following logging, becoming more discharge related than before (Butturini and Sabater 1998). Although a downstream increase in SRP concentration is usually associated with land use (e.g., McClain et al. 1998), in some drainages SRP concentration is naturally elevated.

The Salto River, drains dense tropical rainforest at La Selva Biological Station, Costa Rica. High, natural SRP input, attributed to regional, geothermally modified groundwater, is introduced at the ambient surface water temperature of ~24 °C (Pringle et al. 1990). In this study we compared natural input, output and concentration among upland and lowland reaches of the Salto River and two nearby streams, the Pantano and Sabalo. All three streams had similar geologic and climatic setting, annual day length, and nearly constant annual temperature. The three streams were compared using both short- and long-term approaches. The study had three objectives: (1) to determine long-term trends of SRP concentration from three streams with differing SRP levels; (2) to examine SRP concentration and retention relative to the pore water environment above and below sites of high SRP input; and (3) to examine short-term SRP retention by in situ and laboratory studies. This report examines the first two objectives.

Study area

All study sites were within or adjacent to La Selva Biological Station, a 3300 ha reserve located at the transition between the Caribbean lowland plains and the steep foothills of Costa Rica's central mountain range (Fig. 1). La Selva receives average annual rainfall of ~4 m. The wettest months are July–September and the driest are February–April, although some years lack a definite dry season. Our focus was the Salto River, an ungaged third order stream that drops from 300 to ~36 m above mean sea level where it joins the Puerto Viejo River. The base of this 1120 ha watershed is located in La Selva Biological Reserve and the upper two-thirds lies in Braulio Carrillo National Park. The area of the upper watershed above the sampling site Salto 60, as indicated on Fig. 1, is ~726 ha, while the lower watershed between stations Salto 60 and Salto 30, is ~394 ha. More than 95% of the watershed is roadless, primary, tropical rainforest (Pringle et al. 1990; Pringle et al. 1993).

Upper Salto drains a basalt formation believed to be of Quaternary origin. The stream gradient is steep (0.10) and its bed is composed of large boulders with sand interstices. Lower Salto drains swamp-forest composed primarily of terraces of

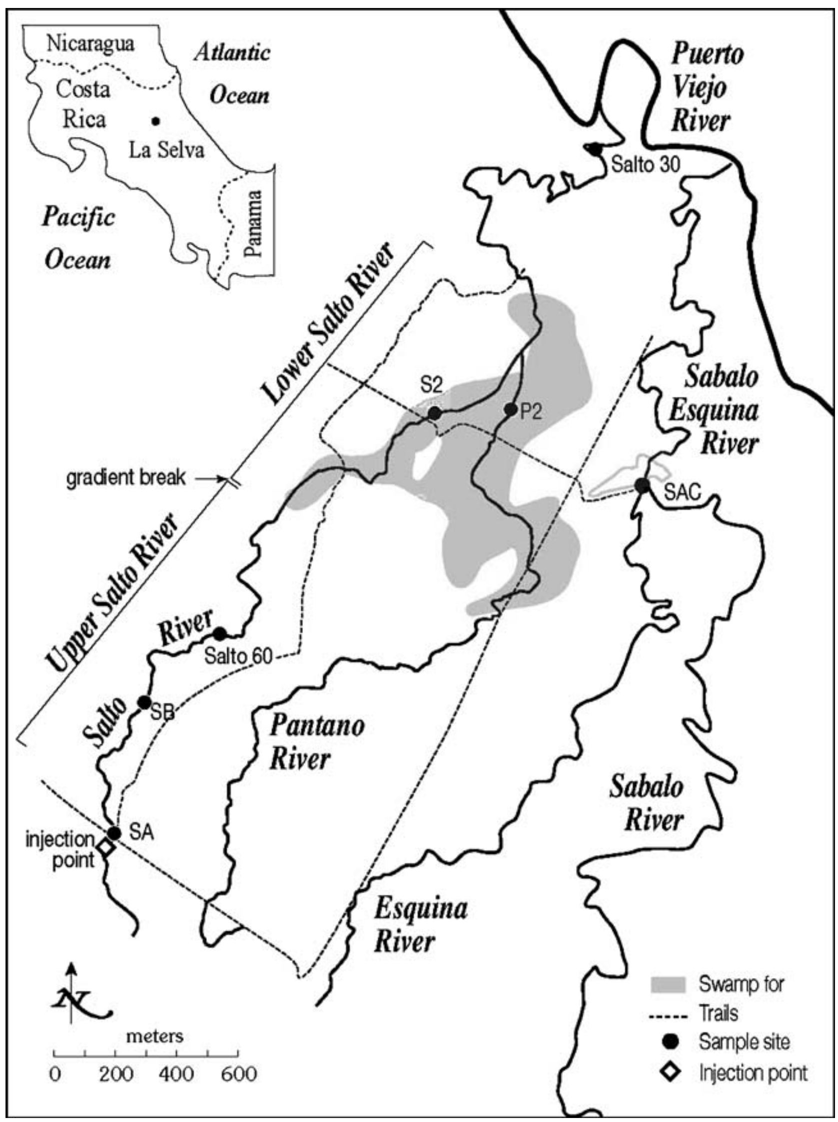

Fig. 1 Map of Salto River basin at La Selva Biological Station indicating its location in Costa Rica and long-term sampling locations in the Salto, Pantano, and Sabalo Rivers

alluvial sands and gravels of volcanic origin (Bourgeois et al. 1972). The Salto mainstem flows along the eastern boundary of the younger of two lava flows at La Selva (Pringle et al. 1990). P-rich springs emerge near the edge of this formation as the channel crosses the gradient break and enters lowland swamp-forest (Pringle and Triska, 1991). Swamp-forest soils are poorly drained, blue-grey and blackish-brown silts and clays. Soils are slightly acidic (pH 4.0–5.2), contain up to 25% organic content, and have a fragile structure (Bourgeois et al. 1972). Due to the high water table access is difficult. The Pantano is a low-gradient (0.06) tributary to the Salto. The Pantano drains swamp-forest above the older Salto lava flow and is low in SRP. Pantano sediments are also fine-grained sands, silts, and clays. The Sabalo River is immediately east of La Selva (Fig. 1). The Sabalo drains a transition zone between upland and lowland. The channel has a pool-riffle geomorphology and does not drain swampy areas. The Sabalo's rainforest was cleared for pasture at least three decades ago. Trees remain along riparian areas but the canopy is open compared to the other densely shaded sites.

Methods

Long-term studies: background nutrients and discharge

Sampling and discharge measurement began in 1988. Grab samples for water chemistry were collected mid-channel, mid-depth approximately weekly 1988–1991, tri-weekly in 1992, and monthly 1993-present. Samples were filtered (0.45 μm membrane) and analyzed for SRP at La Selva Biological Station using an ascorbic acid-molybdenum blue method. TP was determined 1988–1992 from unfiltered, persulfate-digested samples using the same method. The long-term means are arithmetic rather than volume weighted since accompanying discharge data was available for only part of the record. Continuously monitored sites included the Salto River at Site S2, the Pantano at Site P2 (both in swamp-forest), and the Sabalo at Site SAC (Fig. 1). Discharge was determined (1988–1994) within 24 h of nutrient sampling using a Marsh-McBirney current meter. The long-term SRP and TP concentrations were fit with a linear regression through the inverse of discharge since dilution was considered the most likely control of SRP concentration. Before determining if the slope of the regression line was significantly different than zero, residuals were examined for normality using a probability plot correlation coefficient (PPCC) test (Looney and Gulledge 1985). Where residuals were nearly normally distributed, data points corresponding to the extreme outlier residuals ("outside" values), as indicated by a box and wisker plot, were removed and the regression analysis was repeated. All statistical tests were performed using a significance level of 0.05. Monthly discharge measurements were discontinued in 1994 and resumed in 1997 when Salto S2 was replaced with two new sampling sites, Salto 30 (Lower Salto) and Salto 60 (Upper Salto, Fig. 1). SRP concentrations were simultaneously determined with discharge (Salto 60, Salto 30, and P1). The sampling sites were relocated to separately determine upland and lowland contribution to discharge and SRP load (discharge × concentration) in the Salto. Contribution of discharge and SRP load by the swamp-forest were determined by the difference between Salto 30 and Salto 60 measurements, corrected for discharge and SRP load from the Pantano tributary. Due to poor access and time required to complete the discharge measurements, sampling could not always be completed the same day at all three sites, especially during the wet season. As a result discharge-load estimates were eliminated for months where significant precipitation occurred before completion of all measurements. The proportional contribution by the swamp-forest to SRP load and discharge was determined monthly by dividing the swamp-forest load (Salto 60-Salto 30) by that at Salto 30.

Pore water sampling

Surface water exchanges into the bed of the Salto and pore water chemistry were determined in Upper and Lower Salto during March, 1998 to determine if differences in pore water environment were reflected in surface water chemistry. To estimate surface water exchange, the dye tracer Rhodamine WT was continuously injected into the Salto River (FMI Metering pumps) at the upstream La Selva boundary (Fig. 1). After the dye reached plateau concentration, surface and pore water were sampled using a 0.95 cm o.d. stainless steel drive point connected to a peristaltic pump. Both filtered (0.45 μm membrane) and unfiltered samples were taken at various depths in the vicinity of SA, SB, and S2. Samples were returned to the laboratory and background-corrected dye fluorescence was determined using a Turner Model 10 fluorometer. Pore water fluorescence was divided by surface water fluorescence to determine the proportion of surface water entering the bed (Triska et al. 1989). That is, if background-corrected Rhodamine WT concentration was identical in surface and pore water, 100% of pore water presumably originated from surface water infiltration. Filtered SRP samples were refrigerated, acidified (pH ~ 1, ultra pure hydrochloric acid) and returned to our laboratory at Menlo Park, CA for analysis (molybdenum blue, Technicon Method 155–71W). Ferrous iron (Stookey 1970) and ammonium (Bower and Holm-Hansen 1980) were determined immediately upon return to the field laboratory. Separate unfiltered samples collected in 50 ml glass BOD bottles were analyzed for dissolved oxygen (DO) (YSI 5905 stirring BOD probe) and conductivity (Oakton WD 35607).

Results

Long-term SRP

SRP and discharge revealed seasonal and long-term variability within and between sites with a significant impact by ENSO events in 1992 and 1998–1999 (Fig. 2 A–C). Mean long-term SRP concentrations (± s.d.) were 89 ± 53μg/l for Salto S2 (1988–1996) compared to 21 ± 39μg/l for Pantano P2 (1988–1998), and 26 ± 35μg/l for Sabalo SAC (1988–1996). Annual means for SRP at Salto S2 ranged from 70 ± 24μg/l in 1993 to 163 ± 105μg/l in 1992, an ENSO year. After the Lower Salto site was switched to Salto 30 in 1997 the annual mean SRP concentration ranged from 56 ± 18 in 1997 to 213 ± 201 in 1999 (ENSO year). The ENSO impact could also be observed in the long-term mean concentration of 108 ± 103 for the total data set, but only 78 ± 37 if 1998–1999 ENSO data are removed. Annual mean SRP in Lower Salto (S2 or Salto 30) was 70–80 μg/l in 7 of 14 years. Upper Salto 60 had low and consistent SRP concentration. Annual SRP means ranged only between 17 ± 6 and 23 ± 7, and the long-term mean was only 19 ± 8μg/l (1997–2002), slightly higher than the Pantano. Pantano mean SRP concentration (1988–2002) ranged from a low of 2 ± 2μg/l in 2000 to highs of 96 ± 107μg/l in the 1992 and 50 ± 5 in the 1998–1999 ENSO years. In 11 of 14 years annual mean SRP was 20 μg/l or less. The Sabalo, the largest watershed, had low SRP concentration, but typically higher than the Pantano.

Seasonally, SRP concentration was typically highest February–April when annual discharge was lowest. Lowest SRP concentrations typically occurred July–September, midpoint of the wet season. Generalizations were difficult to make since in some years the dry season started early while in others it barely occurred. Dry season SRP concentration was higher than wet season at Lower Salto in 11 of 14 years, although the standard deviations were often high. Mean dry season concentration at Salto 30 was 144 ± 159μg-P/L, but was reduced to 83 ± 27μg/l when ENSO data were omitted. Mean wet season concentration was lower, 88 ± 60μg-P/L and likewise reduced to 52 ± 19μg-P/L by omitting the ENSO data. SRP concentration was consistently low in the Pantano with little seasonal variation except for the 1992 and 1998–1999 ENSO years. In the Sabalo, wet and dry season concentrations were similar. Annual mean SRP ranged from 8 ± 3μg/l in 1996 to 106 ± 92μg/l in 1992 (ENSO year).

A statistically significant relation between SRP concentration and the inverse of discharge was observed at Salto S2 when ENSO samples were omitted but not in either the Pantano or Sabalo (Fig. 3A). TP was positively correlated with the inverse of discharge at all three sites (1988–1992) when ENSO data were omitted (Fig. 3B). The impact of high SRP springs along the lower Salto is readily observed when SRP and the discharge are plotted separately for Salto 60 and Salto 30

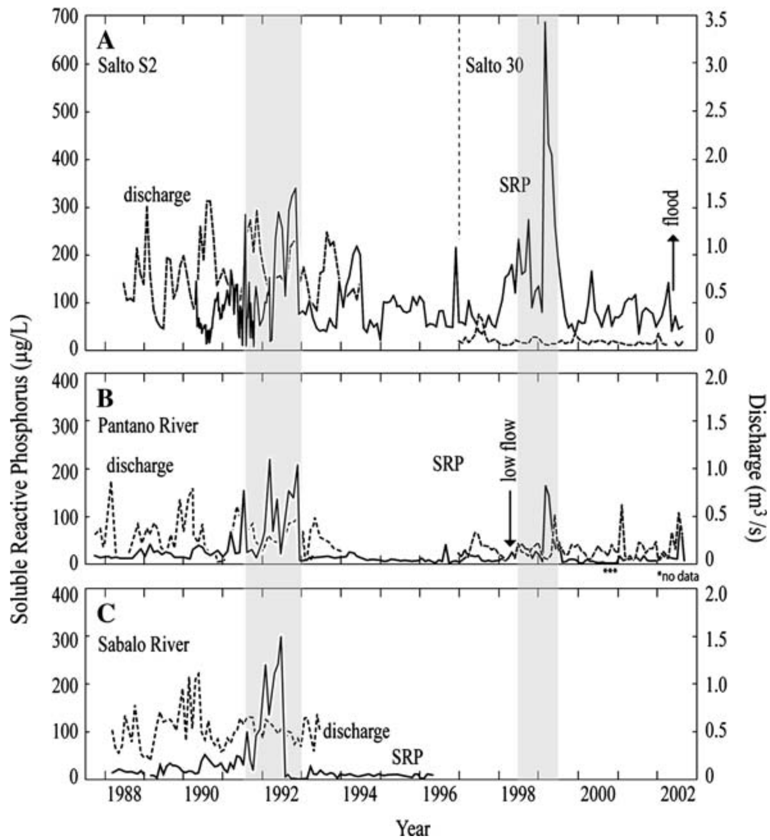

Fig. 2 Discharge and SRP concentration at (**A**) Salto site S2 (1988–1996) and Salto 30 (1997–2002), (**B**) Pantano site P2 (1988–2002), and (**C**) Sabalo site SAC (1988–1996). Shaded areas indicate ENSO periods. Dates where flows were too high or low to be measured are indicated by arrows, (*) indicates no sample

(Fig. 4A, B). At Upper Salto 60 discharge ranged over an order of magnitude (0.25–3.50 m^3/s) and SRP levels tightly clustered between 10 and 30 μg/l. In contrast, typical SRP levels in Salto 30 were 100–275 μg/l at a discharge of 0.50–0.60 m^3/s. At Lower Salto 30, SRP concentration was positively correlated with the inverse of discharge when data from the 1998–1999 ENSO were omitted. The ENSO-related SRP increase observed in 1991–1992 was less than that in 1998–1999 (Fig 2). Moving the sampling site downstream from S2 to S30 possibly added additional geothermal SRP input.

Monthly SRP concentrations in the Lower Salto (1997–2001) were typically highest during the February–April dry season, and decreased July–September, the months with higher discharges (Fig. 5A). The swamp-forest annual groundwater contribution to discharge (1997–2001) was 36% (Fig. 5B) and was proportionally greater in the driest months (February–April) than the wettest (July–August). The swamp-forest contribution to discharge averaged 0.32 m^3/s. The swamp-forest annual groundwater contribution to SRP load (1997–2001) was ~85% (Fig. 5B) and was proportionally constant between wet and dry months. The large groundwater SRP contribution occurred over a small geographic area of the watershed. The proportion of geothermal SRP input was relatively constant while the SRP concentration in the Salto River fluctuated with river discharge.

Annual watershed SRP flux based on monthly discharge-concentration data from 1997 to 2001 was 2.9 kg/ha year (Table 1). Average annual SRP flux from the Upper Salto was estimated to be 0.6 kg/ha year compared to 7.3 kg/ha year in Lower Salto. The Upper Salto SRP flux was fairly consistent despite discharge level or ENSO events (data not shown) whereas in Lower Salto annual SRP flux was variable year to year. For example, in the ENSO year June 1998–May 1999, SRP flux from Lower Salto was twice that of the 5 year average.

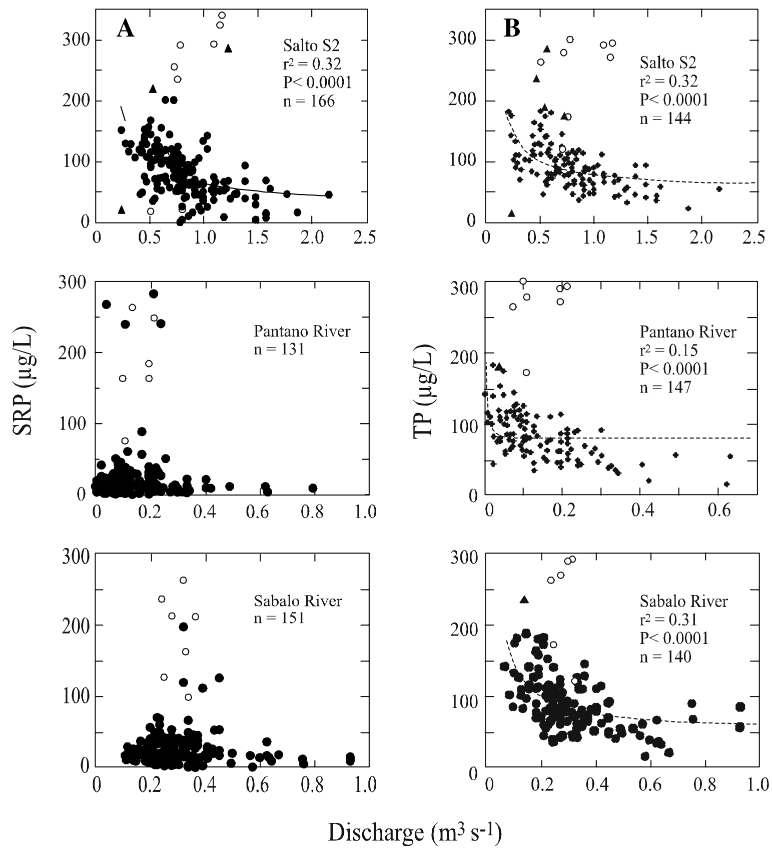

Fig. 3 Plots of (**A**) SRP and (**B**) TP concentration vs. discharge for the Lower Salto (S2), Pantano, and Sabalo Rivers. Dashed lines are best fit regression relationships between concentration and the inverse of discharge. Open circles are ENSO related data, closed triangles are rejected outliers. Fitted line formulae were determined by linear regression of concentration vs. 1/discharge. The plotted lines represent the formulae transformed back into units of concentration vs. discharge. Equations for fitted lines are as follows: (**A**) SRP Salto S2 = 38.1(1/discharge) + 27.2; (**B**) TP Salto S2 = 24.7(1/discharge)+48.6, TP Pantano = 0.274 (1/discharge) + 76.1, TP Sabalo = 10.6(1/discharge) + 45.5

Pore water chemistry

Pore water of Upper and Lower Salto had distinctly different chemical signatures that were reflected in surface water SRP. These underlying differences stem from numerous possible factors including the slope, soil type and gradation, the percentage of water advected into the bed, and geothermal inputs. Rhodamine WT data from Upper Salto revealed surface water penetration to depths of 10–30 cm (Table 2). The surface water component was greatest near site SA where pore water at 10 cm depth was 47 to 100% channel water. Dissolved oxygen concentration was >4.2 mg/l in 7 of 10 Upper Salto samples. One exception was a side channel depositional site, SB1, which had low DO at both 10 and 20 cm depths. Poor hydrologic exchange at this site was attributed to its side location, deposition of particulate organic matter, and fine sediments. Pore water SRP was low and comparable to surface water in 11 of 13 samples. Ferrous iron concentrations were <0.10 mg/l in 5 of 10 SA samples and <0.7 mg/l in all locations except SB1. Upper Salto pore water was low in dissolved solutes. Conductivity was ~30–50 µS/cm. Ammonium concentrations were <10 µg N/L in 8 of 10 SA pore water samples. The highest ammonium concentration was at SB1 (74 µg N/L at 10 cm and 50 µg N/L at 20 cm depth).

Lower Salto (S2) had a low percentage of surface water in the bed (Table 2). In 8 of 9

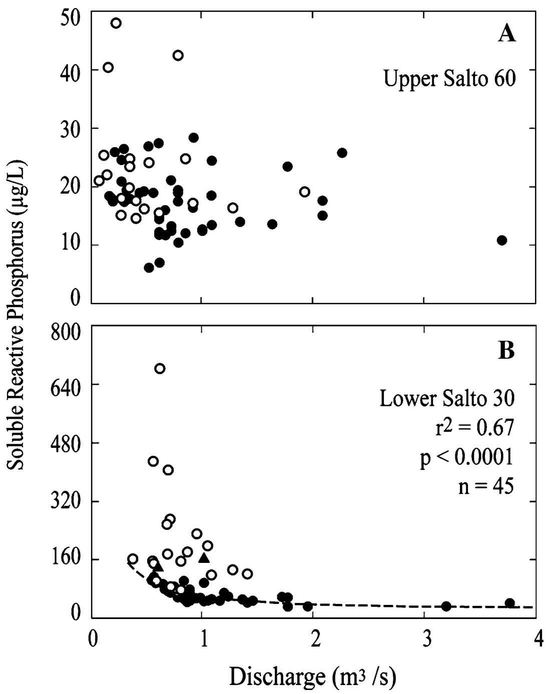

Fig. 4 Plot of SRP vs. discharge (1997–2002) for (**A**) Upper Salto 60 where discharge and SRP concentration are dominated by local groundwater and (**B**) Lower Salto 30 where SRP is dominated by regional groundwater inputs. Dashed line is best fit regression relationship between concentration and the inverse of discharge transformed back into units of concentration vs. discharge. Open circles are ENSO related data (1998–1999), closed triangles are rejected outliers. The equation for the fitted line is SRP = 45.7 (1/discharge)+14.2

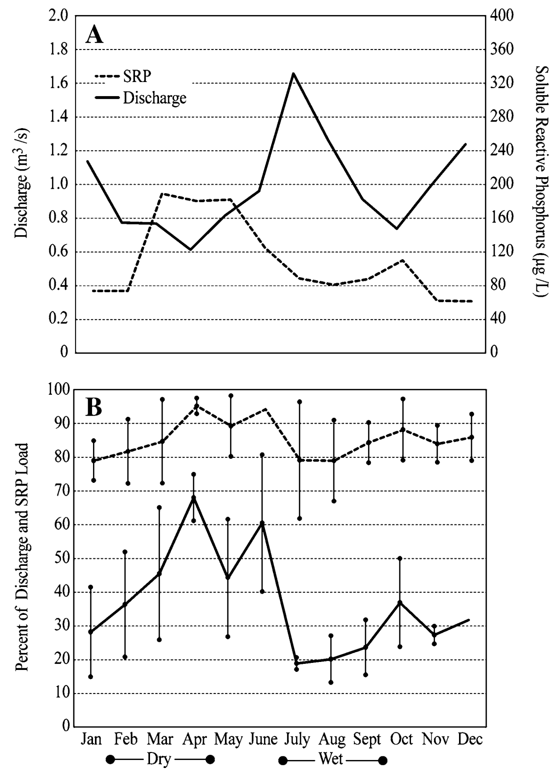

Fig. 5 (**A**) Mean monthly discharge and SRP concentration at Lower Salto 30 (1997–2001) and (**B**) Proportional contribution of discharge and SRP load (monthly mean ± s.d., 1997–2002) by high-SRP geothermal springs and swamp-forest

samples the surface water component was < 12%. Dissolved oxygen was lower and conductivity was higher and more variable than in Upper Salto sediments. All four Lower Salto sample locations were within 30 m of each other yet conductivity ranged from 263–530 μS/cm reflecting variable pore water conditions. Conductivity at a given location was generally consistent with depth. Ferrous iron ranged from 1.3 to 8.0 mg/l in 7 of 9 pore water samples. Pore water SRP concentration was high, similar to surface water. It was also typically more than an order of magnitude higher than pore water in Upper Salto. As a result of the reducing environment, Lower Salto pore water had higher ammonium (10–153 μg N/L) and 4 of 9 samples exceeded the highest concentrations found on Upper Salto.

Discussion

We documented two principal long-term controls, one spatial and one temporal, on SRP concentration and output from the Salto watershed. The first, input of high SRP groundwater from regional sources, was related to the overall volcanic setting, and to the terminus of past lava flows. This control was a function of spatial position. The second, the impact of ENSO events, was temporal.

Long-term SRP concentration was relatively predictable by location considering the high standard deviation in local, seasonal, and inter-annual means. The upland environment (Salto 60) had consistently low SRP concentration for the total period of record (1997–2002), whereas in lowland environments SRP concentration was controlled by the contribution of high-SRP geothermal groundwater. At Lower Salto (Salto 2

Table 1 Mean annual SRP flux from the Salto watershed from 1997 and 2001, during a high-discharge year (1997), an ENSO event year (June 1998–May 1999), and a low-discharge year (2001)

Date	Mean annual discharge Salto 30 (m^3/s)	Total watershed SRP flux (kg/ha year)	Upper Salto SRP flux (kg/ha year)	Lower Salto SRP flux (kg/ha year)
Jan. 1997–Dec. 2001	0.95	2.9	0.6	7.3
Jan. 1997–Dec. 1997	1.53	2.2	0.9	4.6
Jun. 1998–May 1999	0.92	6.0	0.6	16.0
Jan. 2001–Dec. 2001	0.52	1.2	0.4	2.5

and Salto 30) high regional groundwater input both enhanced discharge and dominated SRP loss from the watershed. The strong hydrologic connection to regional geothermally modified groundwater is likely a common but under-investigated property of streams draining geothermally active regions, even in temperate environments (Pringle et al. 1993).

The lowland Pantano and Sabalo received little geothermal groundwater input, but like the Salto responded to ENSO events. After regional geothermal SRP input, most long-term variation in SRP concentration in the Salto and adjacent watersheds was associated with ENSOs in 1992 and 1998–1999, which raised SRP concentration. When data from the ENSO years were removed from the Salto 30 data set, mean dry season, wet season and annual SRP concentration and their standard deviations were all reduced. These results emphasize the importance of ENSO events in the Salto and similar watersheds, and reinforce the importance of long-term monitoring in documenting and understanding interannual SRP flux.

Discharge was a third potential source of variation in SRP concentrations of the three streams, but the relationship was weak. SRP was not correlated with discharge except at Lower Salto and only when ENSO data were removed. Absence of a significant SRP-discharge correlation is consistent with most published literature. Likens et al.

Table 2 Physical and chemical properties of pore water collected at 10–30 cm depth in the Upper (SA, SB) and Lower (S2) Salto River, March 1998

	Depth cm	Stream water %	DO mg/l	Cond µS/cm	Fe++ mg/l	SRP µg/l	NH_4^+–N µg/l
Upper Salto							
Surface water	0	100				16	
SA1	10	48	2.4	94	0.06	19	28
	20	33	2.1	57	0.55	19	5
SA2	10	91	6.3	37	0.11	18	3
	20	80	4.4	33	0.08	17	4
SA3	10	74	4.5	36	0.08	15	8
SA4	10	67	4.3	45	0.15	14	4
SA5	10	100	7.0	34	0.70	14	3
SA6	10	47	2.6	42	0.31	17	18
SA7	10	100	6.7	32	0.41	18	7
	20	94	6.2	36	0.07	15	6
SB1	10	12	1.7	317	0.30	19	74
	20	< 1	1.6	560	3.19	206	50
SB2	10	50	5.9	127	0.21	31	10
Lower Salto							
Surface water	0	100				144	8
S2-1	10	1	2.2	553	4.82	477	123
	20	1	2.4	560	4.13	439	118
	30	0	2.1	507	2.55	349	67
S2-2	10	7	2.3	263	0.96	99	39
	20	4	2.0	281	0.84	104	10
	30	4	1.4	268	1.35	163	48
S2-3	10	42	0.7	371	3.16	150	153
	20	12	0.6	363	6.07	303	94
S2-4	10	1	0.8	489	7.99	525	42

(1977) reasoned that SRP losses bear little resemblance to stream flow at Hubbard Brook because background SRP varies annually over one order of magnitude whereas discharge can vary over many orders of magnitude. Taylor et al. (1971) also found no relationship between SRP and discharge in steams draining woodlands in Ohio, USA. McClain et al. (1998) reported that clear correlations between SRP concentration and discharge are rare in undisturbed streams of the Pacific Northwest, USA. They further noted that where correlations have been reported, the relationship was not consistent in time or between studies. In a synthesis of data from 12 streams throughout the world, Meyer et al. (1988) found that in 10 streams with sufficient data, the relationship of discharge to SRP was positive in four, negative in two, and neutral (i.e. SRP did not change with discharge) in four. Only in reaches like Lower Salto, with a concentrated regional P source, was SRP negatively correlated with discharge and only when ENSO data are omitted. Even then discharge explained only a small part of the variation in concentration (Fig. 3A).

The significant TP-discharge relationship observed at all sites when ENSO data were removed presumably resulted from combined particulate and dissolved P mobilization during rising flows. TP concentrations were higher at medium than high flows (Fig. 3B). Rising flows generate successively higher energy environments mobilizing and transporting increasingly heavier particles. However at some point most readily transportable P is in suspension and further discharge results in greater dilution of dissolved P than addition to particulate P. Once mobilized, particulate P remains suspended until retained by some downstream geomorphic feature, or until energy levels decrease sufficiently to permit redeposition (McClain et al. 1998).

Geothermal groundwater input to the Lower Salto increases the concentration of other solutes including magnesium, chloride, potassium, and sulfate in addition to SRP (Pringle et al. 1990). With conservative solute concentration (e.g. Cl) enhanced 16–25 fold between background and geothermal groundwater, mixing models have estimated geothermal groundwater contribution to stream discharge. A two component chemical mixing model was used by Genereux et al. (2002) to estimate regional groundwater input to several streams draining La Selva. End members included a high solute, high-chloride bedrock groundwater and a low-solute hillslope groundwater. They estimated that Lower Salto consisted of ~41% geothermally modified (regional) groundwater during the dry season. This estimated regional groundwater contribution was comparable to our dry season estimate (44%) calculated from monthly discharge-SRP data at Salto 60 and Salto 30 corrected for the contribution from the Pantano tributary (Fig. 5). Our wet season estimate (July–September) was 20%. Genereux et al. 2002) estimated that the Pantano consisted of ~10% regional groundwater, 14% during the dry season and 9% during the wet season.

While the regional groundwater contribution to Salto discharge was large, the regional contribution to SRP load was larger. The monthly contribution from the swamp-forest to downstream loading averaged 85% of SRP export (Fig. 5B). This consistently high contribution to SRP export, despite variable discharge, emphasized the dominance of SRP-rich regional groundwater inputs.

While little is known of the local ENSO impact in 1992, documented environmental shifts at La Selva in 1998–1999 included enhanced litterfall, higher night time temperatures, and a pH drop in unbuffered Upper Salto water (unpublished data). These observations have led to the hypothesis that enhanced decomposition in hyporheic and riparian sediments increased the size of the reducing environment in swamp-forest resulting in SRP release associated with iron reduction. This hypothesis seems reasonable in light of our pore water studies and previously published data on riparian groundwater in the Lower Salto (Pringle and Triska 1991). SRP sorption/desorption determines SRP levels in interstitial waters (Holtan et al. 1988) and is strongly influenced by mineral composition of sediment, especially ferric oxyhydroxides, aluminum oxyhydroxides, calcium compounds, and clay minerals (Enell and Lofgren 1988). A conceptual model of shifts in hyporheic P flux in streams relative to shifting oxic-anoxic conditions and iron oxidation–reduction was also proposed by Hendricks and White (2001).

We observed dramatic differences in DO and ferrous iron between Upper and Lower Salto pore water indicating distinctly different hydrologic and biogeochemical interfaces within the channel. Upper Salto SRP concentrations were low and Rhodamine WT indicated surface water influx to at least 30 cm depth (Table 2). Pore water was typically aerobic and reduced species such as ferrous iron were low except in scarce depositional environments. SRP concentration of pore water approximated that of surface water and local groundwater. These conditions are conducive for SRP retention by formation of iron oxyhydroxides.

In Lower Salto, sub-channel pore water was indicative of a complex hydrologic and geochemical environment resulting from the low channel gradient, fine sediment, and continuous geothermal SRP input. Positive groundwater pressure gradients and fine grain sediments restricted surface water movement into the bed while the low channel gradient promoted deposition of particulate organic matter. This reducing environment can extend to bankside seeps and many meters into riparian groundwater. Pringle and Triska (1991) reported high SRP and low DO concentrations in Lower Salto seeps and groundwater 10–16 m from the channel. High ferrous iron and low DO in Lower Salto pore water and riparian groundwater could promote dissolution of ferric hydroxide–phosphate complexes and result in active P flux to the stream when the interstitial environment becomes more reducing.

Antecedent conditions appear to be critical for inducing SRP transport related to ENSO events. For example, the most recent ENSO occurred 1997–1998 but the high SRP concentrations were recorded in 1998 and early 1999. Discharge in 1998–1999 was similar to the mean annual 5 year record (0.95 m^3/s, Table 2). However discharge during the 5 months prior to elevated SRP concentrations was low averaging 0.63 ± 0.09 m^3/s. Discharge in this 5 month antecedent period was lower than each respective month in the previous year and the following 2 years. SRP gradually released from sediments to pore water and riparian groundwater at ENSO-induced low flows was presumably mobilized by moderate post-ENSO discharge.

Phosphorus concentrations in most La Selva streams, while low relative to the Lower Salto, are high relative to pristine or near pristine streams in the USA, except in the West at sites on volcanic terrain or uplifted marine sediments with enhanced SRP. In the northeast, monthly averages of SRP at Bear Brook, New Hampshire typically vary between 1 and 4 μg/l and have an annual watershed flux of ~0.02 kg/ha year (Meyer and Likens 1979). Phosphorus-limited streams in the southeast USA such as Walker Branch TN (Elwood et al. 1981), or Hugh White Creek, North Carolina, have SRP levels typically 2–5 μg/l (Webster et al. 1991). Pristine streams in the midwest have SRP concentrations of ~4 μg/l in the region of the Great Lakes and 1–3 μg/l in prairie streams not impacted by agriculture. Except for Alaskan tundra, SRP concentrations in the Western streams approach those of the Pantano or Sabalo. These streams are typically located in mountain settings and many drain volcanic areas. SRP concentrations in the range of 5–12 μg-P/L are common. Examples include Mack Creek in the H.J. Andrews Forest, Oregon (Mulholland et al. 2001) and the mixed geologic setting of the Frank Church Wilderness Area in Idaho (Davis and Minshall 1999). In coastal northern California, Little Lost Man Creek drains uplifted marine sediment, which can also contain enhanced P (9–12 μg-P/L; Zellweger et al. 1986). SRP concentrations higher than the Salto have been reported in rivers draining volcanic landscapes in other parts of the world. Reviewing published work, Golterman (1975) noted high phosphate in tropical rivers in Uganda with concentrations of 160 and 305 μg/l.

Enhanced SRP concentrations and P dynamics observed in La Selva streams are probably more common in pristine streams than generally appreciated, especially in western North, Central, and South American streams draining volcanic terrain. SRP-rich groundwater, introduced to streams like the Salto, is a product of underlying geology, regional tectonic activity, and complex groundwater hydrology that enriches some streams, but not others. Enriched and un-enriched streams in close proximity develop distinct long-term patterns of nutrient chemistry, altered by infrequent meteorological events (e.g. ENSO)

Acknowledgements The authors gratefully acknowledge support from National Science Foundation grants DEB 95-28434 and DEB 00-75349, and from the National Research Program, Water Resources, U.S. Geological Survey. We also acknowledge the field assistance of Minor Hildago, La Selva Biological Station.

References

Bothwell ML (1988) Growth rate responses of lotic periphytic diatoms to experimental phosphorus enrichment: the influence of temperature and light. Can J Fish Aquat Sci 45:261–270

Bourgeois WW, Cole DW, Riekerk H, Gessel SP (1972) Geology and soils of comparative ecosystem study areas, Costa Rica. Contribution No. 11, Institute of Forestry Production, University of Washington, 112 pp

Bower CE, Holm-Hansen T (1980) A salicylate-hypochlorite method for determining ammonia in seawater. Can J Fish Aquat Sci 37:794–798

Butturini A, Sabater F (1998) Ammonium and phosphate retention in a Mediterranean stream: hydrologic versus temperature control. J Can Fish Aquatic Sci 55:1938–1945

Davis JC, Minshall GW (1999) Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. Oecologia 119:247–255

D'Angelo DJ, Webster JR, Benefield EF (1991) Mechanisms of stream phosphorus retention: an experimental study. J N Am Benthol Soc 10:225–237

Devito KJ, Dillon PJ, Lazerte BD (1989) Phosphorus and nitrogen retention in five Precambrian shield wetlands. Biogeochemistry 8:185–204

Dorioz JM, Cassell EA, Orand A, Eisenman KG (1998) Phosphorus storage transport and export dynamics in the Foron River watershed. Hydrol Process 12:285–309

Elwood JW, Newbold JD, Trimble AF, Stark RW (1981) The limiting role of phosphorus in a woodland stream ecosystem: effects of P-enrichment on leaf decomposition and primary producers. Ecology 62:146–158

Enell M, Lofgren S (1988) Phosphorus in interstitial water: methods and dynamics. Hydrobiologia 170:103–132

Genereux DP, Wood SJ, Pringle CM (2002) Chemical tracing of interbasin groundwater transfer in the lowland rainforest of Costa Rica. J Hydrol 258:163–178

Golterman HL (1975) Chapter 2: Chemistry. In: Whitton BA (eds) River ecology. University of California Press, Berkeley CA, pp 39–80

Gonsiorczyk T, Koschel R (1997) Variations of phosphorus release from sediments in stratified lakes. Water Air Soil Pollut 99:427–434

Hall RO Jr, Bernhardt ES, Likens GE (2002) Relating nutrient uptake with transient storage in forested mountain streams. Limnol Oceanogr 47:255–265

Hart BT, Freeman P, McKelvie ID (1992) Whole stream phosphorus release studies: variation in uptake length with initial phosphorus concentration. Hydrobiologia 235/236:573–584

Hendricks SP, White DS (2001) Stream and groundwater influences on phosphorus biogeochemistry. In: Jones JB, Mulholland PJ (eds) Streams and groundwaters. Academic Press, San Diego, pp 221–236

Hill AR (1982) Phosphorus and major cation mass balances for two rivers during summer flows. Freshwat Biol 12:293–304

Holtan H Kamp-Nielsen L, Stuanes AO (1988) Phosphorus in soil, water and sediment: an overview. Hydrobiologia 170:19–34

Kleeberg A, Schlungbaum G (1993) In situ phosphorus release experiments in the Warnow River (Mecklenburg, northern Germany). Hydrobiologia 253:263–274

Likens GE, Bormann H, Pierce RS, Eaton JS, Johnson NM (1977) Biogeochemistry of forested ecosystems. Springer-Verlag, New York

Looney SW, Gulledge TR (1985) Use of the correlation coefficient with normal probability plots. Am Statist 39:75–79

McClain ME, Bilby RE, Triska FJ (1998) Nutrient cycles and responses to disturbance. In: Naiman RJ and Bilby RE (eds) River management and ecology: lessons from the Pacific Coastal Ecoregion. Springer-Verlag, New York

Meals DW, Levine SN, Wang D, Hoffmann JP, Cassell EA, Drake JC, Pelton DK, Galarneau HM, Brown AB (1999) Retention of spike additions of soluble phosphorus in a northern eutrophic stream. J N Am Benthol Soc 18:185–198

Meyer JL (1979) The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem. Limnol Oceanogr 24:365–375

Meyer JL, Likens GE (1979) Transport and transformation of phosphorus in a forest stream ecosystem. Ecology 60: 1255–1269

Meyer JL, McDowell WH, Bott TL, Elwood JW, Ishizaki C, Melack JM, Peckarsky BL, Peterson BJ, Rublee PA (1988) Elemental dynamics in streams. J N Am Benthol Soc 7:410–432

Mulholland PJ, Fellows CS, Tank JL, Grimm NB, Webster JR, Hamilton SK, Marti E, Ashkenas L, Bowden WB, Dodds WK, McDowell WH, Paul MJ, Peterson BJ. (2001) Inter-biome comparison of factors controlling stream metabolism. Freshwat Biol 46:1503–1517

Mulholland PJ, Marzolf ER, Webster JR, Hart DR, Hendricks SP (1997) Evidence that hyporheic zones increase heterotrophic metabolism and phosphorus uptake in forest streams. Limnol Oceanogr 42:443–451

Mulholland PJ, Newbold JD, Elwood JW, Webster JR (1985) Phosphorus spiraling in a woodland stream: seasonal variations. Ecology 66:1012–1023

Munn NL, Meyer JL (1990) Habitat specific solute retention in two small streams: an intersite comparison. Ecology 71:2069–2082

Newbold JD, Elwood JW, O'Neill RV, Van Winkle W (1981) Measuring nutrient spiraling in streams. Can J Fish Aquat Sci 38:860–863

Pringle CM, Triska FJ (1991) Effects of geothermal groundwater on nutrient dynamics of a lowland Costa Rican stream. Ecology 72:951–965

Pringle CM, Triska FJ, Browder G (1990) Spatial variation in basic chemistry of streams draining a volcanic landscape on Costa Rica's Atlantic slope. Hydrobiologia 206:73–85

Pringle CM, Rowe GK, Triska FJ, Fernandez JF, West J (1993) Landscape linkages between geothermal activity and solute composition and ecological response in surface waters draining the Atlantic slope of Costa Rica. Limnol and Oceanogr 38:753–774

Ramirez A, Pringle CM, Molina L (2003) Effects of stream phosphorus levels on microbial respiration. Freshwat Biol 48:88–97

Rosemond AD, Pringle CM, Ramirez A, Paul MJ, Meyer JL (2002) Landscape variation in phosphorus concentration and effects on detritus – based tropical streams. Limnol Oceanogr 47:278–289

Stookey LL (1970) Ferrozene – a new spectrophotometric method for iron. Anal Chem 42:779–781

Taylor AW, Edwards WM, Simpson EC (1971) Nutrients in streams draining woodland and farmland near Coshocton, Ohio. Wat Resour Res 7:81–89

Triska FJ, Kennedy VC, Avanzino RJ, Zellweger GW, Bencala KE (1989) Retention and transport of nutrients in a third order stream in northwestern California: hyporheic processes. Ecology 70:1893–1905

Webster JR, D'Angelo DJ, Peters GT (1991) Nitrate and phosphate uptake in streams at Coweta Hydrologic Laboratory. Verh Internat Verein Limnol 24:1681–1686

Zellweger GW, Kennedy VC, Bencala KE, Avanzino RJ, Jackman AP, Triska FJ (1986) Data on the solute concentration within the subsurface flows of Little Lost Man Creek in response to a transport experiment, Redwood National Park, northwest California. U.S. Geological Survey, Open File Report OFR 86–403WI 28 p