

Soluble reactive phosphorus (SRP) transport and retention in tropical, rain forest streams draining a volcanic landscape in Costa Rica: in situ SRP amendment to streams and laboratory studies

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Abstract Soluble reactive phosphorus (SRP) transport/retention was determined in two rain forest streams (Salto, Pantano) draining La Selva Biological Station, Costa Rica. There, SRP levels can be naturally high due to groundwater enriched by geothermal activity within the surficially dormant volcanic landscape, and subsequently discharged at ambient temperature. Combined field and laboratory approaches simulated high but natural geothermal SRP input with the objective of estimating the magnitude of amended SRP retention within high and low SRP settings and determining the underlying mechanisms of SRP retention. First, we examined short-term SRP retention/transport using combined SRP-conservative tracer additions at high natural in situ concentrations. Second, we attempted to observe a DIN response during SRP amendment as an indicator of biological uptake. Third, we determined SRP release/retention using laboratory sediment assays under control and biologically inhibited conditions. Short-term in-situ tracer-SRP additions

indicated retention in both naturally high and low SRP reaches. Retention of added SRP mass in Upper Salto (low SRP) was 17% ($7.5 \text{ mg-P m}^{-2} \text{ h}^{-1}$), and 20% ($10.9 \text{ mg-P m}^{-2} \text{ h}^{-1}$) in Lower Salto (high SRP). No DIN response in either nitrate or ammonium was observed. Laboratory assays using fresh Lower Salto sediments indicated SRP release ($15.4 \pm 5.9 \text{ } \mu\text{g-P g dry wt.}^{-1} \text{ h}^{-1}$), when incubated in filter sterilized Salto water at ambient P concentration, but retention when incubated in filter sterilized river water amended to $2.0 \text{ mg SRP l}^{-1}$ ($233.2 \pm 5.8 \text{ } \mu\text{g-P g dry wt.}^{-1} \text{ h}^{-1}$). SRP uptake/release was similar in both control- and biocide-treated sediments indicating predominantly abiotic retention. High SRP retention even under biologically saturated conditions, absence of a DIN response to amendment, patterns of desorption following amendment, and similar patterns of retention and release under control and biologically inhibited conditions all indicated predominantly abiotic P flux.

Keywords Costa Rica · Nutrients · Phosphorus · Rain forest · SRP · Streams · TP · Tropical

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Introduction

Within fluvial environments, phosphorus uptake and transport is regulated by numerous biotic and

abiotic factors including assimilation, pH, temperature, sorption/desorption, redox, discharge and concentration. Historically, discharge and concentration impacts on biotic assimilation have dominated fluvial studies. Most research has occurred in oligotrophic, temperate settings, and under assumed P limitation relative to the stoichiometry of nutrient assimilating biota (Redfield ratio). At low background soluble reactive phosphorus (SRP) and low discharge, Meyer and Likens (1979) found that biotic assimilation dominated retention (processing mode) while at high discharge biotic impact was minimal (transport mode). Past work, typically conducted at processing mode, may overestimate biotic SRP retention.

Earlier studies (e.g. Newbold et al. 1981; Elwood et al. 1981) demonstrated high biotic retention using radiotracer P additions kept below biotic saturation. Webster et al. (1991) and Mulholland (1992) reported similar results from other oligotrophic streams using low SRP amendment. Mulholland et al. (1990) compared uptake length at low ($5\text{--}12\ \mu\text{g-P l}^{-1}$) vs. high ($84\text{--}163\ \mu\text{g-P l}^{-1}$) SRP concentration. At low concentration ($<5\ \mu\text{g-P l}^{-1}$), biological processes regulated retention, but increasing concentration eventually saturated biotic P uptake until abiotic processes dominated. Long-term SRP release at low, but potentially higher than uptake saturation ($10\text{--}30\ \mu\text{g-P l}^{-1}$), can increase periphyton biomass, alter community structure (Bothwell 1989; Horner et al. 1990; Stockner and Shortreed 1978) and enhance biomass saturating SRP concentration (Bothwell 1988). Horner et al. (1990) reported saturating SRP levels at $15\ \mu\text{g-P l}^{-1}$ in laboratory periphyton, while a review by Welch et al. (1998), indicated saturation from $7\ \mu\text{g-P l}^{-1}$ to $22\ \mu\text{g-P l}^{-1}$ in Pacific Northwest streams. Thus SRP concentrations $<20\ \mu\text{g-P l}^{-1}$ likely favor biotic retention, while abiotic mechanisms increasingly dominate as concentration increases.

Separating biotic SRP assimilation from abiotic factors, such as sorption and precipitation, is difficult to distinguish in situ without radioisotopes. However, Davis and Minshall (1999) reported uptake N:P ratios of 15.5 in Pioneer Creek and 12.2 in Cliff Creek, two wilderness streams, to indicate dominance of biotic uptake. The authors

cautioned that while biotic retention appeared to dominate SRP retention, further investigation of physicochemical processes was warranted.

Comparable data on SRP retention, and biotic vs. abiotic controls are scarce from tropical settings. Here we examine SRP retention and transport in two tropical, rainforest streams spanning a regionally representative range in natural SRP levels resulting from their volcanic lithology and variable input of regional, geothermally modified groundwater. Tropical streams are advantageous as natural laboratories because they control several key environmental variables. For example, critical seasonal factors in temperate watersheds such as light and temperature are nearly constant ($\sim 12\text{ h}$ light–dark cycles, $\sim 24^\circ\text{C}$) annually. Our objective was to examine SRP retention in tropical stream reaches with naturally high and low background concentration and determine the underlying retention mechanisms (biotic vs. abiotic). We used three approaches. First, we examined in situ SRP retention/transport using short-term SRP plus conservative tracer injections at levels, simulating enhanced, natural input. Second, we attempted to determine the biotic role in SRP retention by examining DIN response to SRP amendment (*sensu* Davis and Minshall 1999). Third, we examined biotic vs. abiotic SRP retention and release in laboratory sediment assays under biologically inhibited and control conditions.

Study area

The study site was Quebrada Salto and a tributary the Pantano, located near the eastern boundary of La Selva Biological Station, a 3,300-ha reserve in Costa Rica ($10^\circ 26'\text{ N}$, $84^\circ 01'\text{ W}$, Fig. 1). The watershed is located at the base of Volcan Barva, which is surface-inactive, but can geothermally modify stream chemistry (Pringle et al. 1993). Average annual rainfall is $\sim 4\text{ m}$. The wettest months are typically July–September and the driest February–April. Our studies were conducted during the dry season.

There were two low-SRP sites (Upper Salto, $12\ \mu\text{g-P l}^{-1}$, upland; Pantano, $16\ \mu\text{g-P l}^{-1}$, lowland), which are near to slightly above biotic P saturation.

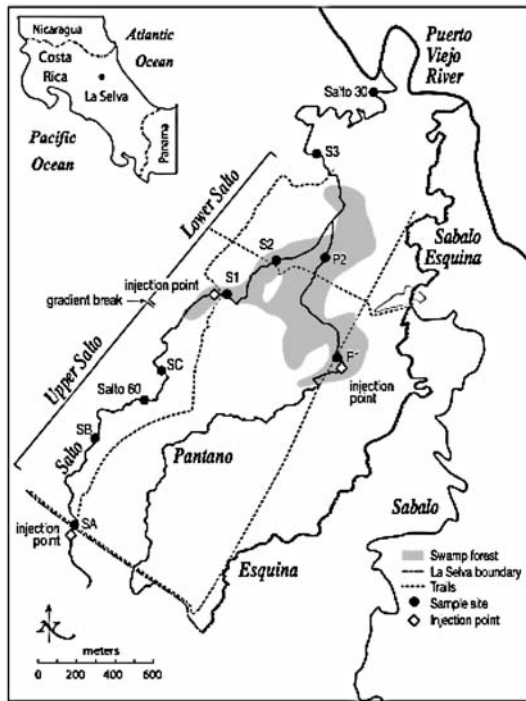


Fig. 1 Map of the Salto watershed at La Selva Biological Station and its location in Costa Rica. Sample locations in Upper Salto are designated SA–SC, in Lower Salto S1–S3, and on the Pantano, P1–P2. Sites of long-term SRP sampling are Salto 60, Salto 30 and P2

The third, a high SRP reach, Lower Salto ($\sim 120 \mu\text{g-P l}^{-1}$), is impacted by interbasin transfer of high-SRP waters (Genereux et al. 2002; Triska et al. 2006) and is not P limited.

Quebrada Salto is an ungauged third order stream that drops from 300 m to ~ 36 m above mean sea level where it joins the Puerto Viejo River. The base of this 1,120-ha watershed is located in La Selva, while the upper two-thirds lie in Braulio Carrillo National Park. More than 95% of the watershed is roadless, primary, tropical rainforest (Pringle et al. 1990, 1993). The streams are shaded by dense multilayered canopy which limits light and periphyton development.

Upper Salto drains a basalt formation believed to be of Quaternary origin. The stream gradient is 0.10, with a bed of large boulders with sand interstices. Lower Salto drains swamp-forest composed primarily of terraces of alluvial sands and gravels of volcanic origin (Bourgeois et al. 1972). The Salto main stem flows along the

eastern boundary of Esquina Andesite, the younger of two lava flows at La Selva (indicated as Sabalo lava flow on a map in Pringle et al. 1990). P-rich springs emerge near the edge of this formation as the channel crosses the gradient break (Fig. 1) and enters lowland swamp-forest (Pringle and Triska 1991). In Lower Salto, forest soils are poorly drained, blue-gray and blackish-brown silts and clays. Soils are slightly acidic (pH 4.0–5.2), have an organic content to $\sim 25\%$, and fragile structure (Bourgeois et al. 1972). A high water table makes access difficult. The Pantano is an ungauged, low gradient (0.06) tributary contributing $\sim 10\%$ to Salto discharge. It drains swamp-forest and is low in SRP. Pantano sediments are also fine-grained sands, silts, and clays.

Methods

Field studies

The study consisted of four in situ SRP-Rhodamine WT (RWT) co-injections. The target SRP concentration, $475 \mu\text{g-P l}^{-1}$, approximated the highest, natural concentration of regional springs (Agrio stream, Poas; Pringle et al. 1993). Although subject to photo-degradation and sorption, RWT was found to be basically conservative at reach lengths used in this study (Jackman et al. 2006). RWT was detectable at single ppb levels and its fluorometric response was highly linear ($r = 0.99$). Injection sites were located at the head of turbulent reaches to enhance mixing and sample sites were also located in riffle areas. RWT and SRP were injected separately to the right and left of center channel to prevent complexation. Reach lengths were as long as possible (1,050 m, 1,330 m) and injection time as short as possible to reduce errors associated with growth, cellular release and mineralization, but reach plateau concentration. Hand sampling was completed before dusk since some sites could not be located after dark and nocturnal reptile populations presented a safety hazard. Dark samples were collected using automated sample collectors (ISCO). Studies were conducted during non-rain days, which

often followed night rains. If significant rain occurred during an injection, it was aborted.

The Upper Salto injection site was upstream of the reserve boundary ~4 km into the rain forest. Downstream station names, locations, background nitrogen and phosphorus levels and distance between for all three reaches are provided on Fig. 1 and Table 1.

RWT and SRP (NaH_2PO_4) were injected continuously to Lower Salto from 1012 h to 1515 h, February 27, 1992 when the RWT pump failed. SRP addition continued for an additional 2 h. We amended Upper Salto for ~9 h, 1020 h–1910 h, March 5, 1992. A slug injection was conducted in the Pantano March 9, 1992 (1530 h), and repeated as a four hour continuous injection, 0915–1320 h, March 9, 1998.

RWT fluorescence was determined in unfiltered samples using a Turner Model 10 fluorometer the evening of sample collection at room temperature (~24°C). All samples and standards for an particular injection were run at the same time and temperature. Discharge, normalized concentration and nominal travel time (the interval required to attain half the plateau concentration) were determined (Triska et al. 1989). Mean background-corrected plateau concentration was estimated between the times, and for the number of samples, indicated on Table 2. Plateau concentrations were calculated using the last samples before cutoff. Increasing discharge

between stations indicated groundwater and tributary spring input.

Proportional SRP recovery was calculated for each downstream station. SRP and RWT samples were corrected for background concentration and normalized as a proportion of the plateau concentration at the most upstream station (Triska et al. 1989, 1993). Normalized RWT is equivalent to predicted SRP assuming conservative transport. SRP retention was estimated as the difference between normalized RWT and normalized SRP at plateau concentration. Retention included both sorption and biological uptake.

Sample collection and analysis

Samples were collected using a peristaltic pump (Geopump) in a zone of active flow. Sampling frequency varied from 2 to 5 min on the rise at the most upstream station, to hourly at plateau concentration. SRP samples were filtered in line (0.45 μm membrane), acidified, refrigerated, returned to Menlo Park, CA, USA, and analyzed as quickly as possible. The maximum period between collection and analysis was six weeks. SRP was analyzed on a Technicon Autoanalyzer II using the molybdenum blue (Technicon Industrial Method 155-71 W) method. SRP from the Pantano 1998 injection were analyzed at La Selva also using a molybdenum blue method. A second filtered, frozen sample was taken to monitor

Table 1 Background physical-chemical conditions in stream reaches experimentally amended with SRP

Location	Reach length (m)	Discharge ($\text{l s}^{-1} \pm \text{sd}$)	SRP ($\mu\text{g l}^{-1} \pm \text{sd}$)	$\text{NO}_3^- \text{-N}$ ($\mu\text{g l}^{-1} \pm \text{sd}$)	$\text{NH}_4^+ \text{-N}$ ($\mu\text{g l}^{-1} \pm \text{sd}$)	Sediments	Gradient	Nominal travel time (min)	Load (mg s^{-1})
Upper Salto									
SA	50	260 ± 8	13 ± 1	252 ± 1	6 ± 1	Boulder-Sand	0.10	5	3.4
SB	600	315 ± 7	14 ± 1	237 ± 1	6 ± 1	Boulder-Sand	0.10	140	4.4
SC	1,050	356 ± 6	15 ± 1	234 ± 1	5 ± 1	Boulder-Sand	0.07	175	5.3
Lower Salto									
S1	40	385 ± 18	127 ± 2	176 ± 1	4 ± 1	Sand-Silt	0.07	4	48.9
S2	460	444 ± 13	116 ± 1	171 ± 6	8 ± 2	Sand-Silt	0.07	144	51.5
S3	1,330	588 ± 24	101 ± 2	162 ± 1	13 ± 2	Sand-Silt	0.06	298	59.3
Pantano (1998)									
P1	30	25 ± 3	12	ns	ns	Sand-Silt	0.06	9 ^a	0.3
P2	660	50 ± 2	16 ± 3	ns	ns	Sand-Silt	0.06	280 ^a	0.8
Pantano (1992)									
P1	25	28	13	142 ± 1	12 ± 2	Sand-Silt	0.06	6 ^a	0.4
P2	650	69	12 ± 6	137 ± 3	ns	Sand-Silt	0.06	176 ^a	0.8

For all sites the injection point is zero meters

^a First arrival of tracer, ns = no sample

Table 2 Background corrected plateau concentration of amended SRP ($\mu\text{g-P l}^{-1}$), normalized RWT and SRP, and loads during experimental amendments to three rainforest streams

Site	Plateau SRP		<i>n</i>	Normalized concentration (%)		Retention% (mg s^{-1})
	Concentration	Time		RWT	SRP	
Upper Salto						
SA	469 \pm 10	1210–1910	8	97 \pm 4	97 \pm 2	0
SB	315 \pm 5	1800–2100	4	80 \pm 2	65 \pm 1	15
SC	266 \pm 7	1535–1824	6	70 \pm 1	55 \pm 2	0
Lower Salto						
S1	387 \pm 20	1044–1240	5	97 \pm 3	96 \pm 4	1
S2	346 \pm 16	1215–1500	9	86 \pm 2	82 \pm 5	3
S3	212 \pm 9	1600–1824	6	61 \pm 1	47 \pm 2	11
Pantano (1998)						
P1	417 \pm 5	0945–1100	5	100 \pm 2	90 \pm 10	
P2	71 \pm 10	1610–1830	11	50 \pm 3	15 \pm 2	

nitrate plus nitrite and ammonia responses to SRP addition. For each sample time RWT, SRP, NO_3^- and NH_4^+ samples were taken. Nitrate + nitrite was determined on a Technicon Autoanalyzer II by cadmium reduction (Technicon Industrial Method 158-71 W), and ammonium-N by a phenol-hypochlorite (Technicon Industrial Method 154-71 W). Methodological precision for nitrate-N and phosphate-P is $\pm 1 \mu\text{g l}^{-1}$ to $100 \mu\text{g l}^{-1}$ and 1% above. Ammonium-N is $\pm 2 \mu\text{g l}^{-1}$ to $100 \mu\text{g l}^{-1}$ and 2% above. Nitrate and ammonium samples collected before the first arrival of RWT were used to determine mean background concentration \pm standard deviation. Nitrate and ammonium samples collected after the arrival of RWT were averaged \pm standard deviation to determine DIN response to SRP amendment.

Mass balance and areal uptake of amended SRP

Mass balance and areal uptake of amended SRP were calculated for each injection. The total injected SRP mass passing each station was the integrated sum of transported SRP mass in each sample interval. Amended SRP mass in each sample interval = mean background corrected SRP concentration ($\mu\text{g l}^{-1}$) \times discharge (l s^{-1}) \times time (s). Areal retention of amended SRP was determined by upstream–downstream difference in mass divided by estimated channel area. Low flow channel width in Upper Salto

varied from 7 m to 9 m total, but low flows were confined to passages between large boulders reducing the wetted channel width to ~ 6.75 m. By the head of Lower Salto channel width was narrower (5.5 m), but wetted area extended bank to bank, and the water was deeper. By Site S2 on Lower Salto the low flow channel widened again to 6.5 m. We used an estimated channel width of 6.75 m for Upper Salto and Lower Salto through S2. At the base of the study reach (S3) channel width was 8.0 m at low flow. Low flow Pantano channel width was 1.9 m. Estimated channel areas are indicated in Table 3.

Laboratory sediment assays

One hour laboratory assays of SRP uptake/release were undertaken using freshly collected S2 sediment in filter-sterilized stream water. Triplicate assays included an untreated control and three modes of biotic inhibition: (1) autoclaving (121°C , 20 min), which guaranteed sterility but disrupted sediment geochemistry, (2) HgCl_2 (40 mg l^{-1}) a potent biocide, and (3) CP (carbonyl cyanide *m*-chlorophenyl hydrozone, 7.5 M), an inhibitor of biological phosphate uptake and cellular P release.

Sediment was wet sieved to <2.0 mm, and 6 ml was added to 50 ml of filter-sterilized stream water in 125-ml Erlenmeyer flasks. Reagents were then added to achieve the final treatments indicated above. Flasks were shaken briefly and

Table 3 Mass balance and areal retention of SRP injected into the Salto and Pantano

Location	Duration (h)	Input (g)	Total retention		Retention (mg)			Area (m ²)
			g	%	m	m ²	m ² h ⁻¹	
Upper Salto								
SA	9.8	4,072	–	–	–	–	–	–
SB	–	3,465	607	15	933	–	–	–
SC	11.3	3,364	708	2	224	79.9	7.5	8,865
Lower Salto								
S1	7.3	3,918	–	–	–	–	–	–
S2	–	3,828	90	2	180	–	–	–
S3	8.5	3,099	819	18	878	86.2	10.9	9,496
P1	4	168	–	–	–	–	–	–
P2	9.3	53	115	68	176	68.0	–	1,190
Pantano (1992)								
P1	slug	205	–	–	–	–	–	–
P2	–	155	50	24	80	42.0	–	1,190

permitted to settle. Ten ml of water was pipetted from each flask into a 12 ml centrifuge tube and spun at 2,000g for 2 min. The sample was decanted, acidified, refrigerated and initial SRP concentration was determined. The remaining flask contents were shaken for 5 s every 10 min for 1 h at 25°C then re-sampled as above. Sediments were dried (80°C), and retention was determined as P uptake g dry wt. sediment⁻¹ h⁻¹. In a second experiment, sediments were treated identically except that SRP was amended to 2.0 mg l⁻¹.

Results

Short-term studies: RWT-SRP co-injections

Upper Salto

RWT-SRP co-injection revealed discharge gain and SRP retention along the reach. Upper Salto discharge increased 27% (Table 1). The longitudinal gain in discharge between SA and SB was 0.10 l s⁻¹ m⁻¹ and 0.09 l s⁻¹ m⁻¹ between SB and SC. Background SRP concentration (samples collected prior to tracer arrival) were low and stable. Background SRP load (discharge × concentration) increased proportional to discharge. Nominal travel time was 175 min.

Normalized SRP concentration during the in situ amendment was less than predicted by RWT indicating retention (Fig. 2a). The normalized plateau concentration exhibited a slight rise, indicating decreasing discharge during the experiment. At plateau, mean, normalized, background corrected SRP indicated 15% retention for the reach (Table 2) and 17% by mass balance (Table 3). Such small differences reflect uncertainty associated with calculation of RWT and SRP plateau values and differences between them. While the approaches were slightly different, the overall within-reach pattern of SRP retention was similar. High retention occurred between SA and SB and low retention between SB and SC (Table 2). The pattern of retention is visually observable by comparing the normalized SRP curves for SB and SC to SA (Fig. 2a). Tailing concentration during the die away indicated SRP release as concentration returned to background levels. Areal reach retention was estimated at 7.5 mg m⁻² h⁻¹ (Table 3).

Lower Salto

The Lower Salto reach was ~30% longer, lower gradient, and nominal travel time was almost twice as long, which potentially enhanced sediment contact (Table 1). Discharge increased by approximately 200 l s⁻¹ (S1–S3) of which the Pantano contributed ~70 l s⁻¹. Discharge

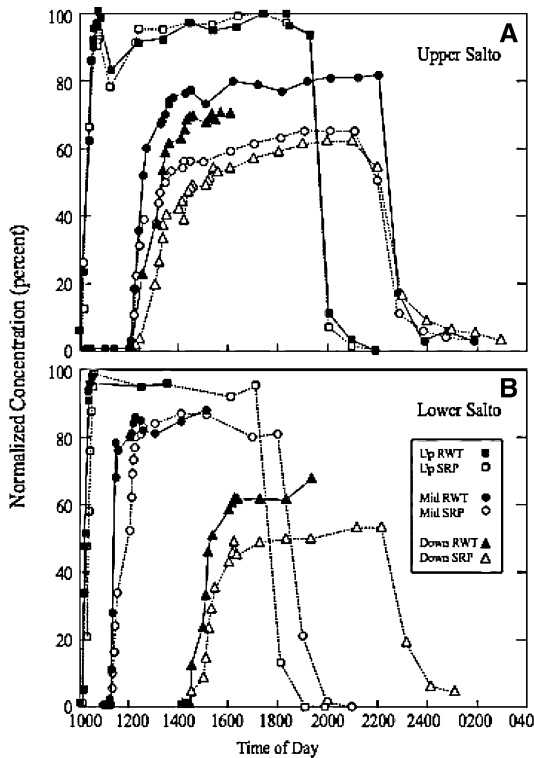


Fig. 2 Normalized concentration (%) of Rhodamine WT and SRP during co-injection studies along the Salto River. **(A)** Upper Salto; solid symbols: Rhodamine WT; open symbols: SRP; SA (up): squares; SB (midreach): circles; SC (down): triangles. **(B)** Lower Salto, solid symbols: Rhodamine WT; open symbols: SRP; S1 (up): squares; S2 (midreach): circles; S3 down: triangles

increased 18% ($0.14 \text{ l s}^{-1} \text{ m}^{-1}$) between S1 and S2, and an additional 14% ($0.08 \text{ l s}^{-1} \text{ m}^{-1}$) between S2 and S3 excluding the Pantano tributary. Including the Pantano tributary, discharge increased ~34% S1–S3.

Background SRP concentration in Lower Salto (injection site, $129 \pm 4 \mu\text{g-P l}^{-1}$) was nearly an order of magnitude higher than Upper Salto. Background concentration decreased and SRP load increased in a downstream direction (Table 1).

During the in situ amendment of SRP normalized, background and dilution corrected plateau concentration indicated 15% SRP retention by normalized concentration (Table 2) but 20% by mass balance calculation (Table 3) Both approaches indicated that most retention occurred between S2 and S3. Estimated SRP

retention between S1 and S2 were 3% and 2% respectively for the normalized concentration and mass balance approaches (Tables 2, 3) Between S2 and S3 estimated SRP retention was 11% and 18%. During the die away normalized SRP indicated greater tailing at S3, than S1 or S2 where normalized concentration dropped quickly to zero (Fig. 2b). Tailing in Lower Salto was also less than Upper Salto sites.

Pantano

The Pantano slug injection indicated high SRP retention and dispersion during transport (Fig. 3a). SRP retention was estimated at ~24% of amended SRP based on mass balance (Table 3). Although the spike was instantaneous, there was already significant dispersion at P1,

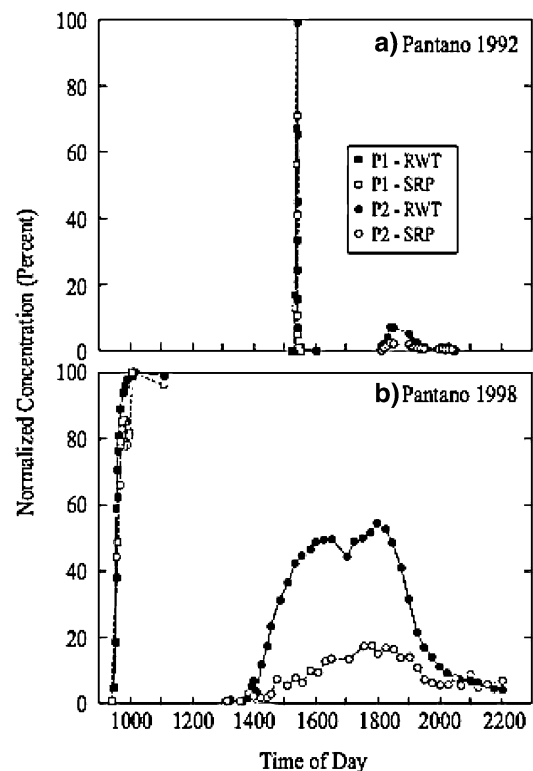


Fig. 3 Normalized concentration (%) of Rhodamine WT and SRP co-injected into the Pantano tributary. **(A)** slug injection; solid symbols: Rhodamine WT; open symbols: SRP; squares: P1; circles: P2. **(B)** 4 h continuous injection; solid symbols: Rhodamine WT; open symbols: SRP; squares: P1; circles: P2

~20 m downstream. The initial rise occurred after 6 min. First arrival of dye was substituted for nominal travel time since the slug injection lacked a plateau. Concentration was $46 \mu\text{g l}^{-1}$ (3 times background) in the final sample 32 min later. High dispersion resulted from slower velocity and long travel time (176 min, P2). At P2 RWT persisted in the last sample, 150 min after first arrival.

The Pantano amendment was repeated in 1998 as a 4-h injection (Fig. 3b). Discharge entering the reach (25 l s^{-1}) was slightly lower than the previous injection and discharge exiting P2 was significantly lower (50 l s^{-1}). Estimated SRP retention by normalized concentration was 25% similar to that of mass balance in the previous slug injection. Using the mass balance approach SRP retention was estimated at 68%. This is a high over estimate since normalized SRP concentration was well above background when the last sample was taken at P2 and the tail indicated a very slow decline (Fig. 3b).

DIN response to SRP amendment

Upper Salto DIN was dominated by nitrate (Table 1). On the date of SRP addition to Upper Salto, nitrate concentration in samples prior to injectate arrival decreased with distance downstream while ammonium-N concentration was nearly constant.

During the amendment DIN (nitrate-N and ammonium-N) was sampled with each RWT and SRP sample. Neither nitrate nor ammonium-N changed during SRP rise, plateau or fall. Mean nitrate concentrations were 251 ± 3 , 233 ± 7 and $231 \pm 5 \mu\text{g-N l}^{-1}$ at SA–SC respectively. The suite of samples collected after RWT arrival was nearly identical to background (Table 1). Ammonium concentrations for the suite of samples taken during the amendment were 6 ± 1 , 5 ± 1 and $5 \pm 1 \mu\text{g-N l}^{-1}$ at SA–SC respectively and also nearly identical to background levels.

Background DIN concentration in Lower Salto was lower than Upper Salto and also dominated by nitrate (Table 1). Like Upper Salto, nitrate-N concentration decreased and load increased going downstream prior to amendment. The Pantano both contributed to DIN load and diluted

concentration between S2 and S3. Lower Salto background ammonium-N concentration increased from $4.0 \pm 1 \mu\text{g-N l}^{-1}$ at S1 to $13 \pm 2 \mu\text{g-N l}^{-1}$ at S3.

During SRP amendment there was no indication of a nitrate or ammonium response during SRP rise, plateau or fall. Over the full suite of samples taken during the injection after RWT arrival mean nitrate concentrations were 174 ± 7 , 169 ± 3 , and $161 \pm 3 \mu\text{g-N l}^{-1}$ and ammoniums were 6 ± 2 , 9 ± 2 and $13 \pm 3 \mu\text{g-N l}^{-1}$ at S1–S3, respectively.

During the slug SRP injection to the Pantano neither nitrate nor ammonium responded to the SRP spike at either P1 or P2. Nitrate averaged $141 \pm 1 \mu\text{g-N l}^{-1}$ and ammonium $12 \pm 2 \mu\text{g-N l}^{-1}$ at P1. Nitrate averaged 131 ± 1 and ammonium averaged $14 \pm 6 \mu\text{g-N l}^{-1}$ at P2, similar to background levels. Ammonium concentrations during the SRP injection were more variable at P2 than at other sites, but it was not related to SRP rise or fall.

Sediment assays

Flask studies using Lower Salto sediment (S2) indicated immediate SRP release when shaken with filter-sterilized stream water (Table 4). During the brief set up period SRP increased significantly in the control and all treatment waters, which continued for an additional hour. Mean SRP release was greatest in the control, but similar to the Hg and CP treatments. Mean SRP release for all flasks, except autoclaved, was $15.4 \pm 5.9 \mu\text{g-P g dry wt.}^{-1} \text{ h}^{-1}$ and was statistically significant at the $P < 0.05$ level (Wilcoxon–Mann–Whitney Rank Sum Test). Autoclaving, involving both heat and pressure, enhanced SRP release. This result was statistically significantly different than the control and other two treatments. Two levels of P binding were indicated, a fraction readily desorbed by contact with background water, and a large tightly bound component released by heat and pressure. The latter fraction likely included phosphorus in the deeper matrix of the sediment particle and possibly digestion of the organic coatings and sediment-associated particulate organics. Significant release

Table 4 Background corrected SRP retention release in laboratory assays (triplicate) of Quebrada Salto sediments (Site S2) and (A) exposed to filter sterilized river water atbackground SRP ($148 \mu\text{g l}^{-1}$) or (B) exposed to filter sterilized water amended to 2.0 mg-P l^{-1} SRP for 1 h

Treatment	A		B	
	SRP release/ flask ($\mu\text{g-P l}^{-1}$)	SRP release ($\mu\text{g-P g}^{-1}$ dry wt. sed.)	SRP retention/ flask ($\mu\text{g-P l}^{-1}$)	SRP retention ($\mu\text{g-P g}^{-1}$ dry wt. sed.)
Control				
1	154	20.0	1,863	233
2	103	13.4	1,825	228
3	193	25.1	1,865	242
	$\bar{x} = 19.5 \pm 5.9 \text{ s.d.}$		$\bar{x} = 234 \pm 7.1 \text{ s.d.}$	
CP				
1	124	15.7	1,855	229
2	110	14.7	1,839	229
3	82	10.7	1,831	229
	$\bar{x} = 13.7 \pm 2.6 \text{ s.d.}$		$\bar{x} = 229 \pm 0 \text{ s.d.}$	
HgCl ₂				
1	49	6.6	1,845	239
2	85	11.5	1,811	241
3	163	21.7	1,812	229
	$\bar{x} = 13.3 \pm 7.7 \text{ s.d.}$		$\bar{x} = 236 \pm 6.4 \text{ s.d.}$	
Autoclaved				
1	1,390	182.9	1,219	160
2	1,414	186.5	1,335	146
3	1,258	163.4	1,075	138
	$\bar{x} = 177.6 \pm 12.4 \text{ s.d.}$		$\bar{x} = 148 \pm 11.1 \text{ s.d.}$	

of SRP at background concentration indicates that sediment SRP stored in naturally high zones could be released when transported to low SRP environments.

High SRP treatment ($\sim 2,000 \mu\text{g l}^{-1}$) produced opposite results (Table 4b). At the time of the initial sample, SRP concentration was already drastically reduced in all treatments. The additional hour of incubation increased P retention. By the conclusion of the experiment mean SRP approached background levels. Mean retention/g dry wt. between the control and Hg and CP treatments was not significantly different statistically. SRP retention for all nine flasks, excluding autoclaved was $233.2 \pm 5.8 \mu\text{g g dry wt.}^{-1} \text{ h}^{-1}$. Similar retention despite biotic inhibition indicated minor biotic SRP retention. As with SRP release, the control, Hg and CP treatments were not significantly different statistically, but the autoclaved treatment retained significantly less SRP. Thus at high SRP levels, sediments readily retained SRP from water, but released it at low concentration.

Discussion

Background SRP concentrations at Upper Salto (low SRP) stations were nearly equal pre-amendment (Table 1), and loads increased proportionally with discharge, indicating that input–output processes were essentially balanced. Long-term concentration (1997–2002) has varied over a narrow range ($10\text{--}30 \mu\text{g l}^{-1}$) despite order of magnitude shifts in discharge (Triska et al. 2006).

Background SRP concentration at Lower Salto was an order of magnitude higher (Table 1) and loads increased in a downstream direction indicating significant input, although concentration decreased. Long-term SRP concentration in Lower Salto is negatively correlated with discharge, essentially constituting a localized SRP source diluted by streamflow (Triska et al. 2006).

SRP was retained in all reaches during the amendment, although retention was not uniform within each reach. Upper Salto retention was greatest from the injection point to SB and declined approaching the gradient break (Tables 2, 3). Lower

Salto retention was least between the injection point and S2, and was greatest S2–S3. Some retention was transient as indicated by a long tails to the SRP die away curves (SA–SC, S3), indicating SRP release upon return to background levels (Fig. 2).

Areal estimates of amended SRP retention (Table 3) were higher than typical published rates. Hill (1982) estimated P retention of $3.3 \text{ mg-P m}^{-2} \text{ h}^{-1}$ and $2.0 \text{ mg-P m}^{-2} \text{ h}^{-1}$ at two reaches downstream of a sewerage treatment plant continuously discharging SRP at $300\text{--}700 \mu\text{g l}^{-1}$, within the range of our amendment. They are also higher than most published amendment studies including: the La Platte River of $4.3 \text{ mg-P m}^{-2} \text{ h}^{-1}$ (Meals et al. 1999), or amendments to two Idaho USA streams, Cliff Creek ($4.9 \text{ mg-P m}^{-2} \text{ h}^{-1}$) and Pioneer Creek ($2.2 \text{ mg-P m}^{-2} \text{ h}^{-1}$, Davis and Minshall 1999). Calculated retention also exceeded the $<1.0 \text{ mg-P m}^{-2} \text{ h}^{-1}$ characteristic of SRP amendments to oligotrophic settings (Munn and Meyer 1990; Hart et al. 1992).

SRP retention is based on a combination underlying factors including sediment geology, magnitude of concentration increase, extent of hyporheic exchange and/or sediment grain size. Geologically, Munn and Meyer (1990) reported higher SRP retention in a volcanic western USA stream than a granitic eastern USA stream under similar SRP amendment. While SRP concentration was raised to similar levels in both Salto reaches, it amounted to a 34-fold increase at SA, but only a 3-fold increase at S1. We expected greater SRP retention in Upper than Lower Salto due to its lower background concentration, similar lithology and proportionally larger concentration increase. However, estimated retention based on mass balance was slightly higher downstream (17% Upper, 20% Lower), perhaps reflecting variable access to sediment surfaces, grain size and/or saturation of sediment sorption sites. Greater surface water exchange in the bed in Upper than Lower Salto (Triska et al. 2006) should have enhanced sediment contact and thus SRP retention. However, a recent hyporheic analysis of storage zone cross-sectional area (the hyporheic surrogate A_s/A , Solute Transport Workshop 1990) estimated less potential storage in Upper than Lower Salto (Jackman et al. 2006). This result was

presumably due to the large component of boulder substrates in Upper Salto which confines storage to sandy interstices, and greater pool and backwater habitat in Lower Salto. Mulholland et al. (1997) found that hyporheic exchange promoted SRP retention when dominated by biota, whereas Hall et al. (2002) found that it was not important when SRP retention was predominantly abiotic. While we did not analyze grain size in this study, previous work indicated that bank soils in Upper Salto are dominated by sand, whereas soils on both east and west banks Lower Salto are dominated by silts and clays (Pringle and Triska 1991). Meyer and Likens (1979) found that P sorption to Bear Brook sediments increased with decreasing grain size and that the silt fraction adsorbed 3.4 times more dissolved P than the sand fraction. Both Meyer (1979) and Hill (1982) suggested that differences in sorption capacity within drainages are more likely regulated by differences in sediment size than biotic uptake. The most likely basis for the observed pattern of higher SRP retention in Lower Salto (S2–S3) was longer reach length, lower gradient, finer sediment grain size (greater surface area) than Upper Salto and its depositional environment all of which would promote sediment contact.

If biotic SRP assimilation was significant some DIN response would have been expected. $\text{NO}_3 + \text{PO}_4$ co-injection to two Idaho USA streams, resulted in an uptake N/P ratio of 12.2 in Cliff Creek and 15.5 in Pioneer Creek (Davis and Minshall 1999). DIN was readily available at all Salto/Pantano sites (Table 1), but measurable uptake response was not detected during the amendment. Passive biotic P retention (not requiring N) is possible at sites with high periphyton, either as some form of luxury uptake or sorption to the polysaccharide matrix (Meals et al. 1999, citing Hoffmann et al. 1996; Lock and John 1979), but was unlikely in the heavily shaded Salto. Biotic P retention associated with organic matter decomposition is a significant SRP sink in many small, oligotrophic, forested streams (Gregory 1978; Elwood et al. 1981; Mulholland et al. 1985; D'Angelo et al. 1991), either as assimilation into biomass or abiotic sorption to organic matter. The absence of a DIN response

argues that most decomposition-associated retention was abiotic.

Dominance of abiotic retention was supported by the laboratory release and uptake studies. Control sediments released slightly more P under background conditions, but were similar to (Hg) treated or (CP) inhibited (Table 4). In the 1 h sorption experiment at 2.0 mg-P l^{-1} , retention was immediate and nearly equivalent despite treatment. Most retention occurred in the first few minutes and was complete within 1 h. Meyer (1979), reported 93% SRP retention within 5 min for silty sediments and 19% for sandy sediments. Meals et al. (1999) reported ~50% of total adsorption within 1 h in La Platte River sediments. Meyer and Likens (1979) found minimal differences between control- and Hg-inhibited sediments after 8 h, in Bear Brook, NH sediments, indicating a dominance of abiotic retention.

Although biotic uptake minimally impacted amended SRP retention, sediment biogeochemistry can shift redox conditions that regulate formation and dissolution of ferric hydroxide-phosphate complexes, and thus impact SRP flux indirectly. Pore water is largely oxidizing in Upper Salto and reducing in Lower Salto (Triska et al. 2006). Gunnars and Bolmqvist (1997) studying alternating oxic-anoxic conditions in lake sediments found that P flux was largely mediated by scavenging and subsequent dissolution of colloidal ferric oxyhydroxides in freshwaters.

Alternate SRP retention/release, depending on concentration, observed in both field and the lab studies, provides a potential mechanism for in situ transient SRP storage until ambient P concentration falls below some equilibrium point triggering release. Both Reddy et al. (1996) and Meals et al. (1999) reported SRP sorption to stream sediments at high concentrations followed by release at lower concentration. Sorption/release is strongly influenced by mineral composition especially ferric oxyhydroxides, aluminum oxyhydroxides calcium compounds and clay minerals (Enell and Lofgren 1988), which largely determine SRP levels in interstitial waters (Holtan et al. 1988). Our brief amendment studies revealed similar retention-release properties.

While amended SRP retention/transport from the watershed was primarily abiotic, biotic response to natural SRP amendment including enhanced organic matter decomposition and secondary production have been observed along natural SRP gradients at La Selva. Rosemond et al. (2002), in a leaf pack study encompassing a wide range of SRP concentration ($5\text{--}230 \text{ } \mu\text{g-P l}^{-1}$), reported that SRP was the most important explanatory variable in leaf decay rate and invertebrate biomass in the lowest P streams, with saturation occurring at $25\text{--}50 \text{ } \mu\text{g-P l}^{-1}$. Although experimental results are sometimes equivocal at nearly saturating concentrations, they suggest that where/when P concentrations are low ($<10 \text{ } \mu\text{g-P l}^{-1}$) the detrital food web is likely controlled from lower trophic levels. Ramirez et al. (2003) similarly reported litter respiration (*Ficus* sp.) positively correlated to SRP concentration in a suite of streams ($5\text{--}350 \text{ } \mu\text{g-P l}^{-1}$), with saturation occurring at $\sim 15 \text{ } \mu\text{g-P l}^{-1}$. Ramirez (2001) also found increased litter respiration during enrichment of a low-P stream at La Selva. Biotic interactions such as enhanced decomposition may minimally impact loads, but could impact SRP flux indirectly through redox shifts in bed sediments. Underlying mechanisms which regulate SRP flux likely shift along the Quebrada Salto river corridor with changes in gradient, SRP input, sediment grain size, organic matter deposition and extent of advective exchange between surface water and pore water.

Control of SRP retention at levels examined in this study was primarily abiotic. This conclusion is based on high SRP retention with simultaneous absence of DIN uptake in both high and low SRP settings. Laboratory assays using biological inhibitors also indicated no evidence of a significant biotic role in SRP uptake and release. Absence of biotic assimilation sufficient to impact DIN in situ may be related to dense canopy which prevents periphyton development, and approximately saturating background conditions, even in low SRP streams, due to their volcanic lithology. The dominance of abiotic processes in SRP retention is likely similar in other high SRP streams draining volcanic terrain, even outside the tropics. Although overall SRP flux was primarily abiotic in Quebrada Salto, other biologic studies at the site indicate that SRP is still critical

in ecosystem function including organic matter decomposition which can shift the sediment redox environment and indirectly interact with abiotic processes to impact SRP flux.

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