Dissolved Inorganic Nitrogen Composition, Transformation, Retention, and Transport in Naturally Phosphate-Rich and Phosphate-Poor Tropical Streams

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The composition, transformation, and transport of dissolved inorganic nitrogen (DIN) was compared in waters associated with two lowland streams in Costa Rica. The Salto River is enriched by geothermal-based soluble reactive phosphorus (SRP), which raises the concentration up to 200 µg/L whereas Pantano Creek, an unimpacted tributary, has an SRP concentration <10 µg/L. Ammonium concentration in springs adjacent to the Salto and Pantano was typically greater than channel water (13 of 22 locations) whereas nitrate concentration was less (20 of 22 locations). Ground waters were typically high in ammonium relative to nitrate whereas channel waters were high in nitrate relative to ammonium. Sediment slurry studies indicated nitrification potential in two sediment types, firm clay (3.34 µg $N \cdot cm^{-3} \cdot d^{-1}$) and uncompacted organic-rich sediment (1.76 µg $N \cdot cm^{-3} \cdot d^{-1}$). Ammonium and nitrate amendments to each stream separately resulted in nitrate concentrations in excess of that expected after correction for dilution using a conservative tracer. SRP concentration was not affected by DIN amendment to either stream. SRP concentration in the Pantano appeared to be regulated by abiotic sediment exchange reactions whereas DIN composition and concentration were regulated by a combination of biotic and abiotic processes.

On a comparé la composition, la transformation et le transport de l'azote inorganique dissous (AID) trouvé dans de l'eau associée à deux cours d'eau qui s'écoulent dans des basses terres du Costa Rica. Les eaux de la rivière Salto sont enrichies par du phosphore réactif soluble d'origine géothermale (PRS), qui porte la concentration à un maximum de 200 µg/L, alors que le ruisseau Pantano, un tributaire qui n'est pas soumis à cet effet, a une concentration de PRS inférieure à 10 µg/L. La concentration d'ammoniac dans des sources contiguës à la Salto et au Pantano est ordinairement supérieure à celle de l'eau du chenal (13 stations sur 22), alors que la concentration d'azote est inférieure (20 stations sur 22). L'eau souterraine est normalement riche en ammonium par rapport à la teneur en nitrate, alors que l'eau dans les chenaux est riche en nitrate comparativement à la teneur en ammonium. Des études faites sur une bouillie de sédiments ont montré qu'il existe un potentiel de nitrification de deux types de sédiments, une argile compacte ($3,34$ µg $N \cdot cm^{-3} \cdot d^{-1}$) et un sédiment non compact et riche en matières organiques ($1,76$ µg $N \cdot cm^{-3} \cdot d^{-1}$). Des amendments pratiqués avec l'ammonium et le nitrate dans chaque cours d'eau séparément ont conduit à l'obtention de nitrate en concentration supérieure aux résultats attendus, après correction pour la dilution au moyen d'un traceur persistant. Peu importe le cours d'eau, la concentration en PRS n'a pas varié par suite d'un traitement à l'AID. La concentration en PRS du Pantano paraissait être régulée par des réactions abiotiques d'échange avec les sédiments alors que la composition et la concentration en AID semblaient régulées par une combinaison de mécanismes biotiques et abiotiques.

Knowledge of factors that regulate nitrogen flux in streams is integral to our understanding of lotic structure and function (Meyer et al. 1988). Studies over the last decade have greatly enhanced our knowledge of nitrogen transport in a variety of lotic systems both temperate and tropical (Vitousek et al. 1979; Meybeck 1982; Newbold et al. 1983; Grimm and Fisher 1984, 1989; Lesack et al. 1984; Sebetich et al. 1984; Richey et al. 1985; Grimm 1987; Saunders and Lewis 1988; Triska et al. 1989a; Munn and Meyer 1990; Webster et al. 1991). The combination of abiotic conditions that influence nitrogen flux in tropical streams can be quite different from their temperate counterparts. For instance, tropical lowland rain-forests on Costa Rica's Atlantic slope receive high annual precipitation (4 m) and lack seasonality in temperature, precipitation, and detrital input. Streams draining primary forest are also severely light limited due to dense multistratal canopies.

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While some information exists regarding nitrogen transport in New World tropical streams draining highly weathered soils of the Amazon (Lewis 1986), virtually nothing is known about nitrogen flux in streams of Central America. Central American landscapes can be of geologically recent volcanic origin (10^2–10^3 yr) and are often underlain by active geothermal systems. Geothermal activity along the volcanic spine of Costa Rica plays a major role in determining patterns of the solute chemistry in surface waters with respect to phosphorus, silica, and major cations and anions such as SO_4, Cl, Mg, and Ca (Pringle et al. 1993).

The Salto River, a stream draining Costa Rica's Atlantic slope, receives groundwater inputs of geothermally based soluble reactive phosphorus (SRP) at a gradient break where the stream drains lowland swamp forest (Pringle et al. 1990; Pringle and Triska 1991). The geothermal origin of solute-rich groundwater entering the stream is indicated by high solute levels (e.g. Cl, Mg, Ca, HCO_3, and SO_4) rather than thermal properties, since temperature cools to that of ambient groundwater during subsurface transport (Pringle 1991; Pringle et al. 1993). SRP input is nearly constant at numerous springs and seeps located in the channel and along the banks; however, channel waters of the Salto range between 50 and 200 μg P/L depending on the magnitude of dilution by recent storm runoff. In contrast, the Pantano tributary is unmodified by geothermal activity, with SRP concentrations typically <10 μg/L.

Nutrient cycles are biologically coupled based on the element ratio required for the production of biomass. Atomic ratios of N/P > 16 can indicate phosphorus limitation of primary production whereas N/P < 16 can indicate nitrogen limitation (Redfield et al. 1963). The input of SRP to the Salto causes the dissolved inorganic nitrogen (DIN)/SRP ratio within the drainage to vary from as low as 3 in the main stem Salto to as high as 55 in the Pantano tributary under base flow conditions. This wide range in N/P ratios raises the question: does high, natural SRP enrichment influence the retention, transport, and transformation of DIN in otherwise similar lowland, tropical streams? We addressed this question in three phases: first, we characterized ammonium levels in springs, seeps, groundwater, and channel water of both streams and evaluated these levels with respect to NO_2 + NO_3-N and SRP data presented in previous studies (Pringle 1991; Pringle and Triska 1991); second, upon finding high ammonium levels in groundwater and high nitrate in stream water of both streams, we assayed two types of channel sediment for nitrification potential using laboratory slurry procedures; third, we separately added ammonium and nitrate to stream reaches to examine the fate of DIN under both high- and low-SRP regimes. We hypothesized effective retention and transformation of ammonium in both streams due to low background concentrations, preference of ammonium over nitrate for biotic uptake, and potential for nitrification in channel sediments. We also hypothesized depletion of background SRP in the Pantano during ammonium amendment due to low SRP concentration, enhanced biotic demand, and lack of significant SRP enrichment from geothermal sources along the reach. Finally, we hypothesized conservative transport of amended nitrate in both streams due to high background concentrations.

Study Site

This study was conducted at La Selva Biological Station, a 3300-ha reserve in northern Costa Rica (10°26′N, 84°01′W)

(Fig. 1), located in the transition between the Caribbean lowland plains and the steep foothills of the central mountain range.

The station receives an average annual rainfall of 4 m. Historically, the wettest months are June–August and the driest February–April; however, some years lack a definite dry season.

The Salto River is an ungauged third-order stream that drops from 300 to ~36 m above mean sea level where it drains into the Puerto Viejo River. The base of the watershed is located in La Selva Biological Reserve and the upper two thirds is within Braulio Carrillo National Park, a corridor of land comprising part of the last continuous altitudinal transect of tropical rainforest spanning elevations from sea level to 2900 m that remains on the Atlantic Slope of Central America. More than 95% of the Salto watershed is in primary, tropical rainforest (Pringle et al. 1985).

The lower Salto watershed, where the experimental reaches were located, is composed primarily of terraces of alluvial clays, sands, and gravels of volcanic origin (Bourgeois et al. 1972) whereas the upper watershed is a basalt formation believed to be of Quaternary origin. The Salto mainstem runs along the eastern boundary of the younger (Esquina) of the two lava flows at La Selva (Pringle and Triska 1991). Phosphate-rich springs emerge near the edge of this formation at numerous locations (Pringle 1991). The Esquina flow overlies the older Salto flow and is andesitic, dating from the early Pleistocene. The Salto flow, which is andesitic/basaltic, is believed to have been deposited in the middle of the early Pleistocene (Sollins et al. 1993). The low-phosphate Pantano tributary drains the Salto lava flow.

A previous study of 24 seeps and springs along the Pantano and Salto indicated that SRP concentrations in springs along the Salto ranged from 2 to 260 μg/L but only 5–15 μg/L along the Pantano (Pringle 1991). Eight springs along the Salto exceeded 200 μg/L, the maximum SRP level observed in channel water. Springs of both high and low SRP concentration were found along the Salto, but only low-SRP waters were observed along the Pantano.

The study reach was located in a swamp forest close to the break in landform. Drainage throughout the site is impeded by the bedrock threshold of the low foothills. Soils in the swamp forest (Fig. 1) are poorly drained, blue–grey, and blackish-brown silts and clays. They are slightly acidic (pH 4.0–5.2) and have a relatively high organic content (~25%) and fragile structure (Bourgeois et al. 1972). Bankside soils in upland reaches of both streams are classified as lithic humitropepts, but within the lowland swamp forest, they are typic, histic, or lithic tropaquepts (Sancho and Mata 1987).

Methods

Ammonium, total DIN concentration, and N/P ratio were determined for surface water (Salto) and 24 bankside springs along the Salto and Pantano (Fig. 1). SRP and NO_2 + NO_3 data from these sites were previously reported in Pringle (1991). The samples, collected September 1988, were filtered in the field (0.45-μm membrane) into new polyethylene bottles rinsed three times with sample. Ammonium was analyzed at the biological station's laboratory using a phenolhypochlorite method (Solorzano 1969). Surface and groundwater chemistry were also compared along four well transects (April 1987). Three transects were on the Salto (upper swamp and east and west banks of midswamp) and one on the Pantano (Fig. 1). Each

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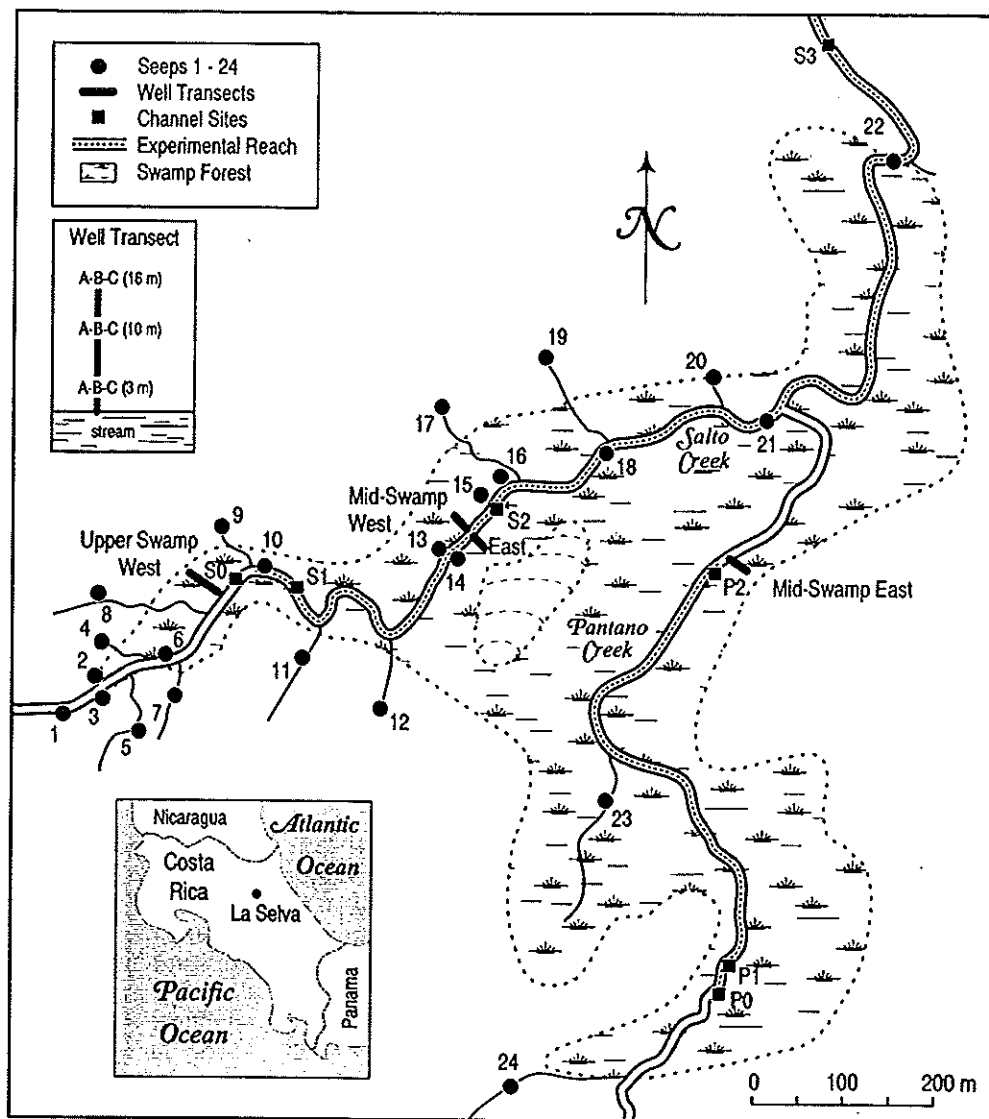*Can. J. Fish. Aquat. Sci., Vol. 50, 1993*

FIG. 1. Map of the Salto and Pantano watershed in Costa Rica showing the location of bankside seeps, groundwater well transects, labeled either west or east, and arrangement of wells along a typical transect. Sample sites for whole-system amendments are labeled S0–S3 along the Salto and P0–P2 along the Pantano (figure modified from Pringle 1991).

transect consisted of two or three well arrays at distances of 3, 10, and 16 m perpendicular to the channel and 1–2 m into the water table. Each array consisted of three wells (A–C) with a minimum of 3 m spacing between wells. Transects were aligned along the anticipated groundwater flow path. Wells were drilled with a power auger and lined with polyvinyl pipe (10 cm) to which a 0.006 wellpoint (slot width of ~130 μm) was attached to the base. Each well was topped with a removable cap. One day prior to sampling, the wells were pumped free of standing water and allowed to refill. The samples were collected using a peristaltic pump connected to an inline filter (0.45-μm membrane filters, Millipore or Gelman metricel) into new polyethylene bottles. Three successive aliquots of sample water were passed through the filter and used to rinse the bottle (as above) before the fourth was saved as the sample. This sampling protocol was also used for water collected in the nutrient amendment studies. The samples were returned to the laboratory and immediately frozen for subsequent analysis.

Nitrification potential of sediments from the Salto was assayed in a 48-h laboratory study (August 1988). Two dominant sediment types, a firm clay and an uncompacted, soft, sandy, organic-rich sediment, were assayed. Six 250-mL flasks of each sediment type contained 20 mL of sediment, 120 mL of stream water, ammonium amended to 1.0 mM as $(NH_4)_2SO_4$, and phosphate to 1.0 mM as K_2HPO_4. Then duplicate flasks of each sediment type were inhibited with nitrapyrin (an inhibitor of ammonium oxidation (10 μL of 22% solution/flask)), heat killed, or left untreated. Water was sampled (10 mL) at 0, 5, 24, and 48 h. Samples were passed through a preleached 25-mm Gelman acrodisc filter (0.45 μm), refrigerated, and analyzed for nitrate within 24 h. Between the taking of samples, flasks were cotton stoppered and shaken to maintain aerobic conditions.

DIN retention–transport was determined under naturally enriched and low-SRP conditions using whole-stream tracer injection techniques (Triska et al. 1989a, 1989b, 1990; Solute

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TABLE 1. Dates and background conditions of whole-system manipulations to Pantano and Salto creeks.

Site	Treatment (target concentration)	Date (1989)	Injection time	Background concentration			
				NO₃ (μg N/L)	NH₄ (μg N/L)	PO₄ (μg P/L)	N/P
Salto	Ammonium (100 μg N/L)	Feb. 19	09:00–13:00	188	7	119	3
Pantano	Ammonium (100 μg N/L)	Feb. 20	09:30–12:30	134	18	6	55
Salto	Nitrate (400 μg N/L)	Feb. 22	08:00–11:00	187	6	124	3
Pantano	Nitrate (400μg N/L)	Feb. 24	08:00–11:00	125	22	6	55

Transport Workshop 1990) during February 1989. The method involved injection of a conservative tracer in conjunction with a reactive solute. The tracer was used to estimate hydrologic parameters such as discharge and dilution whereas the biologically reactive solute was used to estimate biological uptake and sorption after correction for hydrologic properties of the channel. Biotically reactive solutes (BRS) included ammonium (NH₄Cl) and nitrate (NaNO₃). The tracer was rhodamine WT, a dye commonly used as a hydrologic tracer (Wilson et al. 1984). One solute and the tracer were mixed in a polyethylene tank and pumped into the center of the channel using an FMI (Fluid Metering, Inc.) battery-operated pump (5–58 mL/min capacity). Amendment periods lasted 3–4 h (Table 1). In the Pantano, water samples were collected ~3 m upstream of the injection point (site P0) and at two downstream sites, P1 and P2, located 40 and 600 m downstream of the injection point (Fig. 1). In the Salto, four stations were sampled: ~3 m upstream of the injection point (S0) and three downstream sites, S1 (50 m), S2 (460 m), and S3 (1330 m). Dates and details of each injection are described in Table 1. Nutrient samples were frozen and transported to the U.S. Geological Survey in Menlo Park, California, for analysis. Ambient fluorescence and fluorescence produced by rhodamine WT amendments were determined in unfiltered samples using a Turner III fluorometer immediately upon return to La Selva Biological Station's laboratory. Fractional recovery of amended BRS was calculated for each downstream station by correcting for dilution with the rhodamine WT data:

$$\text{BRS calculated} = \text{BRS}_{up} + \frac{[\text{BRS}_t]}{[\text{Rh}_t]} \cdot [\text{Rh}_d - \text{Rh}_{up}]$$

$$\text{BRS measured} = \text{BRS}_d$$

$$\text{Fraction recovered} = \frac{\text{BRS measured}}{\text{BRS calculated}}$$

where BRS = biologically reactive solute concentration, Rh = rhodamine WT concentration, up = upstream concentration, d = downstream concentration, and t = tank concentration. The difference between median calculated and measured plateau concentrations was compared using a t-test on the signed ranks (Iman and Conover 1983).

Nitrate, ammonium, and SRP in samples collected during the amendment studies were measured on a Technicon Autoanalyzer II as follows: Nitrate-(includes nitrite) by cadmium reduction (Technicon Industrial Method No. 158-71 W, December 1972) and SRP by a molybdenum-blue method (Technicon Industrial Method No. 155-71 W, January 1973). Analytical precision was about 1 μg/L for nitrate nitrogen and SRP below 100 μg/L. At higher levels, SRP and nitrate precision was about 1% of the reported value. The precision of the SRP and nitrate methods was estimated by thawing, analyzing, and refreezing three reference samples repeatedly over a 5-12-mo period. Ammonium-nitrogen was analyzed by a phenol-hypochlorite method (Technicon Industrial Method No. 154-71 W, February 1973). Ammonium precision was about 2 μg/L at all levels encountered in this study. Although no reference-sample study was conducted for the ammonium method, the calibration precision as measured by linear-regression analysis, was approximately the same as that of the other two methods. The standard deviation of the ammonium analysis was thus roughly estimated to be <2 μg N/L for concentrations <120 μg N/L.

Results

Synoptic Sampling

The DIN concentration of seeps and springs ranged from 79 to 213 μg/L and, with one exception (Site 13), nitrate exceeded ammonium concentration (Table 2). At 13 of the 22 Salto locations, ammonium in seeps exceeded that in channel water. Ammonium levels were lowest in seeps and springs of the upper swamp (e.g. Sites 1–5) and highest at midswamp locations (Sites 13–15). At 18 of 22 sites, nitrate levels were lower in seeps than in channel water. With the exception of Site 9 on the Salto and Site 23 on the Pantano, DIN/SRP was <16, indicating SRP sufficiency for biotic production.

Groundwater wells within arrays often exhibited high variation in nutrient concentration (Table 3). However, nutrient concentrations in groundwater and stream water and between transects were sufficiently different, such that distinct trends in nutrient concentration were readily observed. For example, SRP in Pantano groundwater was lower than in Salto groundwater, and SRP in groundwater along the west bank of the Salto was lower than in comparable sites on the east bank. The lowest ammonium concentrations were found in groundwaters of the upper swamp. Ammonium exceeded nitrate in 19 of the 27 groundwater wells, and six of the eight exceptions were in the upper swamp where SRP levels were also low. Groundwater ammonium levels greatly exceeded channel concentrations in the midswamp Salto and the 3-m wells of the Pantano. Groundwater ammonium levels generally decreased with distance from the channel. Nitrate in groundwater was always less than in channel water. A general pattern observed in the synoptic sampling was that ammonium concentration decreased (groundwater > seep water or channel water) whereas nitrate concentration increased (groundwater < seep water < channel water) in both streams.

Sediment Nitrification Potential

The high ammonium concentration in groundwater, intermediate concentration in seep water, and low concentration in

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TABLE 2. SRP, nitrate, ammonium and DIN concentrations (µg/L) and DIN/SRP by atoms in seep and spring waters along the banks of Salto and Pantano creeks and in the channel, August 1988. The site numbers correspond to Fig. 1. SRP and nitrite plus nitrate data from Pringle (1991).

Site	SRP	$NO_2 + NO_3$-N	NH_4-N	DIN	DIN/SRP
Salto					
Upper swamp					
West bank					
1	260	80	2	82	0.7
2	231	55	24	79	0.8
4	208	72	18	90	1.0
6	60	115	64	179	6.6
8	32	55	27	82	5.7
9	2	137	20	157	174.4
10	62	110	18	128	4.6
East bank					
3	57	194	15	209	8.1
5	233	121	12	133	1.3
7	158	171	42	213	3.0
11	34	105	16	121	8.1
Midswamp					
West bank					
13	77	94	122	216	6.2
15	33	82	48	130	8.8
16	64	107	24	131	4.5
17	259	47	40	87	0.7
19	106	53	22	75	1.6
20	25	84	50	134	11.91
East bank					
12	219	74	27	101	1.0
14	222	87	50	137	1.4
18	241	57	30	87	0.8
21	27	50	46	96	7.9
22	66	54	53	107	3.6
Upper Swamp					
Streamwater	51	137	27	164	7.1
Pantano					
Upper swamp					
West bank					
23	<5	212	N/A	N/A	94
24	15	38	N/A	N/A	5.6

channel water suggested that nitrification may occur during subsurface and channel transport. To assay for nitrification potential the two sediment types described earlier were collected from the geothermally modified reach of the Salto where high nutrient levels minimized nutrient limitation. Slurries from both sediment types exhibited nitrate increase, and duplicate flasks had nearly identical rates of production (Fig. 2). Nitrate production with the firmer clay substratum ($3.34 \ \mu gN \cdot cm^{-3} \cdot d^{-1}$) was nearly twice that of uncompacted organic-rich sediments ($1.76 \ \mu g \ N \cdot cm^{-3} \cdot d^{-1}$). Both heat killing and nitrapyrin effectively curtailed nitrate production.

Hydrologic Tracer

Although our whole-system amendments were conducted during the dry season, precipitation was common, particularly at night. As a result of the Salto's larger watershed area and the timing of precipitation, discharge varied between experiments in the Salto but not in the Pantano (Table 4). Rhodamine WT dilution indicated that discharge at the downstream station of the Salto (S3) was 544 L/s during the ammonium amendment and 841 L/s during the nitrate amendment. The Pantano

contributed only 35 L/s, less than 10% of the total flow calculated at S3. This is a minimum estimate because the base of the experimental reach, where discharge was calculated, was a significant distance upstream of the confluence (Fig. 1). Discharge within the experimental reach in the Salto increased downstream by 216 L/s on February 19 and by 421 L/s on February 22. This increase, while heavily dependent on recent runoff, also reflected the contribution of seeps, springs, and groundwater inputs. The capacity for nutrient retention was related to both the size of the reach (width and length) and the potential contact time with channel sediments. High discharge reduced the nominal travel time for nutrient transport by 40 min between the two experiments in the Salto whereas travel times were nearly identical for the Pantano experiments.

Ammonium Injection

Amendment into the Pantano raised the ammonium concentration to approximately 100 µg N/L. Measured median plateau concentration at P1 was 104 µg N/L between 09:54 and 12:32 (Fig. 3; Table 5). The median plateau concentration downstream (P2) between 14:40 and 16:00 was 42 µg N/L. The

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TABLE 3. Dissolved inorganic nitrogen and phosphorus concentrations (μg/L) during a synoptic sampling of groundwater wells, bankside seeps, and channel water, April 1987. Each datum is a mean of duplicate samples. Well names and locations are according to Fig. 1 NS = no sampling. Table modified from Pringle and Triska (1991).

	Salto							Pantano Midswamp East bank	
	Midswamp								
	Upper swamp West bank		West bank			East bank			
	3 m	10 m	3 m	10 m	16 m	3 m	10 m	3 m	10 m
Phosphate									
Well									
A	15	75	30	7	12	96	99	7	15
B	37	39	78	75	14	183	93	4	6
C	24	43	15	88	1	235	19	4	3
Seep	20		200			227		NS	
Channel	127		139					20	
Ammonium									
Well									
A	11	14	527	357	215	18	10	685	26
B	13	11	212	537	165	22	27	947	52
C	22	11	324	167	213	28	18	140	120
Seep	22		12			11		NS	
Channel	NS		15					50	
Nitrate									
Well									
A	13	63	5	3	3	4	18	15	88
B	28	66	13	16	7	2	10	6	2
C	47	113	6	25	2	2	3	3	5
Seep	78		120			136		NS	
Channel	167		165					193	

TABLE 4. Estimates of discharge and nominal travel time in experimental reaches of the Salto and Pantano creeks.

	Salto			Pantano	
Date (1989)	Discharge (L/s)	Nominal travel time (min)	Date	Discharge (L/s)	Nominal travel time (min)
Feb. 19			Feb. 20		
S1	328	20	P1	21.7	12
S2	392	85	P2	35	240
S3	544	310			
Feb. 22			Feb. 24		
S1	420	<10	P1	21.1	15
S2	573	50	P2	36.9	230
S3	841	270			

measured concentration was significantly lower than that calculated by rhodamine dilution (95% confidence limits) at both P1 (15.0 μg N/L) and P2 (39 μg N/L) (Table 5). Under plateau conditions, only 36% of upstream ammonium was recovered at P2, indicating significant retention during transport.

Nitrate concentration rose as the ammonium pulse was transported down the Pantano (Fig. 4). Prior to injection, nitrate concentration at P2 averaged 133 ± 3 μg N/L (±SD) but rose to 151 ± 5 μg N/L at the ammonium plateau concentration. The maximum nitrate concentration was 155 μg N/L. The nitrate production of approximately 20 μg/L accounted for approximately 50% of the 39 μg N/L difference between measured and calculated ammonium concentration at P2. The rise, peak, and fall of nitrate concentration lagged that of ammonium
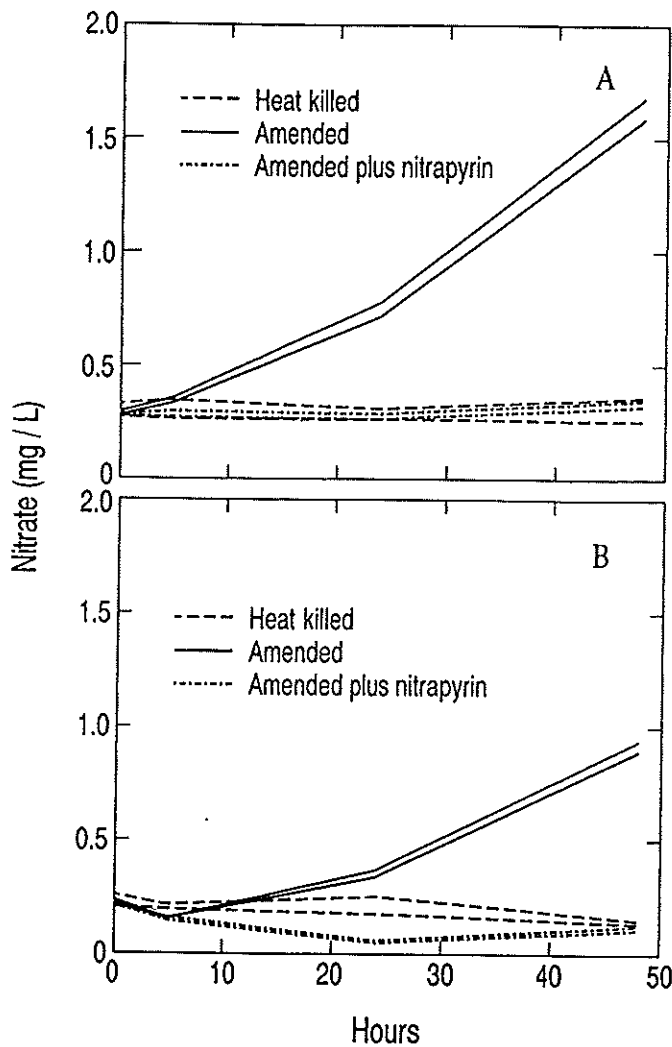
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FIG. 2. Nitrate production in (A) clay sediment and (B) organic-rich sediment slurries in response to 1.0 mM ammonium and phosphate amendment.
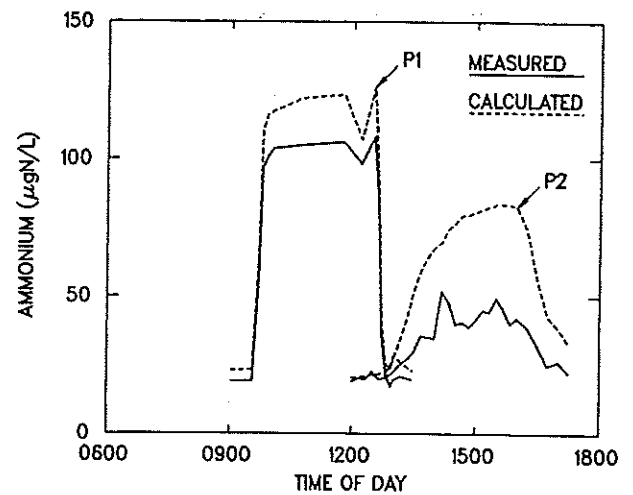

FIG. 3. Comparison of measured concentration of ammonium to that calculated from coinjected rhodamine WT to correct for dilution–dispersion during a whole-system amendment to a reach of Pantano Creek.
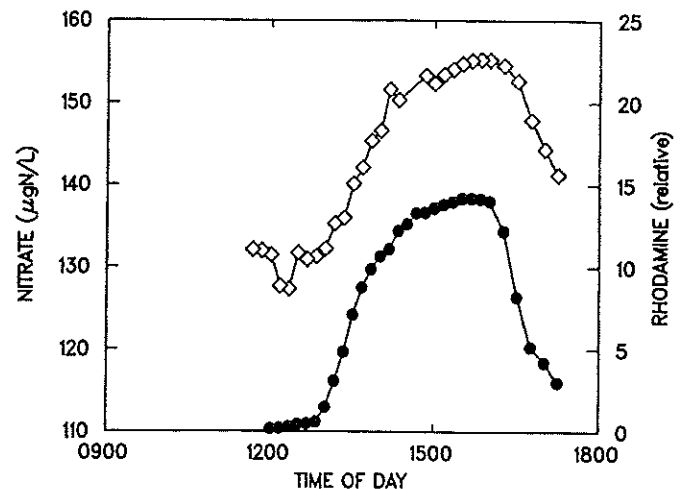

FIG. 4. Timing of nitrate concentration increase (open symbols) at Pantano site P2 in response to ammonium plus tracer amendment as indicated by the conservative tracer plume (solid symbols).

by approximately 30 min. Background SRP was 6.2 μg P/L at P0 and 9.2 μg P/L at P2 and did not change significantly during the experiment.

Ammonium was amended to the Salto at the same target concentration as the Pantano (Fig. 5). Median measured ammonium concentration was 114 μg N/L during the plateau at S1 (09:15–13:05) compared with a median calculated concentration of 119 μg N/L. Median measured and calculated ammonium levels at the midreach station (S2) during plateau were reduced to 95 and 108 μg N/L, respectively (11:40–14:03). At S3, median measured and calculated ammonium levels under plateau conditions were 65 and 86 μg N/L, respectively. The 21 μg N/L difference is significant, indicating effective ammonium retention. Nitrate concentration changed only slightly between S1 and S2 during the ammonium amendment. Between S2 and S3, however, the results were similar to the Pantano in that nitrate concentration increased as the ammonium pulse was transported down the channel (Fig. 6). Prior to arrival of the ammonium pulse at S3, nitrate averaged 170 ± 1 μg N/L but rose to 180 ± 1 μg N/L as ammonium reached plateau concentration. As in the Pantano, the 10 μg/L increase in nitrate during the ammonium pulse was approximately 50% of the

20 μg/L difference between measured and calculated ammonium concentrations at S3. Maximum nitrate concentration was 183 μg N/L. SRP decreased from 119 to 104 μg P/L between S0 and S3 but exceeded that predicted by dilution. Continuous SRP input masked any detectable response to the ammonium amendment.

Nitrate Injections

Nitrate added to the Pantano raised the measured median concentration from 125 to 464 μg N/L at P1 (08:18–11:07) (Fig. 7; Table 5). Median calculated concentration was 497 μg N/L. This difference in median concentrations was significant, indicating nitrate loss between P0 and P1. Measured median concentration at the downstream site (P2) during plateau (13:00–14:30) was 347 μg N/L, 75% of the upstream concentration. Median calculated nitrate concentration was 334 μg N/L at P2. The difference between median measured and calcu-

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TABLE 5. Measured concentration (mean and median) of ammonium or nitrate at plateau concentration during their respective amendments, and the median difference between measured and calculated concentrations, 1989. Positive median differences indicate disappearance in excess of dilution. Negative differences indicate production. The P-value indicates the statistical significance of the difference between median measured and calculated concentrations. P = Pantano, S = Salto, n = number of observations at plateau concentration, SD = standard deviation.

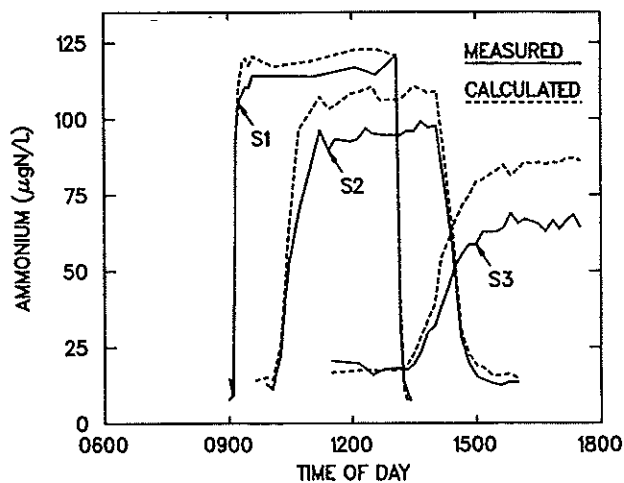| Date (1989)	n	Mean concentration (μg N/L $\pm$ SD)	Median concentration (μg N/L)	Median difference (μg N/L)	P-value
Ammonium amendment					
Feb. 20					
P1	6	104±4	104	15.0	0.036
P2	9	43±3	42	39.0	0.009
Feb. 19					
S1	10	113±4	114	6.0	0.008
S2	15	95±2	95	11.7	0.001
S3	13	66±2	66	20.1	0.002
Nitrate amendment					
Feb. 24					
P1	9	463±13	464	31.7	0.009
P2	10	343±12	347	−12.4	0.032
Feb. 22					
S1	7	565±14	567	18.8	0.022
S2	12	465±9	482	−4.0	0.005
S3	6	393±5	396	−16.8	0.003

FIG. 5. Comparison of measured concentration of ammonium with that calculated from coinjected rhodamine WT to correct for dilution–dispersion during a whole-system amendment to the Salto River. S1, S2, and S3 are sample sites (see Fig. 1).
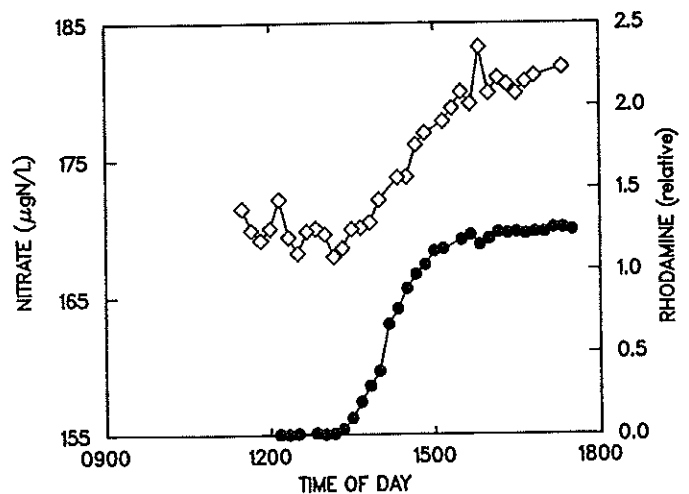

FIG. 6. Timing of nitrate concentration increase (open symbols) at Salto site S3 in response to ammonium plus tracer amendment as indicated by the conservative tracer plume (solid symbols).

lated nitrate was significant, indicating nitrate gain during passage from P1 to P2. Background SRP increased from 5.3 μg P/L at P0 to 9.3 μg P/L at P2 and exhibited no significant response to nitrate amendment.

Nitrate added to the Salto raised the median measured concentration from 189 to 567 μg N/L at S1 (08:18–09:30) (Fig. 8). Median measured (567 μg N/L) versus calculated concentrations (584 μg N/L) were significantly different, indicating nitrate retention between S0 and S1 (Table 5). The opposite was observed between S2 and S3. Between S2 and S3 the

difference in median measured (396 μg N/L) and calculated concentrations (377 μg N/L) was significant, indicating nitrate gain. This represents the minimum amount of nitrate production, since background concentration decreased by approximately 12 μg N/L between S2 and S3 prior to passage of the nutrient pulse. Mean SRP concentration decreased downstream from 123 μg P/L at S0 and S1 to 117 μg P/L at S2 and 107 μg P/L at S3. SRP concentrations remained steady during the passage of the nitrate pulse. Thus, nitrate amendment to the Salto did not affect SRP concentration.
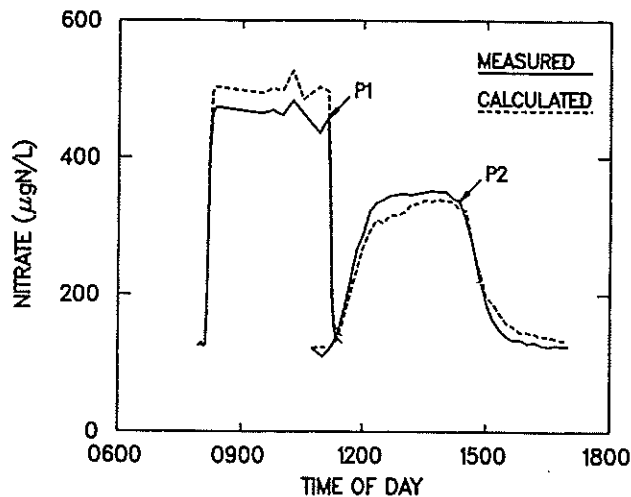
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FIG. 7. Comparison of measured concentration of nitrate with that calculated from coinjected rhodamine WT to correct for dilution–dispersion during a whole-system amendment to a reach of Pantano Creek. P1 and P2 are sample sites (see Fig. 1).
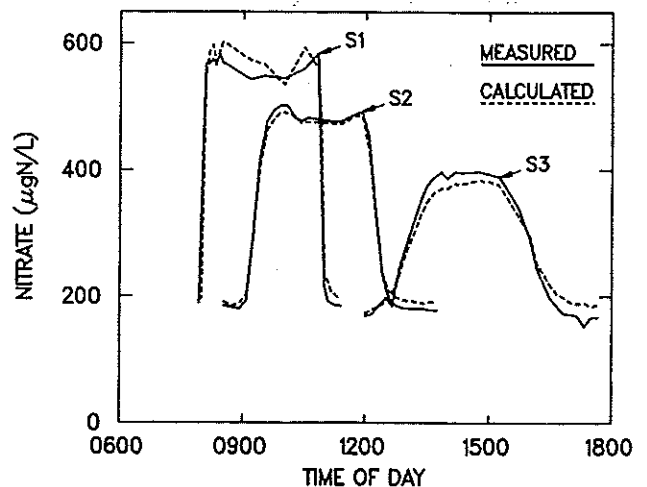

FIG. 8. Comparison of measured concentration of nitrate with that calculated from coinjected rhodamine WT to correct for dilution–dispersion during a whole-system amendment to a reach of the Salto River. S1, S2, and S3 are sample sites (see Fig. 1).

Discussion

While geothermal SRP enrichment of the Salto River constituted a second, separate phosphate source to surface water, DIN in both streams appeared to result from mineralization in the catchment. Only small differences in DIN occurred between the Salto and Pantano in contrast with SRP. Geothermally based groundwaters, high in SRP, appeared to be low in DIN. On the east Salto, especially between midswamp and the confluence of the Salto and Pantano, the drainage is small and entirely swamp forest whereas the west Salto has an extensive contributing area consisting of both upland forest and swamp forest. Where local drainage is aerially extensive (i.e. upper swamp and west Salto transects) or where geothermal groundwater input is minimal (i.e. Pantano), groundwater DIN concentration was high. In the Salto's east bank, where the contributing area of swamp forest is small and groundwater is heavily impacted by geothermal sources, SRP was high but DIN was low. Geothermal waters can be high in ammonium, especially near their source (Cooper 1983). However, the low concentration in the east bank of the Salto indicated absence of a significant geothermal DIN contribution.

DIN composition along both streams reflected local redox conditions. Seep water and groundwater of the Salto's upper swamp were typically oxic (Pringle and Triska 1991). Concentrations of nitrate were higher and ammonium lower than midswamp. Midswamp groundwaters with low dissolved oxygen concentration (<1.0 mg/L) were often found along the west and east transects of the Salto (3-m Wells). At these sites, DIN was dominated by ammonium.

Higher ammonium than nitrate concentration in groundwater and higher nitrate than ammonium concentration in stream water indicated nitrification potential during ammonium transport. Nitrate production in sediment slurries and lack of formation in killed and nitrapyrin-inhibited treatments suggested that nitrate production was a consequence of biological nitrification. Sediments from the Salto had potential nitrification rates of 1.76 μg N·cm^{-3}·d^{-1} for organic-rich sediments to 3.34 μg N·cm^{-3}·d^{-1} for clay sediments. Nitrification has also been reported in soils at La Selva. Robertson (1984) found soil

rates of 4 μg N·g^{-1}·d^{-1} which are at the high end of the range of nitrifying activity (<0.1 to <6.0 μg N·g^{-1}·d^{-1} for tropical soils (de Rham 1970; Tanner 1977; Lamb 1980; Vitousek et al. 1983).

Comparison between the SRP-enriched Salto and the unmodified Pantano under nutrient-amended conditions indicated similarities in nitrogen retention, transformation, and transport. Ammonium recovery at the base of the reach (corrected for background and dilution) averaged only 37% of upstream input in the Pantano and 70% in the Salto, indicating significant retention or transformation during downstream transport. Ammonium amendment resulted in increased nitrate concentration at the base of the experimental reach in both streams. The increase in nitrate concentration accounted for approximately 50% of the difference between mean measured and mean calculated ammonium concentration in both streams. Timing of the ammonium pulse, indicated by rhodamine WT (Fig. 5 and 7), suggests that nitrification in the channel is a reasonable explanation for rising nitrate concentration during the whole-system amendments. Nitrifying activity during ammonium injections to surface water (Newbold et al. 1983; Richey et al. 1985) and hyporheic water (Triska et al. 1990) has also been observed in temperate streams.

We hypothesized SRP depletion in the Pantano due to assimilatory ammonium demand and lack of geothermal SRP enrichment. If the calculated ammonium retention of 39 μg N/L at P2 (Table 5) was exclusively assimilated for biomass production, and coupled to SRP uptake at a ratio of 16/1, SRP concentration would have been depleted by 5.4 μg/L, more than half the background concentration. However, SRP depletion was not observed. There are several explanations. First, while nitrification is coupled to carbon fixation, and SRP uptake might be expected, the ratio of ammonium oxidized to carbon fixed by nitrifying bacteria is higher than the Redfield ratio of 106C:16N:1P (Redfield et al. 1963). Alexander (1961) provided N:C ratios (ammonium-nitrogen oxidized to carbon fixed) of 35:1 for *Nitrosomonas europaea* and N:C ratios from 14:1 to 70:1 for other ammonium-oxidizing species. Thus, nitrification, a major fate of amended ammonium, oxidized large amounts of ammonium for the amount of carbon fixed

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and generated little SRP demand. Second, an unknown increment of retention was sorption rather than uptake. Ammonium is readily sorbed to clays and organic matter (Boatman and Murray 1982), and both are important constituents of bed sediments in the Salto and Pantano. Third, background SRP concentration in the Pantano may be controlled by abiotic rather than biotic processes. Mulholland et al. (1990), studying a small forested stream, found that biologically controlled SRP uptake mechanisms became saturated above approximately 5 µg P/L whereas physical–chemical adsorption continued to increase with increasing concentration. Pringle and Triska (1991) proposed that abiotic control of SRP levels in the Pantano after SRP amendment to the water column (36 ± 2 µg P/L) was effectively reduced to background concentration with no DIN response. Finally, mineralogically identical soils adjacent to the Salto have far more leachable SRP than at the Pantano, presumably indicating availability of additional sorption sites.

Bioassays (15 d) using nutrient-diffusing substrata produced a significant chlorophyll response to SRP in light gaps along the Pantano, but not in the Salto (Pringle and Triska 1991). Thus, ambient SRP level may impact biotic uptake by autotrophs, but biotic uptake does not have a large impact on stream water SRP levels in either stream, most likely due to the high density of shading.

Our final hypothesis was that amended nitrate would be transported conservatively in both streams due to high background concentration. Not only was nitrate transported conservatively in both the Salto and Pantano, but a small increase in nitrate concentration was observed at the base of each reach. The mechanism for this increase is unknown. Previous 15-d bioassays found no significant increase in chlorophyll *a* accrual rates in either the Salto or Pantano using nutrient-diffusing substrata amended with nitrate (Pringle et al. 1986; Pringle and Triska 1991). Conservative to nearly conservative nitrate transport has commonly been reported in streams. Webster et al. (1991) found significant nitrate uptake in only 11 of 58 experiments conducted at Coweeta Hydrologic Laboratory, North Carolina. Richey et al. (1985) reported conservative transport of nitrate but effective retention of ammonium and urea at Bear Brook, New Hampshire. High nitrate retention within short stream reaches is most often attributed to high autotrophic production (Sebetich et al. 1984; Grimm 1987; Triska et al. 1989a, 1989b), although detritus-associated uptake (Munn and Meyer 1990) and denitrification (Hill 1988) can also produce measurable nitrate retention. In the Salto and Pantano, biotic demand was insufficient and uptake length too great for nitrate retention to be detected by our methods.

Our study effectively characterized sources and the fate of transported DIN under naturally high- and low-SRP conditions in tropical streams draining parent material of relatively recent volcanic origin. We found that the proportion of nitrate to ammonium in upper and midswamp locations reflected local redox conditions. The pattern of ammonium concentration was groundwater > spring water > channel water whereas the nitrate pattern was the opposite. Nitrification in channel sediments was confirmed by slurry studies and whole-system amendments. Ammonium retention and transformation were high during down-channel transport. Nitrate production exceeded retention under both nitrate and ammonium amendment. DIN retention, transport, and transformation were not related to SRP levels. Absence of an SRP response to either amendment in the Pantano may indicate a limited role for DIN assimilation compared with sorption and nitrification. The

results support our previous conclusion (Pringle and Triska 1991) that abiotic factors regulate SRP concentration in the Pantano. However, biotic and abiotic mechanisms are both important in regulating DIN concentration and composition. These observations provide an important base for future controlled studies of sediment and biota to examine underlying mechanisms of SRP and DIN retention, transformation, and transport.

Acknowledgements

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