

The dynamics of phosphorus retention during an eight-year P-addition in a Neotropical headwater stream

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Introduction

Understanding the capacity of stream ecosystems to retain nutrients through physical-chemical processes and biotic assimilation has been a central goal of stream ecologists for decades. Currently, most of our understanding of nutrient saturation is based on short-term (<1 day) nutrient addition experiments, while predicting total stream ecosystem response to long-term anthropogenic nutrient loading requires considering the stream's capacity to remove nutrients over extended periods.

Dissolved phosphorus (P) retention results from a combination of biotic and abiotic mechanisms, which could follow different trajectories through time. Short-term biotic P uptake by algae and heterotrophic microbes typically involves direct assimilation from the water column and is saturated at low background soluble reactive phosphorus (SRP) levels (MULHOLLAND et al. 1990). However, during long-term P-loading, the biotic community could also respond by increasing biomass (PETERSON et al. 1985, SLAVIK et al. 2004, but see GREENWOOD & ROSEMOND 2005), temporarily increasing the community's P-retention capacity.

Abiotic P-sorption is an equilibrium process controlled by the relative concentrations of sorbed-P and dissolved-P, although it also depends on sediment size, iron, aluminum, organic content, and pH (MEYER 1979). During long-term P-loading, sediment should become increasingly P-saturated, decreasing abiotic retention. Because biotic and abiotic P-uptake mechanisms could have opposite responses to long-term P-loading, the relative importance of each mechanism will control a stream's retention capacity over time. Specifically, where P-uptake is dominated by biotic pathways, streams could become temporarily more efficient at removing dissolved-P, whereas where P-uptake is primarily abiotic, streams potentially become less efficient.

Here we present data from an 8-year experimental P-addition in a first-order stream, the Carapa, at La Selva Biological Station, Costa Rica. Previous experiments of P-dynamics in the Rio Salto at La Selva indicate that most uptake of P due to the input of naturally P-enriched regional groundwater is due to abiotic sorption (TRISKA et al. 2006). Biweekly measure-

ments of dissolved P concentration upstream and at 3 downstream stations during the long-term P-injection in the Carapa allowed us to calculate P-uptake rates over the 8-year study. Assuming a dominance of abiotic control, we predicted that sediments would become saturated over time, decreasing P-uptake efficiency.

Key words: Costa Rica, headwater stream, nutrient saturation, phosphorus, SRP, uptake

Materials and methods

We performed an 8-year experimental P enrichment in a first-order stream, Carapa, at La Selva Biological Station, Costa Rica. The stream drains dense secondary forest. Allochthonous input into the stream is high, and light availability is low due to the dense multi-stratal canopy (ROSEMOND et al. 2002). From 28 August 1998 to 17 February 2006, phosphoric acid (H_3PO_4) was continuously released from a streamside carboy. Due to the small size of the stream and a series of riffles below the injection site, complete mixing occurred within 10 m. Biweekly water samples were collected 10 m above the P-injection, and at stations 10 m, 50 m, and 100 m downstream, and analyzed on site for SRP using the molybdenum blue method (FUGITA 1969). For quality control, a subset of these samples was frozen and later analyzed for SRP at the Odum School of Ecology Analytical Chemistry Laboratory (University of Georgia, Athens, Georgia), using the ascorbic acid technique (APHA 1992). All sample collections and laboratory analysis at La Selva was performed by the same technician over the 8-year period. Natural background SRP levels on the Carapa were low (averaging $6.5 \mu g L^{-1}$). The target P concentration for the injection was $300 \mu g L^{-1}$ at the station 10 m downstream.

We generated a discharge curve at the upstream station by measuring discharge each month from 1998–2006 using the velocity-area method (GORE 1996). Velocity was measured with a Marsh-McBirney current meter. Stage height was recorded biweekly, providing a discharge estimate for each series of water samples. In February 2006, Rhodamine WT dye was

released to measure dilution over the reach. From February 2005–February 2006, bimonthly measurements of discharge were taken at both the upstream and 100 m stations encompassing a range of discharge levels. Over the year, dilution was nearly constant (plotting discharge at upstream site vs. 100 m downstream site resulted in a linear relationship with $r^2 = 0.94$). Consequently, dilution was calculated for all dates based on the 2006 Rhodamine WT dye results.

P-uptake rates were estimated from the decline in nutrient concentration (corrected for dilution and background concentration) with distance downstream. Short-term nutrient additions assume no regeneration, but in long-term nutrient addition studies, downstream nutrient concentrations reflect both uptake and regeneration; therefore, we calculated distance-normalized net SRP uptake rates (k_{net} ; HAGGARD et al. 2005). The k_{net} was calculated as the negative slope of the log SRP concentration (corrected for background concentration and dilution) versus distance downstream for the 3 downstream sites (STREAM SOLUTE WORKSHOP 1990), with units m^{-1} (k is the inverse of uptake length, S_w). Although the mass transfer coefficient $V_f (= k \times \text{velocity} \times \text{depth})$ is also used as an index of nutrient uptake efficiency, particularly for comparing different streams (HALL et al. 2002), we chose k_{net} to compare changes in uptake efficiency over time because all of our uptake values were within a single small stream with minimal variation in velocity and depth.

Water samples were analyzed for SRP on 775 different dates; however, 90 dates were excluded because of missing data or SRP estimates below the level of detection. From the remaining data, we calculated k_{net} for 685 different days during the 2731-day experiment.

The SRP loading rate was considered to be the SRP concentration at the station 10 m below the injection site (SRP_{10} , with units $\mu\text{g L}^{-1}$). The k_{net} was plotted against SRP_{10} to provide an overall relationship between SRP loading and uptake efficiency. Relationships between SRP_{10} and k_{net} were nonlinear and were modeled using a second-order polynomial equation in JMP® Version 4 (SAS Inc., Cary, North Carolina, USA).

To evaluate changes in P-uptake dynamics over time, the predicted k_{net} value from the polynomial model was compared to the actual k_{net} value calculated for each sampling date. Residuals were calculated and plotted against sampling date. Re-

gression analysis was used to test changes in residuals over time, using JMP®.

Results and discussion

SRP concentrations at the station 10 m below the injection site ranged widely from $10.9 \mu\text{g L}^{-1}$ to $6541.9 \mu\text{g L}^{-1}$ over the course of the 8-year study. Mean stream discharge was 1.7 L s^{-1} (SE = 0.04), with seasonal fluctuations apparent. High discharge was associated with low SRP_{10} values, but at low-to-moderate discharge, SRP_{10} varied widely (Fig. 1).

Although the original goal of the long-term P injection was to maintain a steady SRP concentration downstream, large variations in SRP_{10} resulted from variable uptake rates, discharge fluctuations, and variable H_3PO_4 release rates. The variable P-loading created dynamic conditions for P-uptake and release. Calculated P-uptake rates varied from -0.0237 m^{-1} to 0.989 m^{-1} over the course of the experiment. A second-order polynomial equation best explained the variation in k_{net} with respect to SRP_{10} ($r^2 = 0.487$; Fig. 2). Residual k_{net} values decreased over the course of the experiment ($p < 0.0001$, $n = 685$, linear regression; Fig. 3). Increasing discharge was associated with lower k_{net} values ($p < 0.0001$, $r^2 = 0.04$) and residual k_{net} values ($p = 0.0485$, $r^2 = 0.006$). While discharge influenced P-uptake efficiency, accounting for variance in uptake trends over time, observed trends over the 8-year experiment were not discharge-driven.

Our results show that SRP uptake efficiency increased with background SRP levels up to $3500 \mu\text{g L}^{-1}$ and then decreased (Fig. 2). Prior studies, based on short-term (1-day) SRP additions at low background levels, have found that uptake efficiency (k) decreased with increasing SRP concentration (MULHOLLAND et al. 1990, HART et al. 1992). However, our results are more similar to those of HAGGARD et al. (2005), who measured SRP uptake rate and

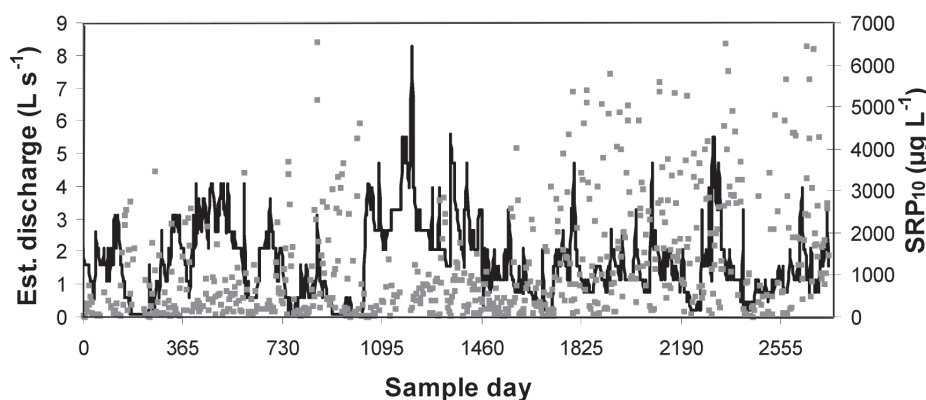


Fig. 1. Estimated discharge (L s^{-1} ; solid line) and SRP at station 10 m below P injection (SRP_{10} , with units $\mu\text{g L}^{-1}$; squares) over the course of the 8-year P-addition.

Fig. 2. Relationship between SRP at station 10 m below P-injection (SRP_{10} , with units $\mu\text{g L}^{-1}$) and net SRP uptake efficiency (k_{net} , with units m^{-1}). The curve is the best-fit second-order polynomial equation: $k_{\text{net}} = 0.0178 + 1.46\text{e-}5 SRP_{10} - 2.71\text{e-}9(SRP_{10} - 1210)^2$ ($r^2 = 0.487$).

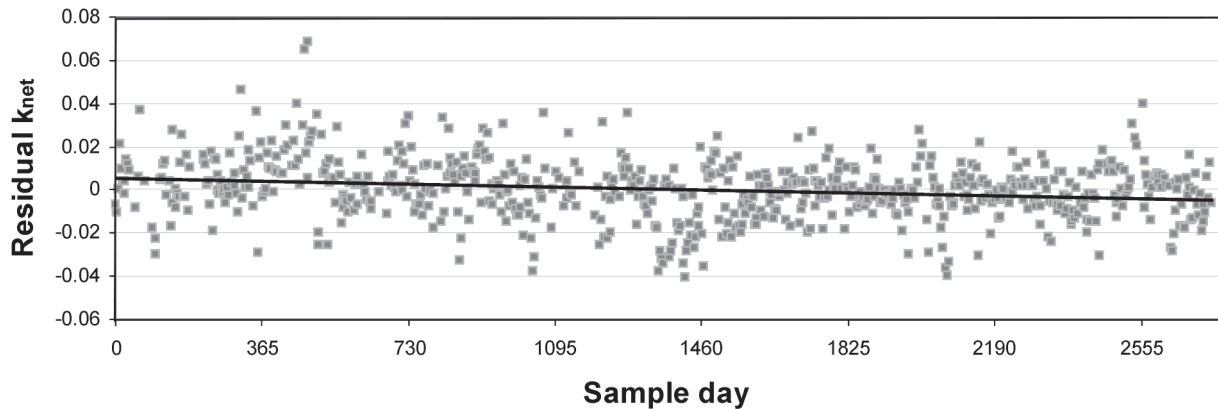
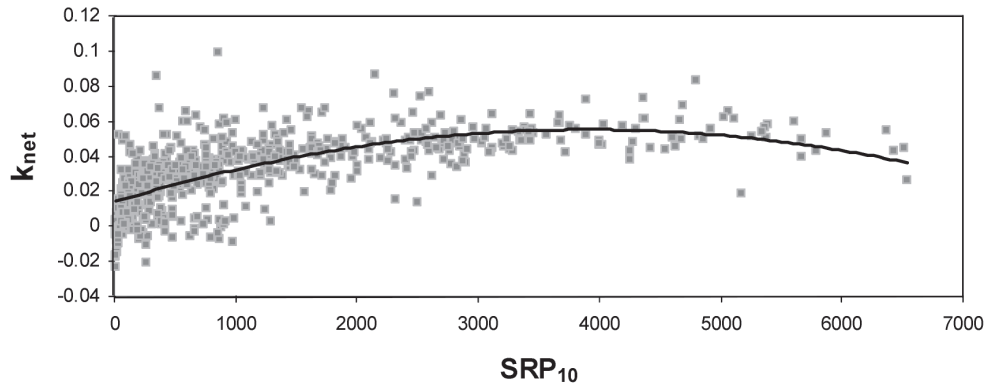


Fig. 3. Residual k_{net} (calculated $k_{\text{net}} - k_{\text{net}}$ from polynomial function) over the course of the 8-year P-addition. The dark line is the best-fit line ($p < 0.0001$, $r^2 = 0.448$, $n = 685$).

efficiency downstream of a wastewater treatment plant in a third-order stream (essentially a long-term nutrient addition experiment). HAGGARD et al. (2005) found that net SRP uptake efficiency was negative at relatively low background SRP concentrations, reached a maximum at approximately $3500 \mu\text{g SRP L}^{-1}$, and declined with further increases in background SRP.

The discrepancy between results from short- and long-term P additions may be explained by temporal uptake and remineralization dynamics. In short-term nutrient addition experiments, remineralization is assumed to be negligible; however, in long-term addition experiments, a dynamic equilibrium between nutrient uptake and remineralization occurs. Because measurements continue for years, subsequent remineralization of added P is implicitly integrated into the measurements of net uptake, altering the apparent uptake measurements. For example, because P-uptake and release from sediments is controlled by the difference between P concentrations in the water column and in the sediment (TRISKA et al. 2006), as sediment becomes saturated, higher water column SRP concentrations are required to generate a positive net uptake.

A decrease in background SRP concentrations can lead to negative k_{net} values. In fact, net P-release was recorded on 42 of the 685 sampling dates, when SRP_{10} fell below $1000 \mu\text{g L}^{-1}$.

Over the course of the experiment, at a given background P-loading rate (SRP_{10}), SRP uptake became less efficient (residual k_{net} values decreased; Fig. 3). This decline in relative uptake efficiency over time was consistent with our prediction that sediment became saturated over the course of the experiment. The negative slope in this relationship supports the hypothesis that P-retention in the Carapa was primarily abiotic. A stream in which P-retention was biotically-driven would be expected to increase its P-uptake efficiency over time if the biomass of algae and microbes increase in response to nutrient addition. We suspect that P-saturation of sediments in the Carapa was slowed because of the input of unsaturated sediment from above the study reach, effectively creating a shallower slope in Fig. 3.

Future studies of stream nutrient dynamics should consider how the capacity of streams to remove nutrients saturates over time, and how biotic and abiotic factors

interact to drive these changes. Only by measuring stream responses to chronic nutrient loading will we be able to understand how anthropogenic nutrient pollution alters the functioning of stream ecosystems.

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References

- [APHA] AMERICAN PUBLIC HEALTH ASSOCIATION. 1992. Standard methods for the examination of water and wastewater, 18th ed.
- FUGITA, D.K. 1969. Standard procedures for water analyses. University of California.
- GORE, J.A. 1996. Discharge measurements and streamflow analysis, p. 53–74. *In* F.R. HAUER & G.A. LAMBERTI [eds.], *Methods in Stream Ecology*. Academic Press, San Diego.
- GREENWOOD, J.L. & A.D. ROSEMOND. 2005. Periphyton response to long-term nutrient enrichment in a shaded headwater stream. *Can. J. Fish. Aquat. Sci.* **62**: 2033–2045.
- HAGGARD, B.E., E.H. STANLEY & D.E. STORM. 2005. Nutrient retention in a point-source-enriched stream. *J. N. Am. Benthol. Soc.* **24**: 29–47.
- HALL, R.O., E.S. BERNHARDT & G.E. LIKENS. 2002. Relating nutrient uptake with transient storage in forested mountain streams. *Limnol. Oceanogr.* **47**: 255–265.
- HART, B.T., P. FREEMAN & I.D. MCKELVIE. 1992. Whole-stream phosphorus release studies: variation in uptake length with initial phosphorus concentration. *Hydrobiologia* **235/236**: 573–584.
- MEYER, J.L. 1979. The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem. *Limnol. Oceanogr.* **24**: 365–375.
- MULHOLLAND, P.J., A.D. STEINMAN & J.W. ELWOOD. 1990. Measurement of phosphorus uptake length in streams: comparison of radiotracer and stable PO₄ releases. *Can. J. Fish. Aquat. Sci.* **47**: 2351–2357.
- PETERSON, B.J., J.E. HOBBI, A.E. HERSHEY, M.A. LOCK, T.E. FORD, J.R. VESTAL, V.L. MCKINLEY, M.A.J. HULLAR, M.C. MILLER, R.M. VENTULLO & G.S. VOLK. 1985. Transformation of a tundra river from heterotrophy to autotrophy by addition of phosphorus. *Science* **229**: 1383–1386.
- ROSEMOND, A.D., C.M. PRINGLE, A. RAMÍREZ, M.J. PAUL & J.L. MEYER. 2002. Landscape variation in phosphorus concentration and effects on detritus-based tropical streams. *Limnol. Oceanogr.* **47**: 278–289.
- SLAVIK, K., B.J. PETERSON, L.A. DEEGAN, W.B. BOWDEN, A.E. HERSHEY & J.E. HOBBI. 2004. Long-term responses of the Kuparuk River ecosystem to phosphorus fertilization. *Ecology* **85**: 939–954.
- STREAM SOLUTE WORKSHOP. 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. *J. N. Am. Benthol. Soc.* **9**: 95–119.
- TRISKA, F., C.M. PRINGLE, J.H. DUFF, R.J. AVANZINO & G. ZELLWEGER. 2006. 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. *Biogeochemistry* **81**: 145–157.

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