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Quantifying phosphorus uptake using pulse and steady-state approaches in streams

Stephen M. Powers, Emily H. Stanley, and Noah R. Lottig*
Center for Limnology, University of Wisconsin-Madison, Madison, WI, USA

Abstract

Steady-state approaches to the study of stream nutrient processing have several limitations. Dynamic (time series) approaches are more flexible, and allow interpretation of nutrient additions introduced as unsteady slugs (pulses). We compared soluble reactive phosphorus (SRP) uptake metrics from experimental nutrient pulses modeled dynamically with those from continuous injections modeled with a steady-state approach. For six southern Wisconsin streams, uptake metrics from these two methods were similar despite low nutrient demand. Linear regression of paired-pulse versus steady-state estimates of the first-order uptake coefficient (λ; $r^2 = 0.84$, slope = 1.21) and uptake velocity (v_f; $r^2 = 0.95$, slope = 1.03) were highly significant. There was a tendency for slightly higher uptake with pulses, possibly due to P sorption. Sampling across five stations of one stream yielded a similar longitudinal pattern between experimental pulse SRP flux and steady-state (plateau) SRP concentration. Conservative transport parameters for pulse and continuously injected tracer data were also similar. These results suggest that unsteady nutrient amendments can provide usable nutrient uptake values, even in low-uptake situations for which uncertainty is high. The flexibility of dynamic approaches to nutrient spiraling facilitates research in poorly understood situations, including conditions of high water residence time, high discharge, and changing discharge or background chemistry.

Introduction

The nutrient spiraling model (Webster and Patten 1979, Newbold et al. 1981) provides informative and well-established currencies for the study of lotic ecosystems. This framework effectively marries internal ecosystem processing with fluid transport and has contributed much to our understanding of nutrient dynamics in streams (Newbold et al. 1982, Mulholland et al. 1985, Valett et al. 2002). Yet conventional application of the nutrient spiraling model in streams involves a steady-state approach that is impractical or inappropriate in many situations of interest. More generally, the highly dynamic nature of lotic ecosystems over ecologically relevant scales of time and space (Martí and Sabater 1996, Dent and Grimm 1999) presents many obstacles to the application of equilibrium-based models.

Most applications of the nutrient spiraling model involve the continuous, experimental introduction of solute to a stream or river under the assumption that a stable, enriched nutrient condition may be achieved. We refer to this strategy as the steady-state approach to nutrient spiraling. Clearly, broad synthesis of results using the steady-state approach has been successful in identifying important patterns, such as short uptake length in small streams (Peterson et al. 2001), relatively low variation in stream nutrient uptake velocity across biomes (Webster et al. 2003) and stream sizes (Wollheim et al. 2001), and substantial cumulative uptake in larger, higher-order rivers (Ensign and Doyle 2006). However, many situations with significance to riverine nutrient transport and processing at large temporal and spatial scales are outside the scope of the steady-state approach. These situations include conditions of fluctuating background flows and fluxes (Fisher et al. 2004), high water residence time (e.g., long flowpaths and those containing wetlands, ponds, or large backwaters), and high discharge (e.g., large rivers, floods). Research in these biogeochemical frontiers would facilitate identifying the

*Corresponding author: E-mail: smpowers@wisc.edu

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places and times at which nutrient removal mechanisms are meaningful to long-term dynamics, and would be valuable within the context of continuing global change. Therefore, methods and models are needed that expand the scope of nutrient spiraling to larger and more complex aquatic ecosystems.

Dynamic models of lotic ecosystems are more flexible than steady-state models, and applicable to situations outside the scope of the steady-state approach to nutrient spiraling. For example, dynamic models allow interpretation of uptake time series from unsteady nutrient amendments (additions that do not achieve a stable experimental nutrient concentration), such as abbreviated continuous injections and instantaneous spikes/slugs (pulses). Although pulse methods present advantages in terms of scope and speed, it remains to be seen how nutrient uptake metrics derived from pulses relate to those derived from steady-state approaches. In this work, we used a dynamic transport model to quantify soluble reactive phosphorus (SRP) uptake velocity from phosphorus (P) pulses for multiple systems, and compared these values to those from paired continuous injections modeled with a steady-state approach. Our interest in this comparison was to evaluate pulse versus steady-state nutrient uptake metrics in situations where both were quantifiable and to facilitate the interpretation of experiments that necessitate the unsteady introduction of nutrients.

The steady-state nutrient uptake approach—The quantification of stream nutrient dynamics using nutrient amendment experiments and steady-state modeling is supported by a rich methodological literature (e.g., Newbold et al. 1981, Stream Solute Workshop 1990, Payn et al. 2005). Although the general approach has been cited as laborious (Fisher et al. 2004), strengths relate to its methodological and mathematical elegance and simplicity. These characteristics have, fortuitously, facilitated widespread application of the model (Ensign and Doyle 2006). Conventional applications of the nutrient spiraling model involve the experimental introduction of ecologically relevant elements by continuous injection at the upstream end of a study reach. Nutrient uptake metrics for individual elements are then calculated from longitudinal declines in solute concentration along the reach during the enriched, stabilized period in the time series (the "plateau"). In its simplest form, the steady-state nutrient uptake approach yields the nutrient uptake length (S_w) defined by

$$S_w = \frac{x}{\ln\left(\frac{C_{up}}{C_{down}}\right)} \quad (1)$$

where x is reach length, C_{up} is the background-corrected steady-state nutrient concentration entering the reach, and C_{down} is the background- and dilution-corrected stable nutrient concentration exiting the reach. In practice, stream ecologists usually sample nutrients at multiple stations with this approach and use basic stream characteristics to calculate associated metrics (Stream Solute Workshop 1990), including areal uptake rate (U) and uptake velocity (v_f).

The value of alternative nutrient uptake approaches—Whereas the steady-state approach to the nutrient spiraling model assumes that nutrient inputs, outputs, and processing within space do not change in time, dynamic transport models can incorporate changing conditions in both time and space, and thus are more versatile. These models can be used to interpret nutrient spiraling metrics when stable concentrations are not achieved (Runkel 2007). Removing this basic constraint has rather profound implications. Because dynamic models permit study in situations where steady nutrient concentrations cannot be practicably attained, they expand the scope of the nutrient spiraling model to many areas of prime interest to stream ecologists. These situations include large rivers (Tank et al. 2008), wetlands, and the changing background conditions of flow and chemistry that often define lotic ecosystems. For example, storm-flushing of nutrients (Jordan et al. 2005), including episodic transport of soluble P (Fig. 1), can be common in agricultural catchments and may contribute substantially to annual river loads. Although ecological influences on nutrient transport are generally presumed to be small during high-flux periods, we lack understanding of the controls and consequences of transport events in open systems. Dynamic modeling approaches provide a framework for examining such anthropogenic pulse fates.

In addition to expanding the scope of nutrient spiraling to many more ecosystems, dynamic approaches provide at least two other key advances over steady-state approaches: (1) reduced sampling time in streams with characteristics otherwise

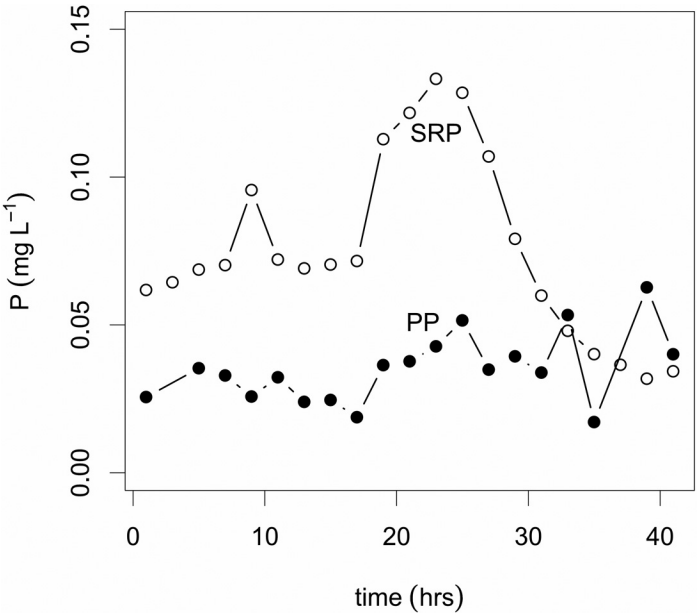

Fig. 1. Dissolved phosphorus pulse initiated by a precipitation event in Big Spring Creek, located in agricultural southern Wisconsin (March 2006). Discharge increased from 400 to 425 L s^{-1} during the period. Note the small change in particulate phosphorus (PP = total P – total dissolved P) compared to soluble reactive phosphorus (SRP). Time is hour of sampling.

amenable to the steady-state approach (e.g., low residence time) and (2) increased mechanistic inference through the use of models that can partition competing processes, such as main-channel versus storage zone nutrient uptake (Runkel 2007), which in lotic ecosystem research have been conventionally treated as a composite. Although estimating nutrient uptake from time series may require more sophisticated models, dynamic modeling approaches used in this work represent a relatively small cost in added model complexity. Currently, few examples of pulse nutrient experiments exist in the literature (but see Meals et al. 1999, Tank et al. 2008). However, the flexibility of dynamic transport models indicates that we are well positioned to expand our understanding of lotic biogeochemistry into several important yet underexplored avenues, and with more rigor than in the past. This progress may involve the use of unsteady nutrient amendment experiments.

Materials and procedures

General study design and rationale—We applied pulse and steady-state approaches to quantifying nutrient uptake in southern Wisconsin streams and attempted to compare SRP uptake velocity in two different ways: (1) across multiple systems using a two-station technique (Fig. 2, $n = 6$ streams: East Branch Boulder Creek, E; German Branch Pecatonica River, G; Lowery Creek, L; Manley Creek, M; Rowan Creek, R; West Branch Boulder, W) and (2) across consecutive reaches ($n = 4$ reaches, or 5 stations) of one stream (second visit to Lowery Creek, $L_{1–5}$). Pulse and continuous injections were conducted consecutively on the same day in two instances (G and R, in which continuous injections were conducted first), 3 days apart to avoid sampling during a precipitation event in one instance (M), and on adjacent days in all remaining cases. Because nutrient uptake metrics are highly sensitive to changes in flow, background chemistry, and weather, we employed this strategy to ensure that paired conditions were similar.

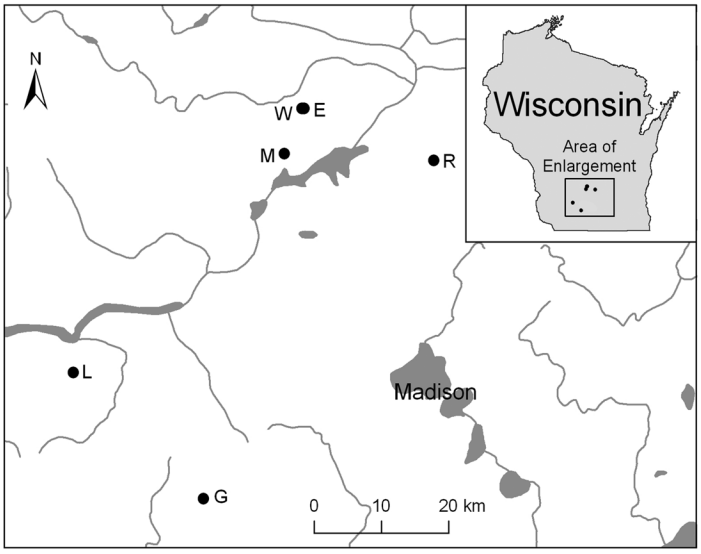

Fig. 2. Map of study area and streams. E, East Branch Boulder Creek; G, German Branch Pecatonica River; L, Lowery Creek; M, Manley Creek; R, Rowan Creek; W, West Branch Boulder Creek. Map center at 43°15.382 N, 89°33.209 W.

Streams in southern Wisconsin are pervasively N-saturated due to contemporary and legacy effects of agricultural activities. Mean background DIN (dissolved inorganic nitrogen, NO_3-N + NH_4-N) for our study sites ranged from 0.93 to 3.85 mg L^{-1}, with >80% in the form of NO_3-N in every stream. Although background SRP was moderately high (mean 0.033 mg L^{-1}, range 0.017–0.051 mg L^{-1}), molar N:P ratios ranged from 54.5 to 205.9, suggesting potential P-limitation. Thus, we chose to add phosphate (PO_4^{3-}), but still anticipated low SRP uptake in these streams. To ensure measurable uptake, we used moderate to long study reaches such that analytical detection limits would not hinder data interpretation.

For calculating steady-state nutrient uptake metrics, Eq. 1 and its variants are well established (Stream Solute Workshop 1990) and have been applied many times (Ensign and Doyle 2006). However, the family of equations typically used to calculate S_w, U, and v_f cannot be used to calculate nutrient uptake from pulses. Further, Runkel (2007) demonstrated that these equations, as commonly applied, include an unintentional hydrologic uptake component. To calculate nutrient uptake metrics from both pulses and continuous injections that are immune to hydrologic effects, we used an advection-dispersion solute transport model with transient storage (Bencala and Walters 1983), and with uptake restricted to the main channel, given by

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}\left(C_L - C\right) + \alpha\left(C_s - C\right) - \lambda C \quad (2)$$

$$\frac{dC_s}{dt} = \alpha\frac{A}{A_s}\left(C - C_s\right) \quad (3)$$

where A is the main channel cross-sectional area (L^2), A_s is the cross-sectional area of the storage zone (L^2), C is the main channel solute concentration (M L^{-3}), C_s is the storage zone solute concentration (M L^{-3}), D is the dispersion coefficient (L^2 T^{-1}), Q is the discharge (L^3 T^{-1}), q_L is the lateral inflow rate (L^3 T^{-1} L^{-1}), t is time (T), α is the storage zone exchange coefficient (T^{-1}), and λ is the first-order uptake coefficient for the main channel (T^{-1}). Per the recommendations of Runkel (2007) for steady-state or time series data sets, we applied the following general procedure for both continuous injections and pulses: (1) simulate conservative (no uptake) transport of the tracer by fitting conservative transport parameters (D, A, A_s, and α) and (2) simulate nonconservative transport of nutrients by fitting the nutrient parameter λ using conservative transport parameters from the previous step. Fitted λ values may then be used to calculate uptake length (S_w = velocity × λ^{-1}) and the associated metrics uptake velocity (v_f = λ × depth) and areal uptake rate (U = v_f × concentration). We obtained velocity and depth for these calculations from a combination of modeled and

measured values (velocity = Q/A, depth = A/width). In some cases, D was held fixed in the modeling procedure (Runkel 2007); if fixed, the value for D was chosen within a range of 0.1 to 0.25 such that Q:A approached an independent estimate of stream velocity (determined from time of passage for the tracer center of mass). F_{med}^{200} (Runkel 2002), a measure of the relative influence of transient storage on conservative solute transport, and Damkohler values (Da, Harvey and Wagner 2000) were also calculated from tracer time series.

We used this general strategy for both pulses and continuous injections, and computed separate *pulse* and *steady* metrics. This allowed us to compare conservative transport parameters and nutrient uptake metrics from each field approach. Specific details regarding the application of these two approaches are discussed below.

Continuous injection methods—In each stream, a continuous injection pump was placed 20–50 m above an upstream (input) sampling station to allow sufficient distance for lateral mixing of solute. Downstream (output) stations were selected to allow at least 30 min of water travel time across the study reach. The enrichment target (approximate) was 25 μg L^{-1} SRP. The experimental solution for continuous injections contained tandem tracers (dissolved NaBr and NaCl) and dissolved P (KH_2PO_4). Cl^- was used to elevate background specific conductivity (SC, 25°C) to sufficient levels (10–50 μS cm^{-1}) for effective high-frequency monitoring of tracer movement with conductivity meters. Water samples for SRP and Br^- determination were collected at the upstream and downstream stations, filtered in the field with Whatman GF/F filters, dispensed into 30-mL polypropylene scintillation vials, and placed in ice chests to protect from temperature and light degradation. SRP samples were collected at background and enriched conditions and analyzed within 36 h of collection using colorimetry on an Astoria Pacific Instruments autoanalyzer (APIA), which is accurate to <1 μg L^{-1}. Corresponding Br^- samples were also quantified by colorimetry with the APIA, and a subset of Br^- values was confirmed on a Dionex DX-500 ion chromatograph, yielding good agreement. We report tracer as translated Br^- from Br^-~SC relationships (see Gooseff and McGlynn 2005). Reported flow measurements from Table 2 were taken using standard dilution-gauging techniques (Gordon et al. 1992).

With continuous injections, we adhered to the modeling recommendations of Runkel (2007) for steady-state data sets. Using nonlinear least squares estimation, the one-dimensional transport with inflow and storage (OTIS) model was used to fit D, A, A_s, and α from continuous injection tracer data and λ_{steady} from background-corrected nutrient data taken during the stable, enriched period. We then calculated steady-state uptake metrics from λ_{steady}, yielding $S_{w\text{-}steady}$, $v_{f\text{-}steady}$, and U_{steady}. Because λ errors from model fits represent a two-station regression in our steady-state procedure, λ standard deviation (SD) for each continuous injection was obtained by sensitivity to changes in background-corrected enrichment concentration (ΔC, altered by 1 SD in separate model runs). λ SD was then used to calculate errors for remaining nutrient uptake metrics.

Pulse methods—Solute pulses were initiated in streams by instantaneous slug introduction of nutrient/tracer solution. We sampled from the same upstream and downstream stations used for continuous injection trials to generate breakthrough curves. To achieve a similar reach-averaged experimental nutrient concentration, we aimed for pulse SRP concentrations such that experimental peaks at upstream and downstream stations bounded the steady-state nutrient concentration from continuous injections. In all but one instance, this goal was met (exception: W, in which the upstream peak pulse concentration was 1 μg L^{-1} below the corresponding steady-state concentration). The required mass of added tracer and nutrient for achieving experimental targets was estimated with a simple advection–dispersion model (Chapra 1997). Solute was introduced 50–150 m above the upstream (0 m) sampling station to allow initial dispersion and lateral mixing of the pulse, so that each pulse passed through the upstream station in a dispersed fashion over 20–60 min. SC was monitored in situ to guide collection of water samples over time. Water samples for SRP and Br^- analysis were collected frequently, Br^-~SC relationships were used, and sample time was recorded with high precision (to ~10 s). In addition to background samples, at least 15 SRP samples were analyzed for each upstream station and 10 samples for each downstream station, to effectively characterize the shape of the nutrient pulse time series. Samples at the downstream station were taken continuously until SC returned to background conditions, and SRP to within 2 μg L^{-1} background conditions. Br^- flux (area under observed concentration curve × discharge) was then calculated from the time series of observations. SRP flux was calculated in the same way, with one modification: when SRP did not completely return to background conditions following amendment, we used simulated SRP values from the OTIS model (extrapolated over time) to calculate SRP flux. The fact that dynamic solute transport models do not require a complete experimental nutrient time series for reach outputs represents yet another advantage of this approach. Water samples from pulses were otherwise collected and analyzed in a manner identical to that of continuous injections.

As discussed earlier, steady-state modeling cannot be used to interpret nutrient uptake velocity from pulses, because these unsteady amendments do not achieve a stable experimental nutrient concentration. Instead, employing nonlinear least squares estimation, we used the OTIS model to fit a second suite of conservative transport parameters (D, A, A_s, and α) from pulse tracer data and λ_{pulse} from background-corrected SRP taken over the time course of the nutrient pulse at upstream and downstream stations. McKnight et al. (2004) and Tank et al. (2008) used similar dynamic approaches for quantifying nutrient uptake. We then calculated pulse nutrient uptake metrics from λ_{pulse}, yielding $S_{w\text{-}pulse}$, $v_{f\text{-}pulse}$, and U_{pulse}. Errors in pulse nutrient uptake metrics were calculated using λ

SD from model fits. Figure 3 demonstrates the success of this dynamic modeling strategy for one pulse sampled at multiple stations ($L_{1–5}$); simulated conservative Br^-, conservative SRP (no uptake), and nonconservative SRP transport values are shown for each station.

Assessment

Comparison of conservative transport parameters from pulses and continuous injections—Conservative transport parameters fitted using tracer data from pulses versus continuous injections demonstrate that the influence of transient storage in these study streams was small (from pulses, mean F^{200}_{med} 4.2%, SD 5.1%; mean A_s/A 8.3%, SD 5.1 %) (Table 1). Deviations in transient storage parameters between paired pulses and continuous injections were also usually small (mean ΔF^{200}_{med} 1.6%; mean $\Delta A_s/A$ 0.35 %), despite variation in D in some cases. Note that selection of long study reaches, necessary to detect nutrient uptake in streams of this work, produced some Da values that were higher than the suggested range (0.5–5.0; see Harvey and Wagner 2000) for fitting transient storage parameters. High Da and small transient storage zone size may have increased uncertainty in conservative transport parameters, and could account for deviations between those fitted from pulses versus continuous injections. In one pulse case ($L_{1–2}$) high Da was clearly related to a low tracer recovery rate.

Payn et al. (2008) compared water residence time distributions using pulse and continuous tracer releases and also found few differences in these tests. However, because continuous injections integrate tracer movements over a longer period than pulses (Gooseff et al. 2008), it is possible that differences in conservative transport parameters could sometimes arise. Further, Wagner and Harvey (1997) found that continuous injections yielded a lower coefficient of variation (CV) for each conservative transport parameter than pulses. However, the pulse approach still yielded CV < 0.2 for D, A, A_s, and α in more than 80% of the situations modeled in that work. Although continuous injections provide the favored method for estimating conservative transport parameters, pulses may be sufficient in many cases. The similarity between conservative transport parameters from pulses and continuous injections in this work likely relate to our use of long mixing reaches for pulses, which helped integrate solute movements over time. Also, the experiment was conducted during an unusual summer drought, which resulted in relatively static hydrologic conditions (exceptions: $L_{1–5}$ and M, which were influenced by recent precipitation events).

Comparison of pulse and steady-state SRP uptake—For consecutive reaches of Lowery Creek ($L_{1–5}$), longitudinal declines in pulse SRP flux and corresponding steady SRP concentration indicated the presence of a measurable P sink (Fig. 4). Similar relative patterns in SRP decline between stations can also be seen for both types of injections in this figure. For this stream, $v_{f–pulse}$ was higher than $v_{f–steady}$ for all reaches with measurable uptake (mean $v_{f–pulse}$ 3.9 mm min^{-1}, mean $v_{f–steady}$ 1.2 mm min^{-1}; see Table 2). However, discharge and background SRP were receding during the experiment due to thunderstorms that occurred 1–2 days prior. These changes probably contributed to higher uptake on the day of the pulse experiment (approximately 5% lower flow and 12 μg L^{-1} lower background SRP on this occasion compared to the corresponding continuous injection; see Tables 1 and 2) and make it difficult to directly compare nutrient uptake metrics from this pair.

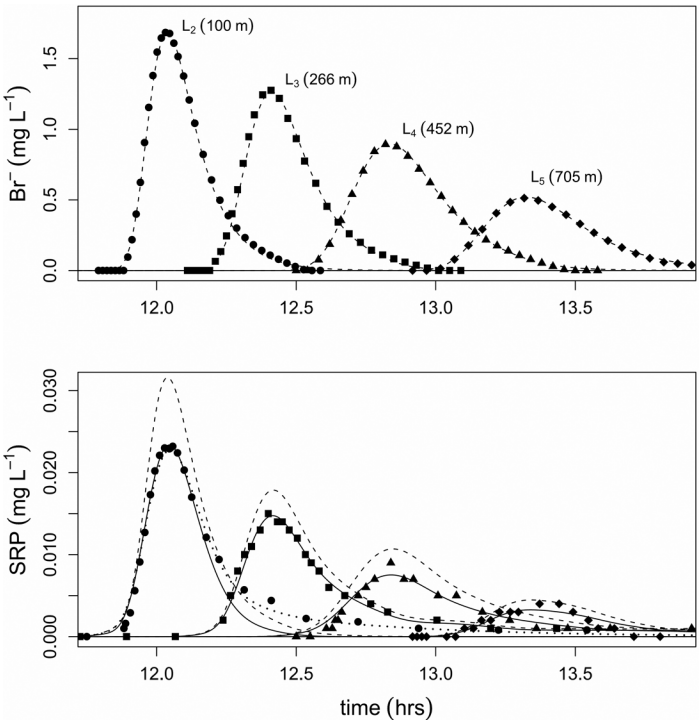

Fig. 3. Propagation of pulse Br^-/SRP amendments across multiple stations in Lowery Creek (L_x) and associated OTIS model simulations. For clarity, upstream boundary conditions at L1 (0 m) not shown. Time is hour of day. Symbols, measured Br^- and SRP; dashed lines, simulated conservative Br^-/SRP transport values; solid lines, simulated nonconservative SRP transport values, with fitted first-order uptake (λ); dotted line, simulated nonconservative SRP transport values for the uppermost reach only ($L_{1–2}$), with fitted K_d sorption (see Appendix 1).

Across multiple systems with similar conditions, nutrient uptake metrics from each method were highly similar. Linear regression of λ_{pulse} and λ_{steady} across these streams yielded a slope of 1.21 (r^2_{adj} = 0.84, P = 0.006), whereas $v_{f–pulse}$ versus $v_{f–steady}$ yielded a slope of 1.03 (r^2_{adj} = 0.95, P < 0.001) (Fig. 5). Each approach had a nearly identical range ($v_{f-pulse}$ range 0.16–4.4 mm min^{-1}, $v_{f-steady}$ range 0.18–4.3 mm min^{-1}). SRP S_w was generally long (range 447–3170 m), but all λ values for our study systems were of the same order as, or one order smaller than, those reported for SRP in McKnight et al. (2004). The magnitude of pulse uptake values was slightly higher than steady-state uptake values for both λ (mean λ_{pulse}:λ_{steady} = 1.23; paired t test P = 0.06) and v_f (mean $v_{f-pulse}$:$v_{f-steady}$ = 1.20; paired t test P = 0.04). Pulse uptake metrics shown in Fig. 5 also had a strong negative correlation with ambient SRP (for λ_{pulse}, r =

Table 1. Physical metrics and conservative transport parameters for south Wisconsin streams determined from paired tracer releases.

Reach	Abbrev.	Date	Amendment	Q, L s^{-1}	Reach length, m	Velocity, m s^{-1}	Depth, m	D, m^2 s^{-1}	A_t, m^2	A_s, m^2	α, s^{-1}	Tracer mass recovered, %	Da	F^{200}_{med}, %	As:A_t, %
Lowery 1–2	L_{1-2}	8/17/07	Pulse	80	100	0.10	0.63	0.25[a]	0.76 ± 0.032	0.15 ± 0.0027	0.0080 ± 0.0050	93.5	49[b]	16.5	20.0
Lowery 1–2	L_{1-2}	8/16/07	Continuous	84	100	0.11	0.61	0.25[a]	0.74 ± 0.020	0.093 ± 0.017	4.2E–04 ± 2.0E–04	99.6	3.4	6.0	13.0
Lowery 2–3	L_{2-3}	8/17/07	Pulse	83	166	0.12	0.53	0.17 ± 0.011	0.63 ± 0.0037	0.040 ± 0.0032	2.0E–04 ± 3.6E–05	102	4.6	1.7	6.3
Lowery 2–3	L_{2-3}	8/16/07	Continuous	87	166	0.13	0.55	0.15[a]	0.66 ± 0.015	0.056 ± 0.013	2.9E–04 ± 1.7E–04	99	4.7	2.8	8.4
Lowery 3–4	L_{3-4}	8/17/07	Pulse	88	186	0.12	0.57	0.35 ± 0.034	0.68 ± 0.0095	0.068 ± 0.0073	2.0E–04 ± 5.4E–05	96.4	3.4	2.6	10.0
Lowery 3–4	L_{3-4}	8/16/07	Continuous	92	186	0.13	0.62	0.20 ± 0.067	0.75 ± 0.015	0.064 ± 0.013	1.2E–04 ± 5.7E–05	98.7	2.2	1.3	8.6
Lowery 4–5	L_{4-5}	8/17/07	Pulse	108	253	0.14	0.53	0.27 ± 0.014	0.75 ± 0.0018	0.050 ± 0.0034	4.7E–05 ± 4.4E–06	98.9	1.4	0.4	6.7
Lowery 4–5	L_{4-5}	8/16/07	Continuous	110	253	0.15	0.53	0.20[a]	0.75 ± 0.017	0.027 ± 0.015	9.5E–05 ± 1.3E–04	100	4.6	0.4	3.6
East Branch Boulder	E	7/31/07	Pulse	17	120	0.087	0.13	0.10[a]	0.19 ± 4.9E–04	0.0034 ± 4.0E–04	5.7E–05 ± 1.9E–05	98.5	4.5	0.2	1.8
East Branch Boulder	E	7/30/07	Continuous	17	120	0.088	0.13	0.089 ± 0.0029	0.19 ± 3.8E–04	0.0062 ± 4.7E–04	3.5E–05 ± 5.9E–06	100	1.5	0.2	3.3
German Branch Pecatonica	G	6/15/07	Pulse	175	497	0.15	0.63	0.17 ± 0.060	1.20 ± 0.063	0.11 ± 0.062	8.7E–04 ± 8.2E–04	94.5	34[b]	5.8	9.2
German Branch Pecatonica	G	6/15/07	Continuous	175	497	0.15	0.61	0.12 ± 0.073	1.15 ± 0.092	0.059 ± 0.005	2.0E–04 ± 4.3E–05	97.1	14[b]	1.1	5.1
Lowery	L	7/26/07	Pulse	44	352	0.08	0.35	0.25[a]	0.53 ± 0.0020	0.028 ± 0.0014	9.4E–05 ± 1.4E–05	97.1	8.2	1.1	5.3
Lowery	L	7/25/07	Continuous	44	352	0.08	0.38	0.25[a]	0.57 ± 0.0050	0.042 ± 0.0047	1.3E–05 ± 4.7E–05	100	0.83	0.2	7.2
Manley	M	8/6/07	Pulse	52	170	0.094	0.37	0.10[a]	0.51 ± 0.0023	0.062 ± 0.0017	7.5E–04 ± 5.9E–05	105	13	8.6	12.0
Manley	M	8/3/07	Continuous	41	170	0.079	0.37	0.10[a]	0.52 ± 0.0096	0.075 ± 0.0085	4.2E–04 ± 1.2E–04	97.6	7.2	8.3	14.0
Rowan	R	7/10/07	Pulse	175	516	0.16	0.38	0.20[a]	1.05 ± 0.012	0.091 ± 0.0099	7.0E–04 ± 1.8E–04	105	28[b]	4.7	8.6
Rowan	R	7/10/07	Continuous	175	516	0.17	0.36	0.20[a]	1.02 ± 0.014	0.10 ± 0.013	5.1E–04 ± 1.5E–04	97.6	17[b]	4.0	10.0
West Branch Boulder	W	7/31/07	Pulse	7.4	200	0.069	0.086	0.030 ± 0.0030	0.10 ± 2.5E–04	0.0035 ± 3.6E–04	3.8E–05 ± 7.4E–06	97.2	3.3	0.4	3.4
West Branch Boulder	W	7/30/07	Continuous	7.4	200	0.072	0.083	0.040 ± 0.0021	0.099 ± 1.9E–04	0.0065 ± 1.8E–04	7.6E–05 ± 5.5E–06	100	3.4	1.2	6.5

Parameter errors are 1 SD from OTIS-P fits. Q, reach-averaged discharge; Da, Damkohler number.
[a]Dispersion coefficient (D) fixed in OTIS-P.
[b]$Da > 10$ (well outside preferred range of 0.5–5.0).

–0.92, $P = 0.009$; for $v_{f\text{-}pulse}$, $r = -0.86$, $P = 0.027$), demonstrating higher uptake at lower nutrient concentration. For continuous injections, ΔC ranged from 2 to 14 µg L^{-1}, median 4 µg L^{-1}. Relationships between uptake and amendment concentration were examined, but none were significant. Overall, nutrient pulses provided a similar characterization of streams along a processing gradient compared to continuous injections, although metrics from pulsed additions were slightly higher than those derived from continuous additions.

For two reaches (L_{1-2} and W), long tails in the SRP time series suggested a release of sorbed experimental P. At station L_2, SRP observations on the falling limb of the pulse exceeded even simulated conservative SRP transport values (Fig. 3, bottom panel, dashed line), likely owing to high enrichment at L_1. W also had a depositional lower segment which contained a large volume of fine sediment. In these two cases only, we used the Akaike information criterion (AIC_c; Akaike 1974) to determine whether sorption provided a better explanation for patterns in the SRP time series than first-order uptake alone, and then used λ values from the favored model to calculate uptake metrics reported in Table 2 and Fig. 5. In this expanded analysis, we compared simulated transport from a λ-uptake model (U) with simulated transport from a sorption model (S) and a combined uptake/sorption model (U + S). Sorption of SRP to sediments in the main channel (A) may be simulated using the OTIS model with three additional parameters: K_d (distribution coefficient, or partition coefficient, L^3 M^{-1}), ρ (mass of accessible sediment per volume of water, M L^{-3}), and $\hat{\lambda}$ (main channel sorption rate coefficient, T^{-1}); see Bencala (1983). Parameter values and model summary statistics for L_{1-2} and W are contained in Table 3, and supporting documentation is contained in Appendix 1. Using AIC_c, we selected the S model for L_{1-2} (Fig. 3, bottom panel, dotted line visible on falling limb), and the U + S model for W. We then used the associated λ values from these models ($L_{1-2} = 0$ s^{-1}; W = 3.2e–5 s^{-1}, open circle in Fig. 5) in

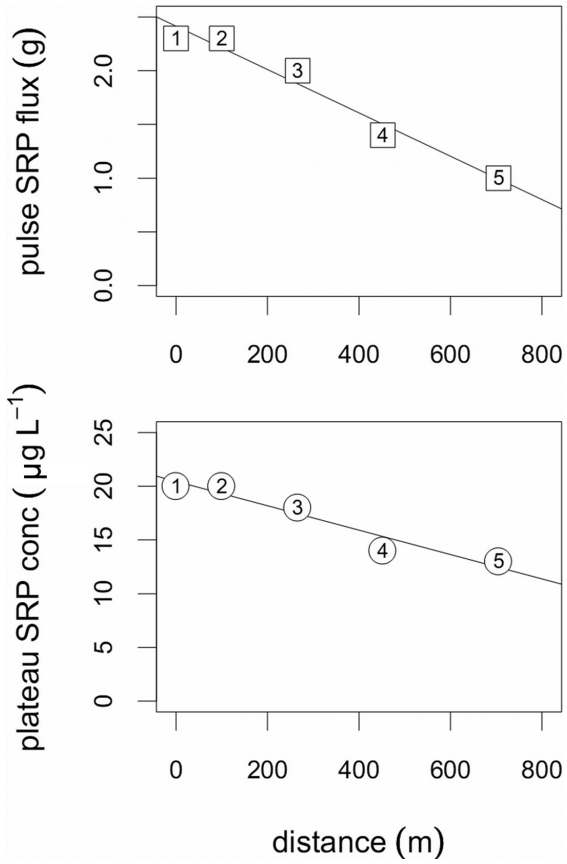

Fig. 4. Similar longitudinal patterns in experimental pulse flux and steady-state (plateau) concentration from paired SRP treatments across multiple stations of Lowery Creek (L_x), WI. Pulse SRP flux values are background corrected (r^2_{adj} = 0.95, P = 0.003). Plateau SRP concentration values are background and dilution corrected (r^2_{adj} = 0.92, P = 0.007).

our comparison of pulse and steady-state nutrient uptake. SRP processing across all other reaches was simulated with first-order uptake only.

Discussion

In this work, we provide evidence that pulse methods can yield nutrient uptake metrics similar to those of steady-state approaches, and therefore allow the successful characterization of nutrient processing rates across streams. Given the need for more versatile tools in lotic ecosystems, this result bodes well for future research applications. In addition, we found that pulse and continuously injected tracer data can yield similar conservative transport parameters in a transient storage model.

Agreement between pulse and steady nutrient uptake documented here is particularly noteworthy given the low nutrient demand of streams in this study. Background SRP concentrations in our study streams were intermediate or high in comparison to most published literature on stream P uptake (Mulholland et al. 1985, McKnight et al. 2004; but see Bernot et al. 2006), and the efficiency of nutrient assimilation (as quantified by v_f) typically decreases with increasing background nutrient concentration (e.g., Mulholland et al. 2008). For these reasons, measurement of v_f at high nutrient concentrations can sometimes be hindered by analytical limits. Situations of low nutrient uptake can also increase the uncertainty of these calculations (Hanafi et al. 2007). Nonetheless, despite potential obstacles presented by conditions of high nutrient availability and low uptake, the pulse approach yielded results broadly consistent with the steady-state approach.

The high degree of similarity between results for these two approaches was somewhat unexpected. Pulse releases can increase the uncertainty of conservative transport parameters (Wagner and Harvey 1997), in part because they do not integrate hydrologic variability over a very long period (Gooseff et al. 2008). Gooseff et al. (2008) also demonstrated that residence time distributions for conservative tracers in transient storage zones differed between pulse and continuous releases. When this happens, the important role of storage zones for nutrient retention (Valett et al. 1996) could serve to amplify differences in whole reach uptake between the methods. Also, because biological uptake rates are influenced by nutrient concentration, if large differences in enrichment concentrations between pulse and continuous amendments occur, uptake metrics should diverge. It is therefore reasonable to suspect that nutrient uptake estimates, which vary as a function of conservative transport parameters, might be sensitive to the nutrient amendment method.

Although we cannot conclusively identify the mechanisms that led to similar uptake metrics between methods in this work, the convergence of our results likely reflects several factors. First, our use of long mixing reaches for pulses allowed substantial solute spreading upstream of the first sampling point. This factor helped to integrate pulse solute movements over time, characterize the pulse time series accurately, and also avoid exceedingly high enrichment concentrations. Second, we achieved similar mean enrichment concentrations for pulses and continuous injections. This factor helped ensure that the mean experimental alteration of inorganic resources was small, or at least equivalent between treatments, compared to biological demand; it also could serve to minimize differences in uptake caused by differential sorption of P to sediments between amendment types. Third, transient storage in most study streams was relatively small, which might prevent the differential loading of transient storage zones (and associated reactive solute uptake) between releases described by Gooseff et al. (2008). But above all, we invite debate on an encouraging general idea: existing models may be used to interpret a wide range of spatial and temporal patterns from stream nutrient amendment experiments, and yield meaningful results. We expand on specific physicochemical and biological considerations of pulses below.

Physicochemical consideration of nutrient pulses—Results from this examination indicate that solute transport models can

Table 2. Pulse and steady-state SRP uptake metrics for south Wisconsin streams.

Reach	Abbrev.	Date	Amendment	SRP, mg L^{-1}			Nutrient uptake metrics				Nutrient mass recovered, %
				Ambient	C_{up}	C_{down}	λ, s^{-1}	S_w, m	U, μg m^{-2} min^{-1}	v_f, mm min^{-1}	
$Lowery_{1-2}$[a]	L_{1-2}	8/17/07	Pulse	0.033	0.055	0.023	0.0	Infinite	0.0	0.0	100.0
$Lowery_{1-2}$	L_{1-2}	8/16/07	Continuous	0.045	0.020 ± 3.E–04	0.020 ± 5.E–04	0.0	Infinite	0.0	0.0	—
$Lowery_{2-3}$	L_{2-3}	8/17/07	Pulse	0.029	0.023	0.015	1.8E–04 ± 0.00001584	650 ± 56	170 ± 15	5.9 ± 0.50	90.5
$Lowery_{2-3}$	L_{2-3}	8/16/07	Continuous	0.043	0.020 ± 5.E–04	0.017 ± 2.E–04	2.3E–05 ± 4.01797E–05	5120 ± 8800	32 ± 55	0.74 ± 1.3	—
$Lowery_{3-4}$	L_{3-4}	8/17/07	Pulse	0.029	0.014	0.009	2.4E–04 ± 0.0000261	510 ± 57	230 ± 26	8.0 ± 0.89	75.1
$Lowery_{3-4}$	L_{3-4}	8/16/07	Continuous	0.042	0.017 ± 2.E–04	0.014 ± 5.E–04	9.4E–05 ± 1.63898E–05	1280 ± 220	130 ± 24	3.2 ± 0.56	—
$Lowery_{4-5}$	L_{4-5}	8/17/07	Pulse	0.027	0.009	0.004	1.8E–04 ± 0.00003596	782 ± 160	150 ± 31	5.7 ± 1.1	70.7
$Lowery_{4-5}$	L_{4-5}	8/16/07	Continuous	0.039	0.014 ± 5.E–04	0.009 ± 3.E–04	3.1E–05 ± 2.00164E–05	4540 ± 3000	38 ± 25	0.98 ± 0.64	—
East Branch Boulder	E	7/31/07	Pulse	0.031	0.048	0.024	1.1E-04 ± 0.00000996	808 ± 75	26 ± 2.4	0.84 ± 0.078	86.4**
East Branch Boulder	E	7/30/07	Continuous	0.029	0.039 ± 4.E–04	0.029 ± 3.E–04	8.5E–05 ± 1.51994E–05	1040 ± 190	19 ± 3.4	0.66 ± 0.12	—
German Branch Pecatonica	G	6/15/07	Pulse	0.040	0.021	0.008	1.2E–04 ± 0.00001484	1300 ± 170	96 ± 12	4.4 ± 0.56	72.7[b]
German Branch Pecatonica	G	6/15/07	Continuous	0.040	0.013 ± 4.E–04	0.008 ± 4.E–04	1.2E–04 ± 2.5826E–05	1280 ± 280	160 ± 36	4.3 ± 0.95	±
Lowery	L	7/26/07	Pulse	0.017	0.037	0.007	1.8E–04 ± 0.00001571	447 ± 39	64 ± 5.6	3.8 ± 0.33	47.5[b]
Lowery	L	7/25/07	Continuous	0.017	0.032 ± 9.E–04	0.015 ± 9.E–05	1.3E–04 ± 7.422E–06	607 ± 34	90 ± 5.1	3.0 ± 0.17	—
Manley	M	8/6/07	Pulse	0.034	0.084	0.021	8.8E–05 ± 0.00001698	1070 ± 210	66 ± 13	1.9 ± 0.38	87.7[b]
Manley	M	8/3/07	Continuous	0.028	0.034 ± 4.E–04	0.023 ± 1.E–04	6.0E–05 ± 7.43499E–06	1310 ± 160	37 ± 4.6	1.3 ± 0.17	—
Rowan	R	7/10/07	Pulse	0.022	0.031	0.008	7.4E–05 ± 0.00001405	2160 ± 410	52 ± 9.9	1.7 ± 0.32	71.1[b]
Rowan	R	7/10/07	Continuous	0.022	0.016 ± 5.E–04	0.013 ± 5.E–05	5.4E–05 ± 8.89162E–06	3170 ± 530	19 ± 3.1	1.2 ± 0.19	—
West Branch Boulder[a]	W	7/31/07	Pulse	0.051	0.034	0.015	3.2E–05 ± 0.00001361	2190 ± 940	8.3 ± 3.6	0.16 ± 0.070	91.7[b]
West Branch Boulder	W	7/30/07	Continuous	0.050	0.035 ± 2.E–04	0.023 ± 1.E–04	3.6E–05 ± 0.00004049	2020 ± 2300	6.2 ± 7.1	0.18 ± 0.20	—

Errors are 1 SD. C_{up} and C_{down} are background-corrected enrichment concentrations (for pulses, peak nutrient concentration; for continuous injections, mean stable nutrient concentration).

[a]For this reach, P dynamics were modeled with a sorption algorithm (see text and Appendix 1).

[b]Simulated SRP values (extrapolated over time) were used to quantify nutrient output flux.

attribute longitudinal nutrient declines to first-order uptake when they may be better explained by other mechanisms such as sorption. As described earlier, sorption of P to sediments in the uppermost reach of the multiple station examination in Lowery Creek (L_{1-2}), and subsequent P release, were evident from a long SRP tail in the pulse time series at 100 m (Fig. 3). The same pattern was evident in W, albeit to a lesser degree. Although the apparently large influence and longitudinal extent of this pattern in reach L_{1-2} was somewhat surprising, its presence was not. Near the additional location in pulse experiments, stream nutrient concentration changes rapidly and attains a high peak, creating large sediment–water nutrient gradients. This should promote adsorption of experimental P to sediments on the rising limb of the pulse (increasing the rate of longitudinal decline for the peak concentration) and desorption on the falling limb (increasing the skewness of the nutrient time series at each station by elevating and extending the tail). Tails in the SRP time series for pulses in systems other than Lowery Creek sometimes existed at the upstream station but were not substantially extended at the downstream station, suggesting minimal sorption influence. It is nonetheless possible that sorption contributed to slightly higher uptake in pulses versus continuous injections, and this effect might have been magnified relative to overall uptake due to consistently low rates of assimilation in our study streams.

Strategies for dealing with sorptive nutrients such as PO_4^{3-} or NH_4^+ in ecological studies of streams and rivers using experimental pulses include the following: (1) construct the input time series from samples collected at a station that is a substantial distance from the enrichment location, in an effort to avoid areas where the effect of sorption is highest; (2) use a multiple reach approach, such as the one we employed in L_{1-5}, to identify the

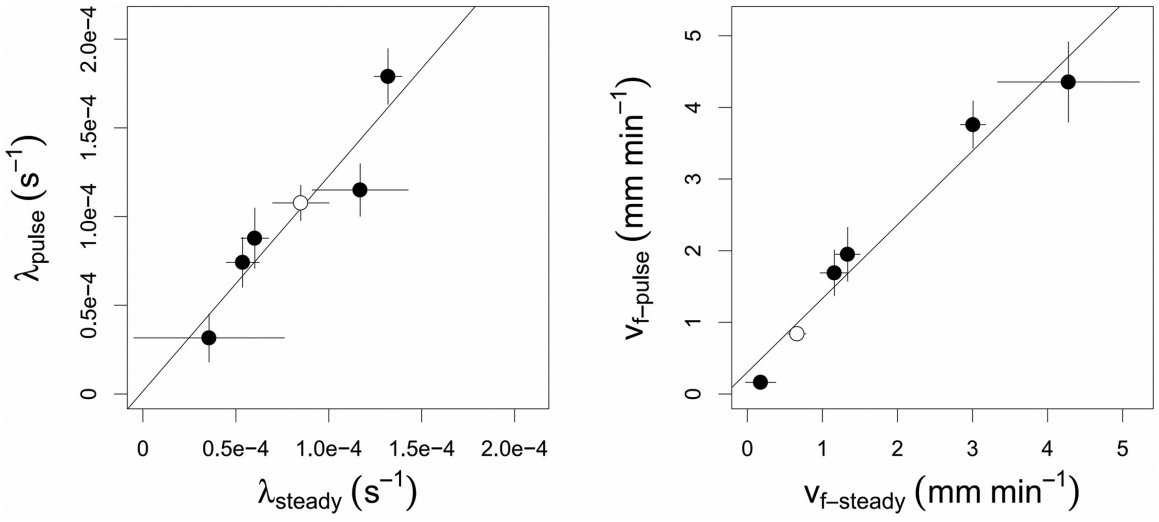

Fig. 5. Similarity in pulse and steady-state SRP uptake rate from paired treatments in multiple streams. For λ, r^2_{adj} = 0.84, slope = 1.21 (P = 0.006); for v_f, r^2_{adj} = 0.95, slope = 1.03 (P < 0.001). Open circle, West Branch Boulder (W), for which a combined model of sorption + first-order uptake was used; error bars, 1 SD.

distance where sorption effects become sufficiently small, and highlight patterns downstream of this point; (3) account for sorption and attempt to partition its influence from first-order uptake with models, as demonstrated for reaches $L_{1–2}$ and W (see Appendix 1), or with field measurements. Further, regarding continuous injections, we add that as the stable experimental nutrient concentration (plateau) is approached, sediments over the study reach may have sufficient opportunity to equilibrate with P-enriched water. If equilibration occurs, this will release P spiraling from sorption control in accordance with equilibrium phosphorus concentration (EPC) considerations. Assuming no other processing mechanisms, P uptake metrics calculated during truly stabilized experimental conditions may thus isolate the gross rate of biotic P assimilation. Yet, because the steady-state approach does not involve the construction of solute time series, it does not provide a means to evaluate experimental successes or failures in achieving steady enriched conditions. Thus, stream researchers may favor continuous injections for ecological questions involving additions of sorptive species, but given the assumptions of equilibrium-based modeling, should find value in the flexibility of time series approaches for continuous nutrient injections.

Biological consideration of nutrient pulses—The influence of nutrient concentration on spiraling dynamics (see Mulholland et al. 2008), such as higher NH_4^+ uptake (v_f) at low nutrient concentrations (Dodds et al. 2002) and longer S_w with non-isotopic PO_4^{3-} releases than isotopic releases (Mulholland et al. 1990), are well established. Strong negative relationships between ambient SRP and pulse uptake metrics reported here demonstrate that pulse approaches can capture these expected patterns. To minimize possible differences in nutrient uptake between pulses and continuous injections caused by differences in experimental concentrations, we sought to achieve peak upstream and downstream pulse nutrient concentrations that bounded the continuous enrichment target (yielding similar reach-averaged SRP concentration). Although we do not have statistical evidence of an enrichment effect on uptake, enrichment magnitude almost certainly influences the biological assimilation of a nutrient pulse to some degree. Because lower nutrient concentrations are known to yield higher (approaching ambient) measures of uptake velocity (e.g., Earl et al. 2006), local uptake velocity will increase longitudinally along a stream as a nutrient pulse disperses if all other factors are held constant. This means that pulse approaches likely underestimate uptake velocity at the upper end of a study reach. On the other hand, in some cases the brevity of the pulse approach may actually serve to minimize unwanted treatment effects (e.g., luxury uptake). Still, interpreting the magnitude of a nutrient pulse, which changes rapidly in time and space owing to hydrologic dispersion, is less straightforward than for continuous injections. For future studies involving nutrient spiraling in lotic ecosystems, tradeoffs between pulse and continuous injection approaches merit thorough consideration during experimental design.

Comments and recommendations

For nutrient spiraling in lotic ecosystems, alternatives to the steady-state, continuous injection approach are rare in the literature. In this work, we provide evidence that short-term nutrient pulses modeled dynamically, which afford fewer constraints in application, can yield meaningful information and results similar to those of more conventional stream methods. The advantages of pulse nutrient spiraling experiments are particularly evident for lotic ecosystems with

Table 3. Comparison of multiple candidate models of soluble reactive phosphorus (SRP) transport from two experimental nutrient pulses, including sorption and first order uptake. In these cases only, SRP release was evident from pulse nutrient time series, suggesting the influence of sorption.

Reach name	Abbrev.	Candidate model	Parameters						
			λ, s^{-1}	K_d, L kg^{-1}	$\hat{\lambda}$, s^{-1}	ρ, g m^{-3}	k	RSS, mg^2 L^{-2}	AIC_c
West Branch Boulder	W	First-order uptake only (U)	1.0E–4 ± 1.1E–5	—	—	—	1	2.10E–05	–192.6
		Sorption only (S)	—	200, fixed	4.9E–4 ± 9.7E–5	1500 ± 240	3	4.60E–06	–214.3
		Sorption + first-order decay (U + S)	3.2E–5 ± 1.4E–5	200, fixed	8.8E–4 ± 2.8E–4	720 ± 240	4	3.80E–06	–214.4
Lowery 1–2	L_{1-2}	First-order uptake only (U)	3.2E–4 ± 2.3E–5	—	—	—	1	5.70E–05	–308.0
		Sorption only (S_1)	—	110, fixed	6.1E–4 ± 1.2E–4	6200 ± 1000	3	1.90E–05	–336.3
		Sorption only (S_2)	—	440, fixed	6.1E–4 ± 1.2E–4	1600 ± 250	3	1.90E–05	–336.3
		Sorption + first-order decay (U + S)	Could not be fitted (high uncertainty, too many parameters)				—	—	—

long residence time or large transient storage zones (e.g., wetland streams, run-of-river reservoirs), which require exorbitant time to achieve stable nutrient conditions required by the steady-state approach.

Certainly, there are tradeoffs in the application of experimental nutrient pulses—which briefly inundate organisms with limiting resources, and cause a large longitudinal gradient in nutrient concentration—and continuous injections—which are not practical in many cases, especially if modeled with the steady-state approach. Although we found similar results from two very different approaches to the quantification stream nutrient uptake, we advise that whenever possible, researchers should select a single method for each study and apply it consistently (see also Gooseff et al. 2008). We also advise that, whereas spike/slug releases are convenient in terms of speed, the control offered by continuous injections is an important experimental consideration. In many cases, the use of nutrient time series from abbreviated continuous injections represents a useful compromise between speed and control. Many questions remain and present opportunities for future research; these include the study of real-world nutrient pulses in agricultural or urban streams and rivers. Application of unsteady releases of experimental nutrients and the use of dynamic biogeochemical models can help us extract new mechanistic information about nutrient spiraling, and also expand the scope of this classic framework to settings that represent gaps in our current understanding of ecosystems.

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