

Benthic sediment influence on dissolved phosphorus concentrations in a headwater stream

Noah R. Lottig · Emily H. Stanley

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Abstract Phosphate interacts with inorganic sediment particles through sorption reactions in streams. Collectively, this phosphorus (P) buffering mechanism can be an important determinant of soluble reactive P (SRP) concentrations. If sorption reactions control SRP concentrations in a stream, then differences in sediment characteristics may cause spatial differences in SRP concentrations. This prediction was tested by examining sediment-buffering characteristics and spatial variation in SRP among reaches with distinct sediment composition (i.e., fine versus coarse particles) in two tributaries of Boulder Creek, a headwater stream in central Wisconsin. SRP concentrations were significantly lower and algal available P and P sorption capacity were significantly higher in the reach dominated by fine sediments. Although fine particles such as sand had the greatest P sorption capacity, no retention could be attributed to biotic processes, whereas over 50% of P retention in coarse particles such as gravel could be linked to biotic uptake. Equilibrium P concentration (EPC_0) assays from different sediment fractions also indicate that biotic uptake is relatively unimportant in sand particles (EPC_{live} 10 $\mu\text{g/L}$; EPC_{killed} 10 $\mu\text{g/L}$) but very important in gravel or larger particles (EPC_{live}

10 $\mu\text{g/L}$; EPC_{killed} 80 $\mu\text{g/L}$). Thus, sediment influence on stream water P concentrations can shift predictably from abiotic sorption in reaches with fine particles to biotic retention in areas dominated by coarse sediments. Consequently, changes in sediment composition due to natural or anthropogenic disturbance have the potential to alter the type and strength of sediment-associated processes determining ambient stream P concentrations.

Keywords Phosphorus retention · Sediments · Equilibrium phosphorus concentration · EPC · Extractable phosphorus · Streams

Introduction

Concerns over anthropogenic enrichment of aquatic ecosystems have lead to a plethora of studies examining internal ecosystem processes regulating ambient nitrogen (N) and phosphorus (P) concentrations. Unlike N, which is strongly regulated by biotic processes, dissolved P in aquatic ecosystems is influenced by both biotic and abiotic dynamics (reviewed by Reddy et al. 1999; Mainstone and Parr 2002). However, studies examining retention of P in streams have tended to emphasize either the role of abiotic processes associated with fine sediment in controlling ambient P, or biotic uptake associated with primary producers or decomposers. Consequently, it

N. R. Lottig (✉) · E. H. Stanley
Center for Limnology, University of Wisconsin, 680 N.
Park St., Madison, WI 53706, USA
e-mail: nrlottig@wisc.edu

is not clear how these two processes interact to determine water column P concentrations.

Biotic processes affecting stream water P include assimilation by both primary producers and decomposers, as well as mineralization of organic P. Studies highlighting biotic control have often relied on reach-scale solute addition methods and demonstrate positive relationships between dissolved P uptake and coarse particulate organic matter (Mulholland et al. 1985), bryophytes (Meyer 1979), algae (Tate et al. 1995), or large woody debris dams (Valett et al. 2002). Measured uptake lengths or rates are often temporally variable, reflecting seasonal or episodic changes in biotic activity in streams (Mulholland et al. 1985; Doyle et al. 2003b).

Abiotic control on P in streams and rivers is often described in terms of a collection of geochemical reactions collectively referred to as the ‘phosphate buffering mechanism’ (Froelich 1988) in which phosphate sorption to and release from suspended and benthic particle surfaces determines water column concentrations. Buffering kinetics may be affected by redox status, pH, cation concentrations, geological variation in sediment composition, and, in particular, by particle size (Froelich 1988; Stone and Murdoch 1989; House and Denison 2000), with small particles being particularly effective in exerting abiotic control on water column P (Klotz 1988; He et al. 1995). Despite various physicochemical influences, the phosphate buffering mechanism can maintain relatively constant concentrations of P within an individual river or stream (Froelich 1988).

Streams are heterogeneous ecosystems, and often, bed materials are composed of mixtures of particle sizes ranging from fine silts to large boulders. Thus, it is reasonable to assume that both biotic and abiotic processes may be involved in determining water column phosphate concentrations, or that the dominant type of control might vary spatially or temporally. Given the potential for both abiotic and biotic processes to affect phosphorus concentrations in streams, we asked: can spatial variation in benthic particle size composition affect water column phosphate concentrations? More specifically, we hypothesized that, all else being equal, differences in sediment size among streams can affect P concentrations by both shifting the balance between abiotic and biotic processes and influencing the overall magni-

tude of sediment-associated P processes such as uptake.

We expected that as particle size increases, the proportion of biotic P uptake will also increase relative to abiotic processes. We also expected that as particle size increases, the total magnitude of P uptake associated with sediment would decrease due to decreases in total particle surface area. The goal of this study was to test this hypothesis by: (1) characterizing sediment particle size composition in two adjacent streams to document differences in bed materials; (2) determining water column and sediment phosphorus concentrations in these streams; and (3) conducting a series of experiments to explore the relative contributions of abiotic and biotic processes to phosphorus uptake across a range of benthic sediment particle sizes. This study was done in a relatively pristine study system so that confounding effects associated with anthropogenic pollution (e.g., heavy metal or other contaminant interactions with P; Gainswin et al. 2006; Lottig et al. in press or larger-scale processes controlling input and retention of P in human-dominated systems; Haygarth et al. 2005) were minimized, allowing us to focus on effects of variability in sediment size on P dynamics.

Study site

The Boulder Creek watershed is a second-order catchment draining a relatively steep region of Pre-Cambrian quartzite with small deposits of sandstone and limestone derived from glacial drift (Martin 1965) in south-central Wisconsin, USA (43°27′30″N, 89°38′00″W; Fig. 1). The 40.6 km² watershed is dominated by a mature red oak (*Quercus rubra*) and sugar maple (*Acer saccharum*) forest, and the entire stream system lies within the forest cover. Because of the well-developed canopy, the stream is highly heterotrophic, and the relatively depauperate autotrophic community characterized by diatoms (Rodgers et al. in review). Sampling efforts focused on two 360-m reaches within separate first-order streams in the upper watershed. Both channels originate from a single wetland and flow ~1.5–2 km before joining to form a second-order channel. Stream width varied from ca. 0.5 upstream to ~1 m at the downstream end of both reaches. Larger rocks and gravel are

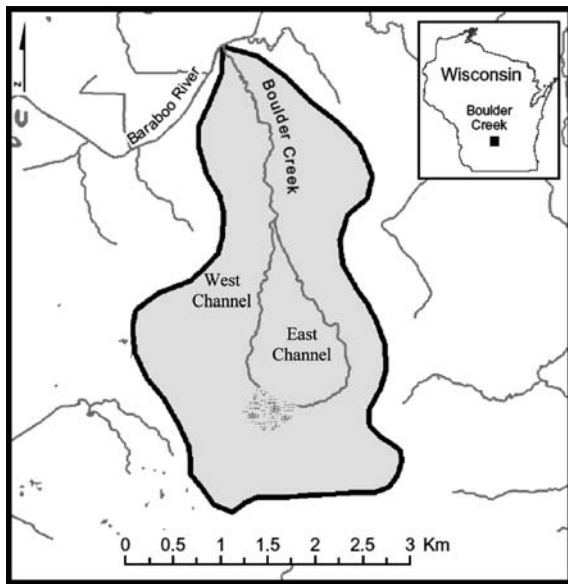


Fig. 1 Map of Wisconsin (USA) showing the location of Boulder Creek (inset) and the Boulder Creek catchment. Study reaches were the downstream-most 360 m of each first order tributary prior to forming Boulder Creek

conspicuous in the western channel, whereas finer-grained materials are obvious in the eastern branch. The differences in sediment composition appear to be due to local differences in hillslope steepness and erosion. Water quality in Boulder Creek is considered relatively high, as baseflow suspended sediment and total P concentrations are low (<50 mg/L TSS; <0.060 mg/L total P). Dissolved organic carbon concentrations also tend to be low during spring, summer, and winter (<4 mg/L); consequently, organic P represents a small fraction of the total P pool during most months. pH in both channels ranged from 7.3 to 7.8. Discharge in the east channel (17 ± 5 L/s) was typically double those observed in the west channel (7 ± 1 L/s).

Methods

Stream bed sediment composition

Benthic sediment composition was determined every 15 m within each stream in June 2003 (25 grids/channel). A 0.5 m^2 gridded quadrat was placed in the center of the channel and sediment composition was

drawn to scale at each site to create a set of maps of bed composition (after Weinberg 1981). Quadrats covered anywhere from 30 to 100% of the stream channel width. Benthic particle classes were divided into six categories (after Bunte and Abt 2001): clay (<0.0039 mm), silt (0.0039 – 0.063 mm), sand (0.063 – 2.0 mm), gravel (2 – 64 mm), cobbles (64 – 256 mm), and boulders (>256 mm). Particle sizes larger than 2 mm were determined by direct measurements in the field, and identification of areas of sand and fine depositional fractions (i.e., clay, silts, and organic matter) were based on visual inspection. Hand-drawn maps of stream bed sediments were scanned and digitized to determine the distribution of each particle category using a sample area-analysis program (Burkett and Gusftason 1995).

Five sediment cores (5-cm diameter, 3–5-cm deep) were taken from random areas identified as sand or depositional sediment in each channel to validate visual classification of these fractions. No areas of depositional sediment large enough to core were observed in the eastern channel and consequently only sand fractions were collected. Sub-samples were ashed at 500°C for 4 h to determine organic content. Particle sizes of each core was determined using a hydrometer with aggregate dispersion following Elliott et al. (1999). Field-defined sand and depositional fractions were subsequently adjusted to account for laboratory texture and organic matter analysis results. Differences in sediment distribution between the east and west branches were determined by standard *t*-tests on arcsin-square root transformed data.

Longitudinal water chemistry surveys

Two water samples for nutrient and anion analyses were collected at 15-m intervals from both first-order streams on a single day in August 2002, April 2003, and July 2003 (50 samples per channel). An additional two-field replicate samples were collected at three transects in each reach (top, middle, and bottom; six samples per reach). Field replicate samples differed by $<2\%$; consequently, we report mean concentrations for each transect. Samples were filtered through a $0.45 \mu\text{m}$ Millipore HA syringe filter immediately after collection and stored on ice in acid-clean polyethylene bottles until returned to the laboratory. Additional unfiltered samples for cation

analysis were taken every 75 m and stored on ice in acid-clean polyethylene bottles until returned to the lab where they were acidified with ultra-pure 10% HCl.

Calcium (Ca) and magnesium (Mg) were determined on a Perkin-Elmer Optima 4300 DV inductively coupled plasma optical emissions spectrometer (ICP-OES). Soluble reactive phosphorus (SRP) was determined by the ascorbic acid method (APHA 1995) within 24 h of collection to minimize errors associated with sample instability (Haygarth et al. 1995). Additional aliquots of each sample were analyzed for nitrate-N ($\text{NO}_3\text{-N}$), sulfate (SO_4), and chloride (Cl) using a Dionex DX-500 ion chromatograph with an AS14A column following USEPA standard methods (1993). The specific conductivity of each filtered sample was immediately measured upon return to the laboratory using a bench-top conductivity probe (WTW Cond340i) after removing aliquots for nutrient analyses.

Spatial patterns in SRP profiles were analyzed by analysis of covariance (Ott and Longnecker 2001). Background water chemistry samples were analyzed with two-way ANOVA with reach (east and west) and location (head or base) as factors. Tukey *t*-tests were used for all post hoc multiple comparisons when an interaction was present.

Sediment/phosphorus interactions

To identify effects of particle size on stream P dynamics, a series of experiments were conducted to characterize sediment P content and uptake characteristics. Benthic sediments were collected from the top 1–5 cm of stream bed at 60-m intervals using a polyethylene corer (4 cm in diameter). Sediments in the sand size class were collected from the east channel and gravel was collected from the west channel. Due to the lack of adequate sediment distribution among the reaches, we were not able to collect sufficient sand samples from the west channel or gravel from the sandy eastern channel. Two gravel size fractions were collected: small gravel particles ranged from 5 to 10 mm and large gravel particles ranged in size from 15 to 30 mm. Sediment samples were stored on ice and returned to the laboratory where they were refrigerated until analysis. At no stage did the sediments freeze, and all sediment analyses were initiated within 12 h of collection.

Algal-available SRP associated with sediments (hereafter sediment P) was determined by NaOH–NaCl extraction following methods of Pionke and Kunishi (1992). Briefly, ~3–4 g of large gravel, 1–2 g small gravel, or 0.3 g sand were placed into polyethylene cups with a 40 mL mixture of 0.1 N NaOH and 0.1 M NaCl on a shaker table for 16 h. A 15 mL aliquot was removed, filtered, and analyzed for SRP. Sediment samples were then dried at 60°C for dry weight (dw) determination and all results are reported as $\mu\text{g P extracted/g dw sediment}$. Differences between size classes were analyzed with a one-way ANOVA and longitudinal changes within each size class were assessed by regressing sediment P against distance downstream.

Sediment phosphorus uptake (SPU) was determined for intact (live) and HgCl_2 -amended (killed) sediments to assess the relative contribution of biotic and abiotic uptake of P. Sorption by live sediments represents both biotic and abiotic processes while sorption by killed sediments is a function of abiotic processes alone (Meyer 1979; Klotz 1988). Biotic uptake can then be calculated by subtracting abiotic sorption from total (live) sorption. Sediment samples were incubated in a 100 $\mu\text{g/L PO}_4\text{-P}$ solution buffered with 50 mg/L CaCl_2 and 30 mg/L MgCl_2 to match natural stream water ionic strength (Klotz 1988, 1991) at a 1:10 (g sediment : mL solution) ratio. Samples were continually agitated, and after 24 h, the aqueous and sediment phases were separated by filtration. SRP was determined as previously described. SPU ($\mu\text{g g}^{-1} \text{ h}^{-1}$) was determined as:

$$\text{SPU} = \frac{\text{SRP}_{\text{initial}} - \text{SRP}_{\text{final}}}{\text{sediment dw} \times t}, \quad (1)$$

where *t* is incubation time in hours.

Phosphorus sorption index (PSI), a measure of the sediments ability to sorb large amounts of phosphorus (Bache and Williams 1971; Klotz 1985), was determined on live and killed sediment treatments as previously described for uptake measurements. One hundred mL of filtered stream water was added to 20–30 g of wet sediments and spiked with a KH_2PO_4 stock solution to achieve a final concentration of 2,000 $\mu\text{g P/L}$. Samples were shaken for 10 s every 15 min. After 1 h, a 15-mL aliquot was removed, filtered, and analyzed for SRP as described previously. Sediment

samples were dried at 60°C after extraction for dw determination. PSI was calculated as:

$$\text{PSI} = \frac{\left(\frac{(\text{SRP}_{\text{initial}} - \text{SRP}_{\text{final}}) \times \text{vol}}{\text{sediment dw}} \right)}{\log (\text{SRP}_{\text{final}})} \quad (2)$$

The equilibrium phosphorus concentration (EPC_0 sensu Froelich 1988) is the ambient concentration at which phosphorus is neither released nor taken up by sediments, and thus it provides a metric for assessing whether sediment acts as a source or sink of P depending on the water column SRP concentration, and consequently its potential to control water column P concentrations (Taylor and Kunishi 1971). EPC_0 of both live and killed sediments were determined by the techniques described by Froelich (1988), Klotz (1991), and House and Denison (2000). Four phosphorus solutions (0, 25, 50, 100 $\mu\text{g/L}$) were made by diluting a KH_2PO_4 stock into a 50 mg/L CaCl_2 + 30 mg/L MgCl_2 solution (again, to match natural stream water ionic strength; Klotz 1988, 1991). To compensate for decreases in number of particles per gram while maintaining a 1:10 ratio (g sediment : mL solution) across the range of particle sizes, we incubated ~10 g of sand or small gravel in 100 mL of each solution and 30 g of large gravel in 300 mL of each solution. All samples were stirred gently on a shaker table for 24 h (House and Denison 2000). The aqueous and sediment phases were separated by filtration for SRP determination. The change in phosphorus ($\mu\text{g P/g dw}$ sediment) was regressed against the final SRP concentration, and EPC_0 was calculated as the x -intercept of this plot (Froelich 1988).

We used a two-way ANOVA with sediment type (sand, small gravel, and large gravel) and treatment (live or killed) as factors to identify differences in SPU, PSI, and EPC_0 values. Tukey t -tests were used for all post hoc multiple comparisons when an interaction was present. All data were checked for normality using the Shapiro–Wilk test. Non-normal data were appropriately transformed if possible to satisfy normality tests and transformation used noted in text. All statistical tests were performed using SAS (Version 9.1 SAS Institute Inc., Cary, NC, USA).

Results

Stream bed sediment composition

Benthic sediment composition between the east and west channels differed significantly (Fig. 2). The east channel was characterized by extensive areas of 100% sand, while the west channel was composed of primarily large cobbles and rocks interspersed with small gravel. Areas of fine depositional sediments were rarely observed in either reach and both sand and depositional sediments constituted <4% of the total benthic substrate in the west channel (Fig. 2).

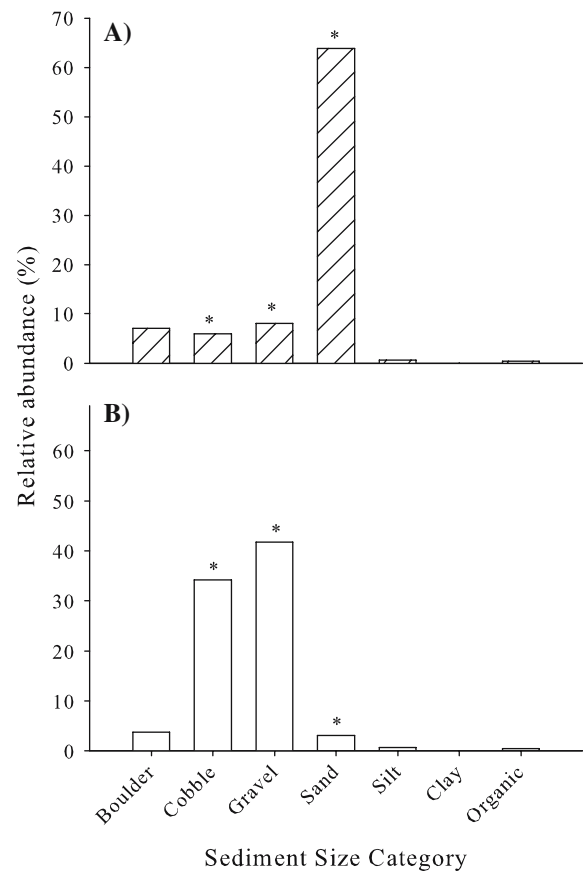


Fig. 2 Relative abundance of sediment categories in the east (a) and west (b) channels of Boulder Creek. Error bars (mean \pm SE) are represented within the thickness of the line. Data were arcsin-square root transformed prior to statistical analysis. Significant differences ($P < 0.05$) between reaches with regard to the proportion of sediment present in a given size category are identified with an asterisk following standard t tests

Gravimetric analysis of sediment cores collected from areas identified as sand in both the east and west channels indicated that these areas were dominated by sand-sized particles and included a small percentage of silt and clay (Table 1). As previously noted, no areas of depositional sediment were observed in the east channel; areas defined as depositional sediments in the west channel were composed primarily of sand (59.3 ± 4.1), silt (25.3 ± 5.0), and organic matter (12.9 ± 0.1 ; Table 1). However, when these results were scaled up to the entire reach, they indicated that silts and clays composed <1% of the benthic sediment in the west channel (Fig. 2).

Longitudinal water chemistry surveys

Water chemistry characteristics of the two channels were generally similar, although some significant differences were observed (Table 2). Cl concentrations were relatively low (4.48–5.15 mg/L) and not significantly different between channels ($F = 1.68$ and $P = 0.19$). $\text{NO}_3\text{-N}$ was significantly different between channels ($F = 20.79$ and $P < 0.01$). However, concentrations were typically <10% higher in the west channel. SO_4 concentrations were similar at the head of either channel ($t = 1.85$ and $P = 0.07$), but were significantly higher at the base of the east channel (13.53 ± 0.09 mg/L, $t = 6.09$ and $P < 0.01$) relative to the west channel (12.51 ± 0.01 mg/L). Similar to Cl, no significant differences were noted in Ca (57.7–65.7 mg/L) between the two channels ($F = 2.79$ and $P = 0.10$). Although significant ($F = 5.47$ and $P = 0.04$), Mg concentrations were <1 mg/L higher in the east channel and did not vary longitudinally in either channel. No statistics were run on conductivity data due to non-normally distributed data (Shapiro–Wilk $W = 0.94$ and $P = 0.03$), but we observed substantial overlap in the range of conductivity values (486–534 $\mu\text{S/cm}$) between the two streams (Table 2).

The most conspicuous difference in water chemistry between the east (sand) and west (gravel) channels was seen in the longitudinal SRP profiles (Fig. 3). SRP concentrations in the west channel (36–52 $\mu\text{g/L}$) were significantly higher ($F = 4,718.34$ and $P < 0.01$) than in the east channel (20–28 $\mu\text{g/L}$) and increased by 5–10 $\mu\text{g/L}$ over the 360 m reach on all sampling dates ($F > 77$ and $P < 0.01$). SRP concentrations in the west channel also varied by up to 70% among the three survey dates, while SRP in the east channel remained relatively constant among over time. Consequently, SRP concentrations always increased significantly more in the west channel ($F = 353.14$ and $P < 0.01$) over the course of the study.

Sediment/phosphorus interactions

The amount of algal available P differed significantly among sediment size classes ($F = 63.82$ and $P < 0.01$). Sandy sediments contained the largest quantities of extractable P (11.6 ± 1.2 $\mu\text{g/g}$), and the amount of extractable P decreased with increasing particle size (large gravel 1.3 ± 0.5 $\mu\text{g/g}$; Fig. 4). Extractable P on sand fractions collected from the east channel was significantly correlated with distance downstream ($r^2 = 0.27$, $F = 5.91$, and $P = 0.03$), while no significant correlation was observed with either small or large gravel fractions collected from the west channel (Fig. 5).

Sediment P uptake rates varied among particle size categories and live versus killed sediments ($F = 29.71$ and $P < 0.01$; Fig. 6). Greatest uptake rates were measured for the sand fraction (0.023 ± 0.002 $\mu\text{g g}^{-1} \text{h}^{-1}$) and decreased by ca. 1× for small gravel (0.011 ± 0.006 $\mu\text{g g}^{-1} \text{h}^{-1}$) and 1.5× for the large gravel fraction (0.009 ± 0.007 $\mu\text{g g}^{-1} \text{h}^{-1}$). Over all size fractions, live sediments exhibited greater uptake relative to killed samples ($F = 5.52$ and $P = 0.03$): 100% of uptake for the sand fraction, 63% for small gravel,

Table 1 Gravimetric analysis of sediments identified as sand and depositional fractions in the field from the east (sand) and west (gravel) reaches

Sediment type (Reach)	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Organic (%)
Sand (East channel)	3.0 ± 0.7	95.3 ± 0.7	1.1 ± 0.1	0.0 ± 0.0	0.6 ± 0.0
Sand (West channel)	5.9 ± 2.4	89.1 ± 2.5	3.8 ± 0.4	0.6 ± 0.3	0.6 ± 0.0
Depositional (West channel)	2.4 ± 1.2	59.3 ± 4.1	25.3 ± 5.0	1.2 ± 0.4	12.9 ± 0.1

Values are mean ± 1 SE

Table 2 Stream water concentrations for dominant anions and cations in two tributary channels of Boulder Creek

Reach	SRP (mg/L)	NO ₃ -N (mg/L)	SO ₄ (mg/L)	Cl (mg/L)	Ca (mg/L)	Mg (mg/L)	Cond. (µs/cm)
East (sand)							
0 m	0.024 (0.019–0.027)	1.58 (1.37–1.69)	13.1 (12.4–13.7)	4.48 (3.80–5.21)	62.9 (61.8–65.7)	34.4 (33.4–35.0)	519 (506–534)
360 m	0.026 (0.024–0.027)	1.47 (1.42–4.49)	13.5 (13.1–14.4)	4.75 (4.02–5.34)	60.0 (59.6–60.5)	32.4 (31.8–32.9)	511 (486–527)
West (gravel)							
0 m	0.040 (0.036–0.043)	1.81 (1.58–2.02)	12.8 (12.6–12.9)	5.15 (4.85–5.55)	60.3 (57.7–61.4)	32.1 (31.0–32.6)	514 (508–521)
360 m	0.048 (0.044–0.052)	1.61 (1.47–1.72)	12.5 (12.2–12.8)	4.56 (4.23–5.25)	60.5 (59.3–61.9)	32.0 (31.8–32.8)	502 (489–507)

Values are the annual mean (range) for the head and base of both the east (sand) and west (gravel) reaches

and 47% for large gravel were accounted for by abiotic sequestration of phosphorus. However, despite similar uptake rates for live and killed sand fractions, and apparently lower rates for killed treatments of gravel, there was no significant interaction between treatment (i.e., live versus killed sediments) and particle size ($F = 2.13$ and $P = 0.14$).

As with SPU, there were significant differences in PSI values among sediment size classes (Fig. 7). As expected, small size fractions (sand) had the greatest potential to remove phosphorus from solution ($PSI = 0.87 \pm 0.05$), while the largest fraction had the least potential ($PSI = 0.16 \pm 0.03$) of all size fractions in the study ($F = 261.18$ and $P < 0.01$). We found a significant interaction between particle size and treatment (live versus killed) on PSI values ($F = 6.91$ and $P = 0.01$) due to significantly higher PSI values for the killed treatment relative to live sediments for large gravel ($t = 5.42$ and $P < 0.01$).

EPC₀ for killed sediments displayed a strong particle size effect (Fig. 8), with decreased buffering capacity associated with increasing particle size. Among the killed particle size fractions, sand had the lowest EPC₀, and, therefore, the largest capacity to maintain low water column SRP concentrations, while large gravel had the highest EPC₀ values and thus the least ability of all fractions to buffer water column SRP. Killed sediments in the gravel size fraction had EPC₀ values that were marginally significantly different from sand ($t = 2.78$ and $P = 0.09$) but not large gravel ($t = 1.54$ and $P = 0.64$), while EPC₀ of killed sand was significantly different from killed large gravel ($t = 4.95$ and $P < 0.01$).

In contrast, live sediments had consistently lower EPC₀ values than killed samples and displayed less variability among size fractions. The maximum difference between live EPC₀ for the three sediment categories was $\sim 9 \mu\text{g/L}$, compared $65 \mu\text{g/L}$ for killed EPC₀, although the difference between live and killed treatments was not significant for the small gravel fraction ($t = 2.70$ and $P = 0.11$). Large gravel exhibited the lowest EPC₀ values, followed by sand and small gravel; however, the difference between sand and large gravel was not significant ($t = 1.09$ and $P = 0.88$). Small gravel EPC₀ was significantly higher than both sand and large gravel ($t \geq 3.81$ and $P < 0.01$).

Discussion

Several studies have examined the role of sediments in controlling phosphorus concentrations in lotic ecosystems (e.g., Meyer 1979; Klotz 1988; House et al. 1995; McDowell et al. 2003). In some cases there appears to be a close coupling between sediment buffering capacity (abiotic mechanism) and SRP concentrations (Meyer 1979; Klotz 1988, 1991), while other studies have emphasized the role of biota in regulating SRP concentrations (e.g., Elwood et al. 1981; Munn and Meyer 1990; Valett et al. 2002). The two streams in this study present an unusual opportunity for considering the relative contribution of abiotic sorption processes versus biotic uptake and for addressing the variable contributions of these two processes types on stream water P dynamics. The shared origin from a small upstream

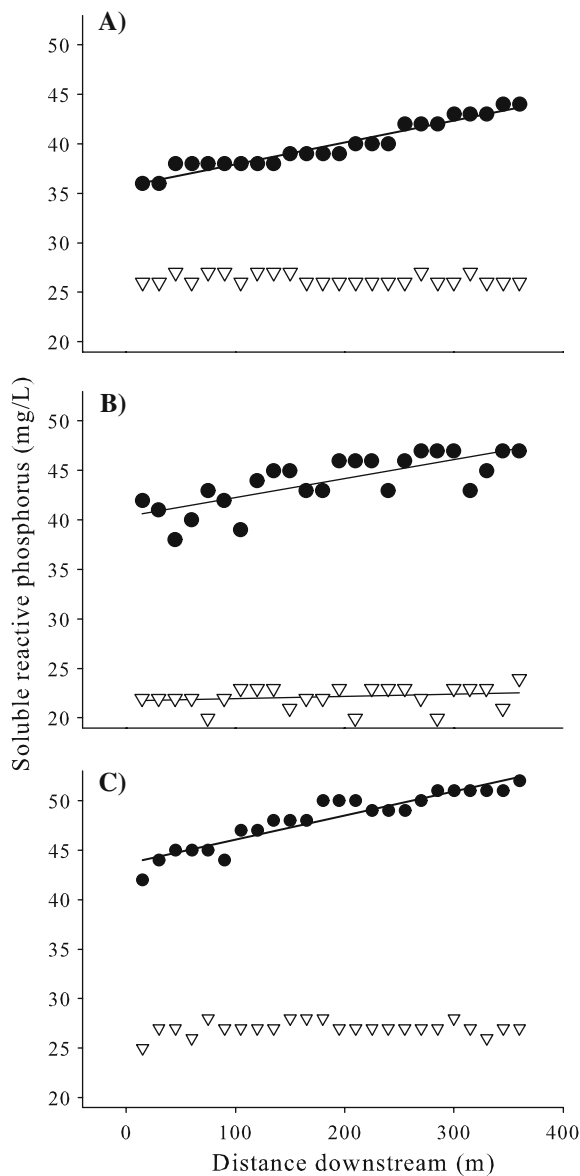


Fig. 3 Seasonal soluble reactive phosphorus profiles for sand (open triangles) and gravel (closed circles) reaches from Boulder Creek, Wisconsin. Samples were collected in **a** August 2002, **b** April 2003, and **c** July 2003. Each point represents a mean of 2–5 samples taken at 15 m intervals along each 360 m study reach. Regression lines indicate significant relationship between SRP concentrations and distance downstream ($P < 0.05$)

wetland, the close proximity of the two streams, and the lack of consistent, substantial differences in water chemistry (except for SRP) all suggest that the source water for both reaches is virtually identical. Thus, the difference in bed sediment composition represents a natural experiment (*sensu* Cody 1974) to assess

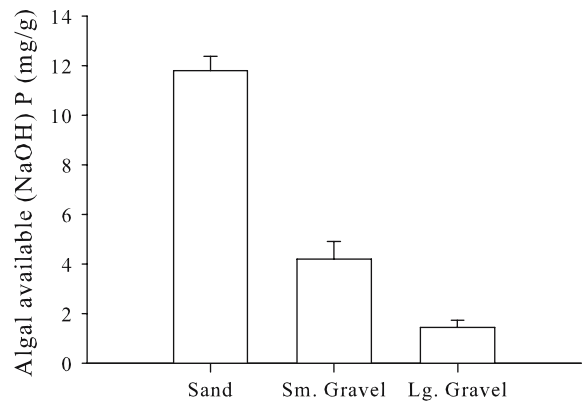


Fig. 4 Algal available P for three difference sediment size categories in Boulder Creek. Bars are mean \pm SE with $n = 18$ per category

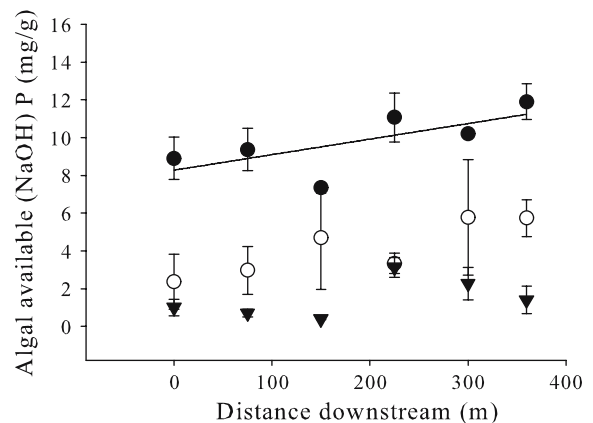


Fig. 5 Algal available P for three sediment size categories versus distance downstream in the East and West Boulder Creek tributary streams. Regression lines are shown only when sediment P versus distance downstream relationships were significant ($P < 0.05$). Closed circles—sand, open circles—small gravel, closed triangles—large gravel

effects of particle size on water column P at the whole-stream scale.

Soluble reactive phosphorus was consistently low and did not vary with distance downstream in the eastern channel, which contrasted the relatively high and longitudinally increasing SRP profile of the west branch. In the context of this natural experiment, the distinct nutrient patterns strongly suggest a role for sediment size in creating differences in ambient SRP concentrations, consistent with the first part of our hypothesis (i.e., differences in sediment composition can affect stream P concentrations).

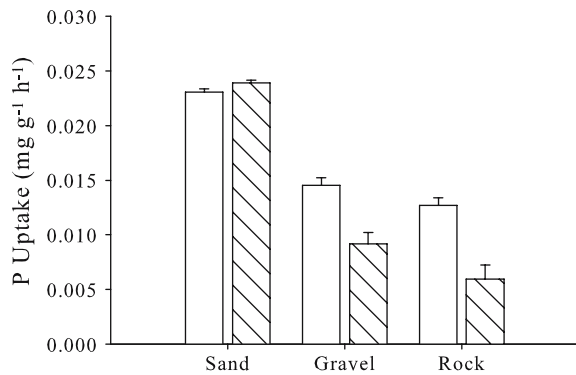


Fig. 6 Sediment P uptake (SPU) for live (open bars) and killed (hashed bars) for three sediment categories in Boulder Creek. Bars are mean \pm SE with $n = 6$ per group

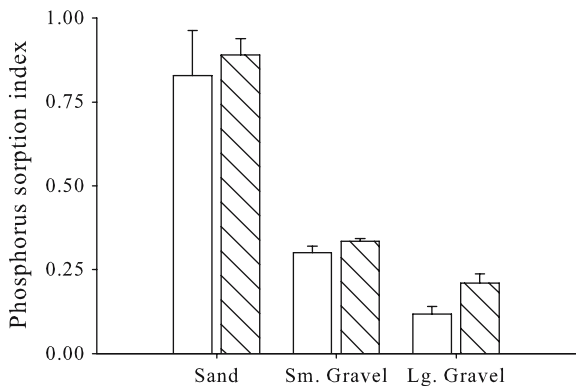


Fig. 7 Phosphorus Sorption Index values of live (open bars) and killed (hashed bars) for three sediment categories in Boulder Creek. Bars are mean \pm SE with $n = 6$ per group

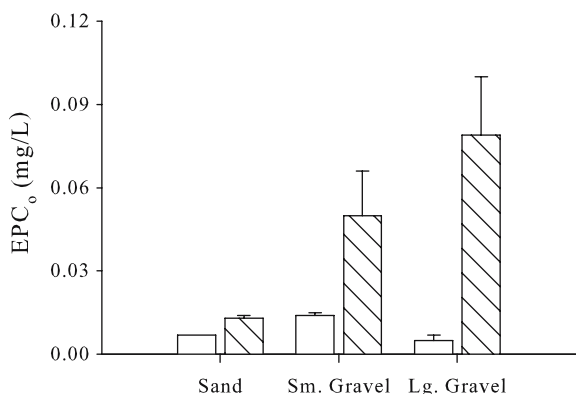


Fig. 8 Zero Equilibrium P concentrations of live (open bars) and killed (hashed bars) treatments for three sediment categories in Boulder Creek. Error bars represent mean \pm SE with $n = 6$ per group

Results of small batch experiments with different benthic sediment size classes provided support for the second component of our hypothesis: that the sediment effects on water column P reflect a shift in the balance between abiotic and biotic processes associated with differences in sediment size. Smaller particle sizes that dominated the east channel had high uptake rates (SPU), and EPC_0 values were lower than ambient SRP concentrations for both live and killed samples, demonstrating that these sediments were able to retain SRP (Froelich 1988). Another line of evidence indicating that these smaller sediments were removing SRP from the water column was the significant downstream increase in sediment-bound phosphorus in the fine sediments of the east channel. The potential for sediments to remove SRP and the downstream accumulation of P on these sediments both support the conclusion that the observed low and constant water column SRP concentrations were being maintained by sediment uptake along the length of the east channel. Further, the lack of difference between live and dead treatments for all sediment-phosphorus measures (EPC_0 , PSI, and SPU) for the sand fraction suggests that this uptake is largely abiotic. However, the addition of a biocide potentially confounds this conclusion, as killing the microbes may lead to the release of their internal P stores into solution. If microbial P release is substantial, sediment P metrics for killed sediments would be under-estimated and in turn the significance of biotic uptake would be over-estimated. However, additions of HgCl_2 did not cause rapid increases in solution P (Lottig and Stanley, unpublished data), which would be expected if there was substantial release of microbial P. Thus, while we cannot completely discount the effects of the biocide on sediment rate estimates, we do not have reason to believe that this was a major source of error in our assays.

Just as experimental evidence suggested that low and relatively constant SRP concentrations were being mediated by abiotic sediment processes in the east channel, it also suggested that was not the case in the west channel. The dominant sediment in the west channel had killed EPC_0 values greater than water column SRP concentrations, implying that no abiotic retention was occurring. In contrast, we observed very low EPC_0 values for live large gravel fractions and moderate uptake rates by live gravel classes,

which emphasize the role of algal and/or microbial communities in P uptake and in affecting SRP dynamics in the west channel.

The one counterintuitive outcome from our sediment experiments was that the PSI values for killed samples were higher than the live sediments, although this difference was significant only for the large gravel fraction. These are somewhat conflicting results because the live treatments should always be at least the same if not larger than killed treatments since they incorporate both biotic assimilation and abiotic sorption (Haggard et al. 1999). Regardless, ambiguous PSI results may not be surprising given the extremely high level of the addition (2,000 $\mu\text{g/L}$). While this experiment is useful for considering the consequences of an acute short-term P addition, it may have been too large for any discernable difference between live and killed treatments to be observed (Munn and Meyer 1990).

Our laboratory experiments clearly demonstrated differences in relative and absolute rates of biotic and abiotic P uptake as a function of particle size. From these results, we suggest a simple conceptual framework to describe the shift from abiotic to biotic uptake and changes in the rate of uptake along a particle size gradient (Fig. 9). While the effects of particle size on P uptake have been described previously in streams (Klotz 1988; Stone and Murdoch 1989; Munn and Meyer 1990), we were able to identify particle sizes in which biotic uptake emerged as a contributor to P uptake, and further, that fractions

are generally considered to be relatively coarse (i.e., the sand size class) can support substantial abiotic uptake at the whole-reach scale.

The transition from abiotic to biotic pathways along a particle size gradient is not surprising given the basic physical properties of different sediment classes. On one hand, small sediments provide a relatively unstable substrate for establishment of biota (limiting biotic uptake) because of their ease of mobility, but these fine-grained particles offer extensive surface area for P sorption. On the other hand, larger, more stable sediments can be more rapidly colonized by microbial and algal communities (Duffer and Dorris 1966) but offer less surface area for abiotic sorption. Thus, it is expected that studies emphasizing the phosphorus buffering mechanism are dominated by systems with high silt and clay fractions (e.g., Hill 1982; Klotz 1991; House and Denison 1998; Smith et al. 2005), whereas those focusing on biotic mechanisms of P retention typically have stream beds dominated by gravel, cobble, and boulder substrates (e.g., Newbold et al. 1983; Munn and Meyer 1990; Marti and Sabater 1996). Often, it is assumed that the potential for biotic uptake to affect water column P is limited (e.g., see Macrae et al. 2003) because of low concentrations at which biota become P saturated (1–10 $\mu\text{g/L}$; Bothwell 1985; Mulholland et al. 1990). The contrast between low and constant SRP concentrations in the sorption-dominated east branch versus the high and increasing SRP profile of the west branch where biotic uptake assumed greater relative importance demonstrates this reduced potential for biota to affect water column P illustrated in Fig. 9. However, Mainstone and Parr (2002) argue that growth rates and standing crops of primary producers can be affected by P concentrations as high as 200–300 $\mu\text{g/L}$, suggesting that even at concentrations >10 $\mu\text{g/L}$, biota should be able to influence stream water P.

There are two notable implications of these demonstrated particle size effects on rates and mechanism of P uptake in Boulder Creek and other similar streams. The first point relates to the capacity of sands to regulate P in this stream. Relative to finer silts and clays, sands have less uptake capacity and retain less P. For example, concentration of sediment-bound P in Boulder Creek averaged 10 $\mu\text{g/g}$, approximately an order of magnitude lower than concentrations observed for silts (<0.25 mm) in

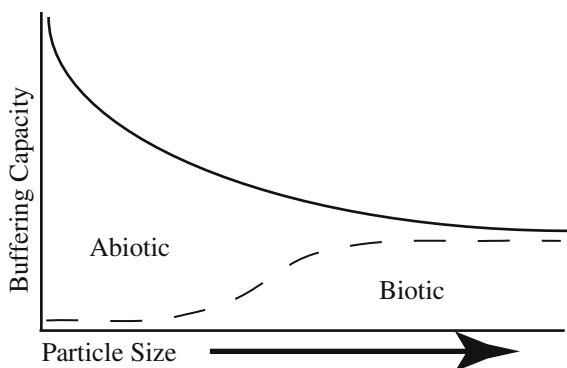


Fig. 9 Conceptual diagram of the sorption potential and mechanisms responsible for uptake of phosphorus in benthic sediments across a particle size gradient. The solid line represents the total buffering capacity and the dashed line represents the transition from uptake being primarily abiotic to primarily biotically mediated by periphyton communities

Hoxie Gorge, NY (Klotz 1988) and suspended sediments (<2 mm) in the Susquehanna River basin, PA (Pionke and Kunishi 1992). However, in all likelihood, the modest uptake capacity of sands (as measured in laboratory experiments) coupled with high mobility of this size fraction mean that the effectiveness of this P sink may be greater than expected. While fine sediments have substantial P sorption capacity, significantly higher velocities are needed to mobilize and transport these particles relative to sand (Knighton 1998). Thus, the abiotic P sink might ‘fill up’ over time in a clay- or silt-dominated system if scouring floods do not occur, and sediments will shift from P sinks to P sources (e.g., Schulz and Herzog 2004, Jarvie et al. 2005). In contrast, frequent transport of sand occurs during moderate flows in Boulder Creek (Orr et al. 2006) and input of new sediments from bank erosion or other disturbances can replenish the sediment P sink (Meyer 1979). Thus, sediments in the 1–2 mm size class represent an optimization of P sorption and sediment turnover that can maintain a relatively stable, long-term buffering mechanism in these systems.

Second, changes in particle size composition could have important consequences for P cycling and productivity in some streams. Fine sediment inputs often increase following natural disturbances (e.g., Lamberti et al. 1991), but sand and silt inputs to streams are also strongly associated with anthropogenic activities such as road construction, agricultural and urban land uses, etc. (Waters 1995) and may have important consequences for P storage and transport. For example, widespread siltation allows P to accumulate in many UK Rivers, and may eventually lead to greater riverine eutrophication (Mainstone and Parr 2002). Similarly, dam construction and removal profoundly alter downstream bed sediment composition (Collier et al. 1996, Doyle et al. 2003a) and P retention in rivers (Stanley and Doyle 2002). The differences in water column P profiles in the two Boulder Creek tributaries associated with divergent sediment composition suggest that common anthropogenic activities that modulate sediment supplies also have the potential to alter P cycling in streams.

In addition to changing the amount or size of sediments delivered to channels, human use of streams and rivers often modulate flow regimes and increase P loading. It will be challenging to predict

the consequences of increased P loading given coupled changes in sediment composition and transport (Mainstone and Parr 2002). While we have shown that differences in particle size have consequences for water column P and pathways of P retention, it is not clear how much change in particle size is needed to trigger ecologically meaningful changes in water column P or P storage in bed sediments. Making quantitative connections between P inputs, sediment-P interactions, biotic responses, and sediment transport dynamics will likely be required to understand interactive effects of human activities on stream phosphorus dynamics.

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