

Relationships between Benthic Sediments and Water Column Phosphorus in Illinois Streams

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Sediments can be important in regulating stream water P concentrations, and this has implications for establishing nutrient standards that have not been fully investigated. We evaluated abiotic and biotic processes to better understand the role of sediments in determining stream water dissolved P concentrations. Sediment and stream water samples were collected during low discharge from 105 streams across Illinois and analyzed for equilibrium P concentration at zero release or retention (EPC_0), P sorption characteristics, stream water P concentration, and sediment particle size. In addition, four east-central Illinois streams were repeatedly sampled to examine temporal patterns in sediment P retention and biotic processing of P. Median dissolved reactive P (DRP) and total P concentrations across the state were 0.081 and 0.168 mg L⁻¹, respectively. Sediment EPC_0 concentrations were related to stream water DRP concentrations ($r_s = 0.75$). Sediment silt+clay (and co-correlated organic matter) was related to sorbed P ($r_s = -0.49$) and the reactive sediment pool of P ($r_s = 0.76$). However, for most sites this pool was small given the coarse textures present (median silt+clay was 5.7%). Repeated sampling at the four intensive sites showed little variation in EPC_0 values or alkaline phosphatase activity, suggesting overall stream conditions regulated the biotic processing. Biotic retention of P was 32% of short-term P removal. We conclude that sediments in Illinois streams are a reflection of and partially affected by stream water P concentrations through both abiotic and biotic processes. Sediments seem unlikely to alter annual stream P loads, but may affect concentrations at low discharge.

POOR water quality in many areas across the globe has been attributed to anthropogenic nitrogen (N) and phosphorus (P) additions to surface waters (Diaz, 2001). These nutrients can cause eutrophication in bodies of water and associated impacts such as loss of biological diversity, hazardous algal blooms, low dissolved oxygen, and recreational and economic losses (Carpenter et al., 1998). Eutrophication of streams and lakes is a common impairment throughout the U.S. (USEPA, 2000). One consequence of nutrient enrichment can be seen in the Gulf of Mexico where a hypoxic zone forms each summer due to N and P inputs from the Mississippi River (Turner and Rabalais, 2003). Conventional wisdom is that in marine systems, N is generally the limiting nutrient for phytoplankton growth, although P is also a factor (Sylvan et al., 2006). In contrast, freshwater ecosystems are generally considered P limited (Correll, 1999). Nutrient limitation in lotic ecosystems is less consistent, with N and P limitation occurring with about equal frequency (Francoeur, 2001). Where P occurs in excess in streams and rivers, the main source is typically agricultural runoff or sewage effluent discharged by water treatment plants (WWTPs) (Correll, 1999).

In Illinois, both agriculture and WWTPs are important sources of P to streams and rivers in the state, with about 47% of the P exported by rivers coming from WWTPs (David and Gentry, 2000). In agricultural watersheds in Illinois, most of the riverine export of P occurs during periods of high flow, with both surface runoff and tile drains contributing dissolved reactive P and particulate P to streams (Royer et al., 2006; Gentry et al., 2007). Maintenance practices to improve drainage, such as dredging of ditches and streams, can also enhance P release and transport from sediments (Smith et al., 2006).

Sewage effluent from WWTPs is usually more important to stream P concentrations during low flow periods, when nonpoint sources are

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Published in *J. Environ. Qual.* 38:607–617 (2009).
doi:10.2134/jeq2008.0094
Received 19 Feb. 2008.

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Abbreviations: APA, alkaline phosphatase activity; BLS, Black Slough; DDW, distilled-deionized water; DRP, dissolved reactive phosphorus; EMC, Embarras at Camargo, IL; EMM, Embarras at Meander; EPC_0 , equilibrium phosphate concentration at zero release or retention; LOI, loss on ignition; OM, organic matter; PSI, phosphorus adsorption index; Q, discharge; r_s , Spearman's correlation coefficient; RSP, reactive sediment pool of phosphorus; SF, Salt Fork in the Vermilion watershed; WWTP, wastewater treatment plant.

reduced. This is also the period when algal productivity can affect stream dissolved oxygen dynamics, all in response to higher P concentrations (Morgan et al., 2006). Therefore, it is important to understand which factors potentially control stream water P concentrations during low flow, such as benthic sediments.

Both abiotic and biotic sediment processes can regulate stream P concentrations, and controls on their relative importance are not well understood. Froelich (1988) described sediments in the context of a phosphate buffer mechanism, referring to the ability of sediments to control DRP in the water column. This buffering capacity was primarily due to abiotic geochemical and physical processes (precipitation/dissolution and adsorption/desorption) (Froelich, 1988). However, because P is an essential nutrient for biota, benthic microorganisms also play a potentially important role.

The ability of benthic sediments to regulate water column P concentrations is commonly assessed with P adsorption isotherms (e.g., Klotz, 1988; McDowell et al., 2003; Haggard et al., 1999, 2007). These studies have found that equilibrium P concentrations (EPC_0) of benthic sediments, where P is neither adsorbed nor desorbed, were related to stream water DRP concentrations. EPC_0 values greater than stream water dissolved reactive P (DRP) concentrations suggested the sediments were a potential source for water column P, whereas EPC_0 values less than stream water DRP implied the benthic sediments were serving as possible P sink (Froelich, 1988).

The objective of this study was to evaluate benthic sediment-water column P relationships in streams and rivers throughout Illinois. We studied both abiotic adsorption relationships as well as biotic controls mediated by microbial activity. Our goal was to better understand the importance of benthic sediments in controlling stream P concentrations, particularly during low flow periods. The successful development of nutrient standards requires a full understanding of the in-stream sources, sinks, and transport of P; therefore, we discuss our results in the context of implementing a P standard for Illinois streams and rivers and present calculations of the size of the sediment P pool relative to water column P loads for an agricultural river in east-central Illinois.

Materials and Methods

We sampled sediments in streams throughout the state, coordinated with work on bioassessment and nutrient-chlorophyll relationships (Heatherly et al., 2007; Royer et al., 2008). We chose 105 sites that were accessible for sediment collection, were well distributed throughout the state, and included a wide range of watershed sizes. Sediment and water samples were collected between 10 Sept. 2004 and 6 Oct. 2004 (Fig. 1) during a period of generally low stream discharge (Q). We hereafter refer to this as the low-Q survey to signify that the results reflect low discharge conditions and to be consistent with other reports based on this statewide monitoring program (Royer et al., 2008). Repeated sampling was limited due to the scale of this statewide monitoring program; therefore, we focused an intensive study on four streams in east-central Illinois that have been previously studied for water quality, including P and algal concentrations

(Figuroa-Nieves et al., 2006; Morgan et al., 2006; Gentry et al., 2007). Sediments from these four sites were sampled on a bi-weekly basis between March 2005 and August 2006 (Table 1).

Site Description

Illinois has an area of ~150,000 km², with a land use distribution of 76% agriculture, 12% forest, 6% urban, 4% wetland, and 2% other uses (Illinois Department of Agriculture, 2001). The row crop agriculture is primarily corn (*Zea mays* L.) and soybeans (*Glycine max* L.), with large inputs of N and P fertilizer (David and Gentry, 2000). Nonpoint source P loads have been well studied (e.g., Gentry et al., 2007; Algoazany et al., 2007) and both tiles and surface runoff are known to be important pathways. However, Illinois had an estimated 2007 population of 12.8 million people (U.S. Census Bureau, 2007), and effluent from WWTPs contributes to high P loads in many rivers (David and Gentry, 2000; Bedore et al., 2008; Jacobson et al., 2008).

The intensive study was conducted within two east-central Illinois watersheds: the Embarras and the Vermilion (Table 1). Three sites were located in the Embarras watershed: Black Slough (BLS), Embarras at Camargo (EMC), and Embarras at Meander (EMM). The fourth site (SF) was located in the Vermilion watershed near Homer, IL. Soil parent material in these watersheds is loess over glacial till and the landscape is low gradient with glacial moraines providing some relief. The soils in this region are poorly or very poorly drained Mollisols, with land use dominated by row crop agriculture that is tile drained (David et al., 1997). Mean annual rainfall in the Embarras and Vermilion watersheds is approximately 1270 mm (ISWS, 2006). Each of the streams receives P from agricultural nonpoint sources (see Gentry et al., 2007), but the Salt Fork Vermilion site is also downstream of a WWTP effluent discharge located in Urbana, IL, approximately 40 km upstream from the sampling site.

Statewide Sampling Procedures and Analysis

In most streams the sediments were sampled by wading, with sediment collected using 120 mL plastic cups (7 cm tall). Cups were plunged into the sediment, capped with a spatula, and then pulled from the streambed and placed into a bucket. This was repeated within the stream reach (32 m) at eight sampling points located in the middle of the stream channel, moving upstream each time. This sediment sampling technique is assumed to represent the top 5 to 7 cm of benthic sediment within each stream reach. The eight 120-mL cups of sediment were composited and homogenized in the field, and then sieved (4 mm). The <4 mm sediment was placed in a 500 mL HDPE bottle and stored in a cooler until arrival at the laboratory. An Eckman dredge was used to collect sediment samples at sites where wading was not possible due to depth of the stream. Eight dredge samples were collected and homogenized in a bucket, before sieving as above.

Stream water grab samples were collected simultaneously with sediment samples from the thalweg of each stream in a 500 mL HDPE bottle. Water temperature at each site was taken in situ using a portable meter (Digi-Sense Thermocouple, Cole-Parmer, Vernon Hills, IL). Water samples were then stored on ice in a cooler until arrival at the laboratory.

Immediately upon arrival at the laboratory, P adsorption isotherms were determined on the fresh sediment samples. For the 105 samples collected during 2004, we used a series of KH_2PO_4 concentrations in distilled-deionized water (DDW) for the equilibrium solution. For each site, 40 mL of the equilibrium solution was added to 6 g wet sediment sample and placed in a 50 mL centrifuge tube. The samples were shaken for 12 h, then filtered through a Whatman GF/F 0.7- μm filter, and analyzed for DRP using the ascorbic acid method on a Lachat QuikChem 8000 Flow Injection Analysis system (Hach Company, Loveland, CO).

To evaluate native P sorbed on the sediment at the time of collection, we applied the initial mass isotherm, which is suitable for soils or sediments where there is sorbate already present (Nodvin et al., 1986; Vance and David, 1992). In the initial mass method, P adsorbed or released (normalized to sediment mass) is regressed against the initial P concentration in solution (normalized to sediment mass). A linear relationship is typically found, and nearly all the coefficients of determination (r^2 values from the regression) were greater than 0.99 for the 105 sediment samples— an example initial mass isotherm for P is shown in Fig. 2. The isotherm is described as the amount of P adsorbed or released (RE) relative to the initial amount of P added to solution with respect to the mass of sediment (X_i):

$$\text{RE} = mX_i - b \text{ (all units mg P kg}^{-1}\text{)} \quad [1]$$

Values on the y axis <0 represent a release of P; whereas positive values represent a removal of P (Fig. 2).

The slope (m ; unitless) represents the partition coefficient (fraction of total reactive P in a sediment/water system that is retained by the sediment), whereas the intercept ($-b$) describes the unretained (i.e., amount desorbed when $X_i = 0$) portion of the reactive sediment pool. The amount of P present in the sediment that can be readily released is the reactive sediment pool (RSP, mg P kg^{-1}). The RSP is calculated as:

$$\text{RSP} = b/(1-m) \quad [2]$$

Another measure of the affinity of a substance for sediment is K_d ($\text{m}^3 \text{kg}^{-1}$), the distribution or partition coefficient. This K_d represents the affinity of P for the sediments in this case, while taking into account solution volume to sediment mass; it is calculated as:

$$K_d = m/(1-m) * (\text{solution volume})/(\text{sediment mass}) \quad [3]$$

We also wanted to compare EPC_0 values from the adsorption isotherms to stream water DRP concentrations as well as other sediment characteristics. For this type of analysis, EPC_0 is calculated using several concentrations of P added to stream water where P is already present (Meyer, 1979). This is done to simu-

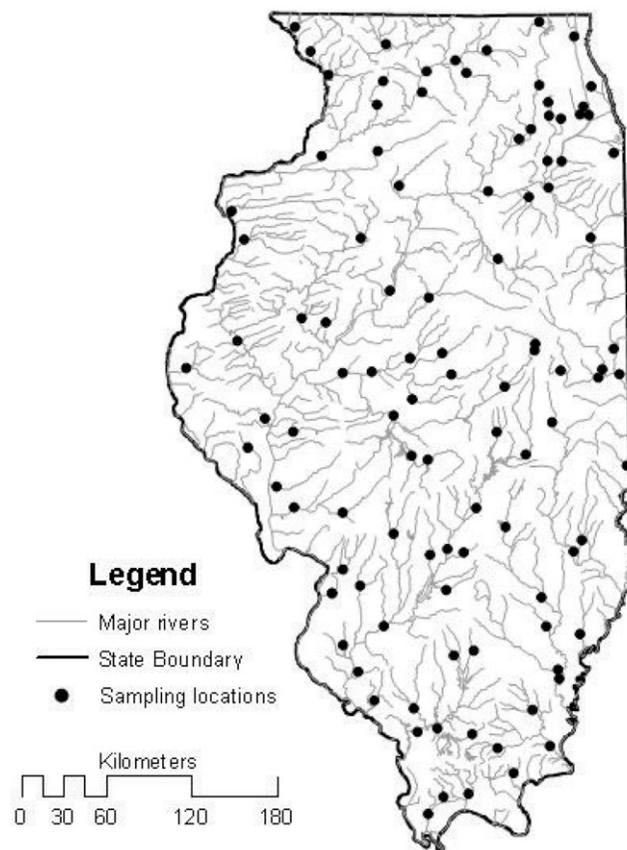


Fig. 1. Map of Illinois showing major river network and the stream sites sampled during the low-Q period of 2004 ($n = 105$).

late the natural ionic strength and composition of the stream water— which has been shown to influence EPC_0 (Klotz, 1988, 1991). Stream water was filtered with a Fisherbrand cellulose acetate/cellulose nitrate filter, pore size 0.45 μm , immediately upon returning to the laboratory. For the stream water isotherm analyses, the amount of DRP (mg P kg^{-1} of sediment dry weight) removed or released was plotted against the equilibrium P concentration (see Fig. 2 for an example). A regression of P sorbed against the final DRP concentration allowed the evaluation of the point on the x axis where the line crosses and there is negligible P adsorption or release from the sediments to the solution, or EPC_0 (Bache and Williams, 1971). To transform the 105 EPC_0 in DDW values (used to calculate RSP) to EPC_0 in stream water concentrations, we developed a regression equation using sediments from 31 sites sampled during the summer of 2006 or 2007 for which isotherms were evaluated using both DDW and stream water as a solute. The relationship ($n = 31$, $r^2 = 0.80$, $y = 0.4555 * \text{EPC}_0$ in DDW) allowed us to estimate the EPC_0 in stream water for the 105 samples collected in 2004.

Table 1. Site information for the four streams intensively sampled in east-central Illinois. BLS, Black Slough; EMC, Embarras at Camargo, IL; EMM, Embarras at Meander; SF, Salt Fork in the Vermilion watershed.

Site name	Site ID	Coordinates	River basin	Watershed area (km^2)	Stream order (Strahler)
Black Slough	BLS	39° 57' 09" N; 88° 10' 08" W	Embarras	25	2
Embarras at Camargo	EMC	39° 47' 30" N; 88° 11' 09" W	Embarras	473	4
Embarras at Meander	EMM	39° 58' 53" N; 88° 12' 22" W	Embarras	57	3
Salt Fork Vermilion at Homer	SF	40° 03' 44" N; 87° 56' 22" W	Vermilion	839	4

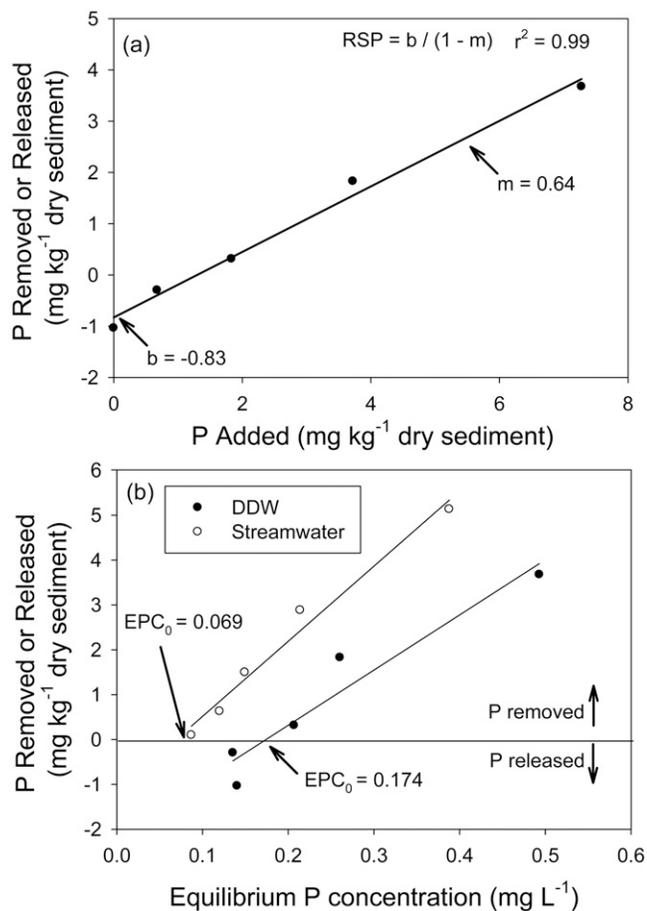


Fig. 2. Sediment isotherms for a typical site (Salt Creek near Greenview, IL), showing (a) initial mass plot using distilled-deionized water (DDW) and (b) Langmuir plots with EPC_0 estimates using DDW (containing 0, 0.1, 0.25, 0.5, 1, and 5 mg dissolved reactive P [DRP] L^{-1}) and stream water (same concentrations as used in DDW added to stream water, which had a DRP concentration of 0.097 mg L^{-1}).

Texture (gravel, sand, silt+clay) for all sediment samples was determined by wet sieving using 2- and 0.053-mm sieves to separate particle sizes. The percentage of organic matter for each sediment sample was determined by loss on ignition (LOI) at 500°C. Each of the 105 sediment samples was analyzed for total P and total N by Kjeldahl digestions and QuikChem Methods 13-115-01-1-B and 13-107-06-2-D, respectively.

Sampling Procedures and Analysis for Intensive Sites

Biweekly sediment samples collected from the four intensive sites were analyzed for alkaline phosphatase activity (APA) following Saylor et al. (1979). APA was expressed per gram of organic matter because other studies have used it successfully as a biotic metric for APA expression (Bonin et al., 2000; Drouillon and Merckx, 2005), and the amount of organic matter (OM) in sediments has been shown to be correlated with microbial biomass (Bott and Kaplan, 1985; Nannipieri et al., 2003). During the intensive study, the 1 Aug. 2005 sediment samples were analyzed for total P by Kjeldahl digestion followed by Lachat using QuikChem Method 13-115-01-1-B. One set of sediment samples from each site was also analyzed using a NaOH extraction to determine total

P, organic P, and inorganic P (Dai et al., 1996), and pH with a volumetric ratio of 1:2.5 (sediment to DDW). On a quarterly basis P adsorption isotherms were also conducted on fresh sediment samples from the intensive sites using P added to filtered stream water on the same day they were collected.

Three times during the high-temperature, high-microbial-activity period of 2006 (late summer), P sorption indices (PSI) were measured for the sediment samples according to the method of Bache and Williams (1971). The analyses were conducted on 25 July, 30 Aug., and 9 Oct. 2006. Procedures were modified by shaking the sediment samples for 12 h as opposed to 1 h, and 6 g of sediment was placed into a 50 mL centrifuge tube. For each site, there was a control with stream water as well as a spiked sample with an addition of 2000 $\mu g P L^{-1}$ to the stream water. The samples were placed in a shaker for 12 h, filtered through a Whatman GF/F glass fiber filter (pore size of 0.7 μm), and analyzed for DRP within 48 h of filtering on a Lachat QuickChem system. PSI was calculated using the equation $X/(\log_{10} C)$, where X is the P sorbed by the sediments ($\mu g P L^{-1}$), and C is the final P concentration ($\mu g P L^{-1}$). To determine the biotic contribution to the P uptake by sediments, the PSIs were measured on “live” sediments and “killed” or autoclaved sediments. Autoclaved sediments were exposed to an average temperature of 121°C and pressure of 117 kPa for 1.5 h, and autoclaved sediments were assumed to represent killed sediments. Phosphorus release due to lysis was calculated as the difference between a control and an autoclaved sample without P additions. After subtracting the P release due to lysis, the percentage of biotic contribution to P uptake was calculated as: $(PSI_L - PSI_K)/PSI_L$.

All stream water samples were preserved upon arrival at the laboratory (APHA, 1998). An unfiltered aliquot was used to determine total P via Kjeldahl digestion and analysis on the Lachat QuickChem (method 10-115-01-4-U). Dissolved reactive phosphorus was measured on the Lachat (method 10-115-01-1-B) following filtration (Fisherbrand cellulose acetate/cellulose nitrate filter, pore size 0.45 μm). Phosphorus detection limits were 5 $\mu g P L^{-1}$. Particulate/organic phosphorus was estimated as the difference between total P and DRP.

Nitrate (NO_3-N) concentrations were determined using a Dionex DX-120 ion chromatograph, with a detection limit of 0.1 mg $NO_3-N L^{-1}$. Analysis of dissolved organic carbon (DOC) was performed using a Dohrmann-Xertex DC-80 TOC analyzer with a minimum detection limit of 0.5 mg DOC L^{-1} . The unfiltered water samples were also analyzed for TKN by digestion with sulfuric acid, copper sulfate, and potassium sulfate in an aluminum block digester (Lachat BD-46). This process converted organic N compounds to ammonia in the aliquot, which was then analyzed via Lachat method 10-107-06-2-H using the sodium salicylate method.

Data Analysis

Statistical analyses were performed using SAS v9.1 (SAS Institute, 2003). All variables were tested for normality using the univariate procedure. No variable was normally distributed. Therefore, the Spearman's nonparametric correlation procedure was used to assess correlations among variables. The Kruskal-Wallis

Table 2. Distribution of water and sediment chemistry from 2004 state-wide low-Q survey ($n = 105$). DRP, dissolved reactive P; DDW, distilled-deionized water; EPC₀, equilibrium phosphate concentration at zero release or retention; RSP, reactive sediment pool.

	Minimum	25th percentile	Median	75th percentile	Maximum
Water chemistry					
DRP (mg L ⁻¹)	< 0.005	0.029	0.081	0.373	2.80
Total P (mg L ⁻¹)	0.007	0.118	0.168	0.474	2.80
Nitrate-N (mg L ⁻¹)	< 0.1	0.2	1.6	3.9	18.0
Total N (mg L ⁻¹)	0.2	1.0	2.5	5.0	18.7
Sediment chemistry					
DDW EPC ₀ (mg L ⁻¹)	0.003	0.092	0.183	0.400	2.6
Stream water EPC ₀ (mg L ⁻¹)	0.001	0.042	0.083	0.182	1.18
Initial mass slope (m)	0.21	0.63	0.84	0.97	1.0
Initial mass-b (mg P kg ⁻¹)	0.0	0.73	1.2	2.2	8.1
Initial mass RSP (mg P kg ⁻¹)	1.2	4.8	10.6	27.2	232
Initial mass K _d × 10 ⁻⁴ (m ³ kg ⁻¹)	20	124	391	1740	75700
Organic matter (%)	0.2	0.8	1.4	2.3	25.6
Total P (mg kg ⁻¹)	120	270	360	670	2340
Total N (mg kg ⁻¹)	120	220	340	580	4360
Sediment texture					
Gravel (%; 4.0–2.0 mm)	0.0	1.0	7.2	17.3	55.2
Sand (%; 2.0–0.05 mm)	1.7	62.8	76.8	88.7	98.9
Silt+clay (%; < 0.05 mm)	0.3	1.6	5.7	23.1	98.3

test was used as a non-parametric version of analysis of variance (ANOVA). Significance was set at $\alpha = 0.05$, and correlation coefficients are expressed as Spearman's correlation coefficient (r_s).

Results

Sediments across Illinois

Median values of stream water DRP and total P were 0.081 and 0.168 mg L⁻¹ during the low-Q survey, with a range of total P from 0.007 to 2.8 mg L⁻¹ (Table 2). The 25th percentile of total P values was 0.118 mg L⁻¹, indicating the high P concentrations in streams throughout Illinois. Total P was highly correlated with DRP ($r_s = 0.85$, $p < 0.0001$).

When EPC₀ values determined using DDW were compared to values calculated using filtered stream water, the DDW-based values were typically two times greater (Table 2). The results presented below are based on estimated stream water EPC₀ values.

Benthic sediments reflected the stream water P concentrations, with EPC₀ values correlated ($r_s = 0.75$) with DRP concentrations (Fig. 3). The relationship between EPC₀ values and stream water DRP concentrations was much stronger than the relationship between water column total P and sediment total P ($r_s = 0.21$, $p = 0.03$). This demonstrates that adsorption/desorption of reactive P (as measured by EPC₀), although a small proportion of sediment total P, best reflected concentrations in the streams. The median EPC₀ concentration was 0.083 mg L⁻¹ for the 105 stream sites, compared to a median stream water DRP concentration of 0.081 mg L⁻¹. Generally, when concentrations of DRP were <0.09 mg L⁻¹, the corresponding EPC₀ values were greater than DRP concentration, suggesting that sediments would be a potential source of P. At DRP concentrations > 0.09 mg L⁻¹, most sediments would likely sorb P from the water column, based on their EPC₀ values. The total P concentration of the sediments was not correlated with EPC₀.

The benthic sediments from throughout Illinois were generally coarse textured, with median values for sand, gravel, and

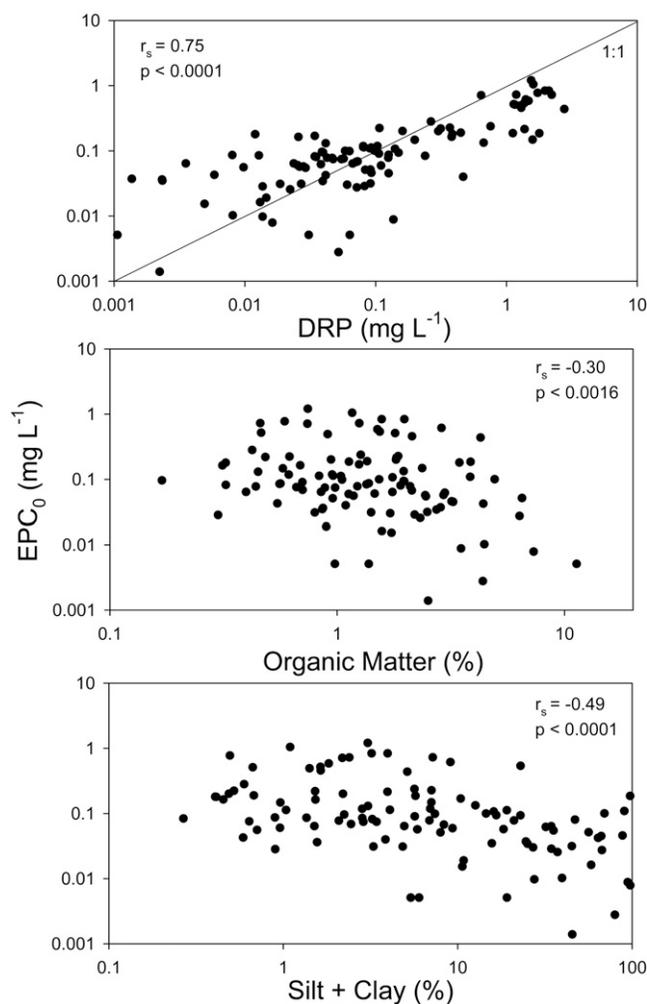


Fig. 3. Sediment equilibrium phosphate concentration at zero release or retention (EPC₀ in stream water) for all stream sites during the low-Q period of 2004 plotted against dissolved reactive P (DRP), sediment organic matter, or sediment silt + clay.

silt+clay of 76.8, 7.2, and 5.7%, respectively, and with little organic matter (median value 1.4%). However, some streams contained fine-textured sediments with large amounts of organic matter (silt+clay was significantly correlated with organic matter, $r_s = 0.70$, $p < 0.0001$) and sediment EPC_0 values displayed a significant, inverse relationship with both organic matter and silt+clay (Fig. 3).

The median initial mass isotherm slope (m) was 0.84, with 75% of the values >0.63 , suggesting most sediment samples had a great affinity for the added DRP—this was also shown by the distribution coefficient, K_d (Table 2). For the initial mass isotherm analysis, DDW was used and all sediments desorbed P when no DRP was added. The reactive sediment pool of P (RSP) from the initial mass isotherms varied from 0 to 232 $mg\ P\ kg^{-1}$, with a median value of 10.6 $mg\ P\ kg^{-1}$. This pool represents the P sorbed on sediments that could be released to stream water by abiotic sorption processes.

The $-b$ values (the unretained portion of the RSP) were much smaller than the RSP values, and ranged from 0 to 8.1 $mg\ P\ kg^{-1}$ (Table 2). As would be expected, the $-b$ and EPC_0 values were strongly correlated ($r_s = 0.93$), as the readily released P would be the pool that determines the EPC_0 concentration. The RSP was not correlated with water column total P concentrations suggesting much of the total P was in forms that were not readily sorbed or desorbed (Fig. 4). Water column DRP also was not correlated to RSP ($p > 0.05$, data not shown). Sediment total P concentrations were correlated with RSP ($r_s = 0.63$, $p < 0.0001$).

Sediment total P values were correlated with initial mass isotherm slope ($r_s = 0.32$, $p < 0.008$; Fig. 5), indicating that sediments with the highest affinity for P also had the greatest concentration of P. The RSP values were best correlated with

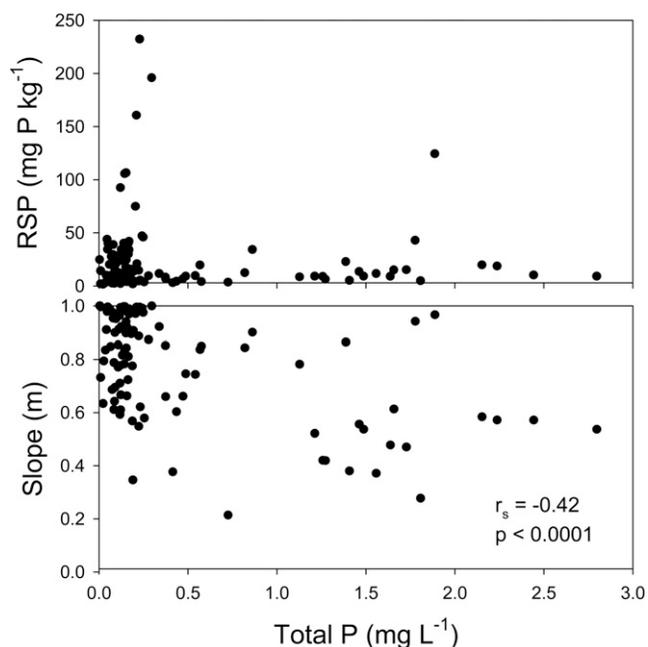


Fig. 4. Initial mass isotherm slope (m) and reactive sediment pool (RSP) plotted against stream water total P concentration for all stream sites during the low-Q period of 2004.

silt+clay ($r_s = 0.76$, $p < 0.0001$) because fine-textured sediments with organic matter were able to retain large P pools.

Sediment Phosphorus Dynamics at Intensive Sites

Stream water concentrations of DRP (and total P) varied greatly at the four sites, from a mean of 0.016 $mg\ L^{-1}$ DRP at EMM to 0.691 $mg\ L^{-1}$ at SF, which was downstream of a WWTP (Table 3). Dissolved reactive P as a percentage of total P ranged from 47% (EMM) to 91% (SF). The total P and DRP means for each site were statistically different (Kruskal–Wallis test, $p < 0.0001$). Typically, the greatest stream water P concentrations occurred during late summer and early fall (Fig. 6) in conjunction with a period of low flow.

The stream sediments consisted mostly of sand and gravel with little temporal variation in composition (Table 3). The EMC site had the finest textured sediment (silt+clay was 12%), as well as the greatest percentage of organic matter at 1.7% of dry weight. The largest fraction of P within the sediments was inorganic P. EMC had the greatest sediment total P concentration of 185 $mg\ kg^{-1}$, and also the largest fraction of organic P (Table 3).

Sediment isotherms were determined repeatedly ($n = 6$) to examine temporal dynamics. The EPC_0 values as a whole, when compared to in-stream DRP, indicated that sediments were acting mainly as sources for P throughout the year; the exception was late summer and early fall when DRP concentrations at each site exceeded the EPC_0 (Fig. 7). Overall, EPC_0 values showed no clear temporal patterns. Similar to sediments from across the state, EPC_0 values in these sites were directly correlated with DRP ($r_s = 0.59$, $p = 0.0033$) and inversely related to silt+clay content ($r_s = -0.58$, $p = 0.0071$). However, no significant correlation existed between EPC_0 and sediment organic matter.

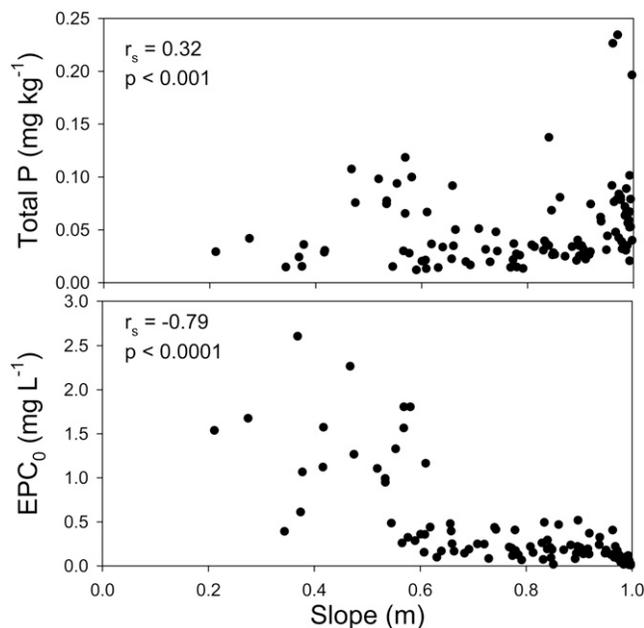


Fig. 5. Total sediment P and equilibrium P concentrations at zero release or retention (EPC_0 in distilled-deionized water [DDW]) plotted against initial mass isotherm slope (m) for all stream sites during the low-Q period of 2004.

Table 3. Water and sediment chemistry for four east-central Illinois stream sites ($n = 31$ for BLS, EMC, and EMM; $n = 22$ for SF). Sediment total P and pH were measured on only one set of samples. BD = below detection. Means shown along with range in parentheses. DRP, dissolved reactive P; DOC, dissolved organic C; EPC_0 , equilibrium phosphate concentration at zero release or retention; BLS, Black Slough; EMC, Embarras at Camargo, IL; EMM, Embarras at Meander; SF, Salt Fork in the Vermilion watershed.

	BLS	EMC	EMM	SF
Water temperature and chemistry				
Temperature (°C)	14.4 (3.4–27.5)	18 (2.8–28.8)	15.4 (3.2–31.2)	18.1 (3.6–30)
DRP (mg L ⁻¹)	0.051 (BD-0.202)	0.063 (0.005–0.198)	0.016 (BD-0.070)	0.691 (0.238–1.67)
Total P (mg L ⁻¹)	0.07 (0.014–0.307)	0.099 (0.015–0.268)	0.034 (0.010–0.127)	0.759 (0.282–1.75)
Nitrate-N (mg L ⁻¹)	6.1 (0.1–13.4)	6.6 (0.2–14.4)	5.0 (0.1–11.5)	7.1 (2.2–11.3)
Total N (mg L ⁻¹)	6.4 (0.5–13.4)	7.0 (0.5–14.4)	5.6 (0.6–11.5)	7.7 (2.6–11.6)
DOC (mg L ⁻¹)	2.2 (1.3–5.7)	2.9 (1.5–5.5)	2.9 (1.6–5.8)	3.4 (2.2–5.5)
Sediment chemistry				
Organic matter (%)	0.8 (0.6–1.1)	1.6 (0.8–2.7)	0.6 (0.5–0.8)	0.7 (0.4–1.1)
pH	8.4	7.9	8.5	8.5
NaOH-extractable P (mg kg ⁻¹)	80.0	184.8	33.9	118.7
NaOH-extractable organic P (mg kg ⁻¹)	3.7	25.3	5.5	1.4
Total P (mg kg ⁻¹)	276	328	203	360
EPC_0 (mg L ⁻¹)	0.056 (0.035–0.087)	0.047 (0.023–0.067)	0.029 (0.019–0.053)	0.310 (0.251–0.347)
Alkaline phosphatase activity (mg p-NP L ⁻¹ g Om ⁻¹ h ⁻¹)	1430 (840–2640)	1050 (516–2552)	1620 (1009–2206)	1530 (836–2864)
Sediment texture				
Gravel (%; 4.0–2.0 mm)	26 (14–41)	16 (4–27)	29 (13–46)	37 (20–56)
Sand (%; 2.0–0.05 mm)	71 (57–83)	72 (55–84)	67 (50–85)	62 (43–79)
Silt+clay (%; < 0.05 mm)	3 (1–5)	12 (1–22)	4 (1–8)	1 (0–2)

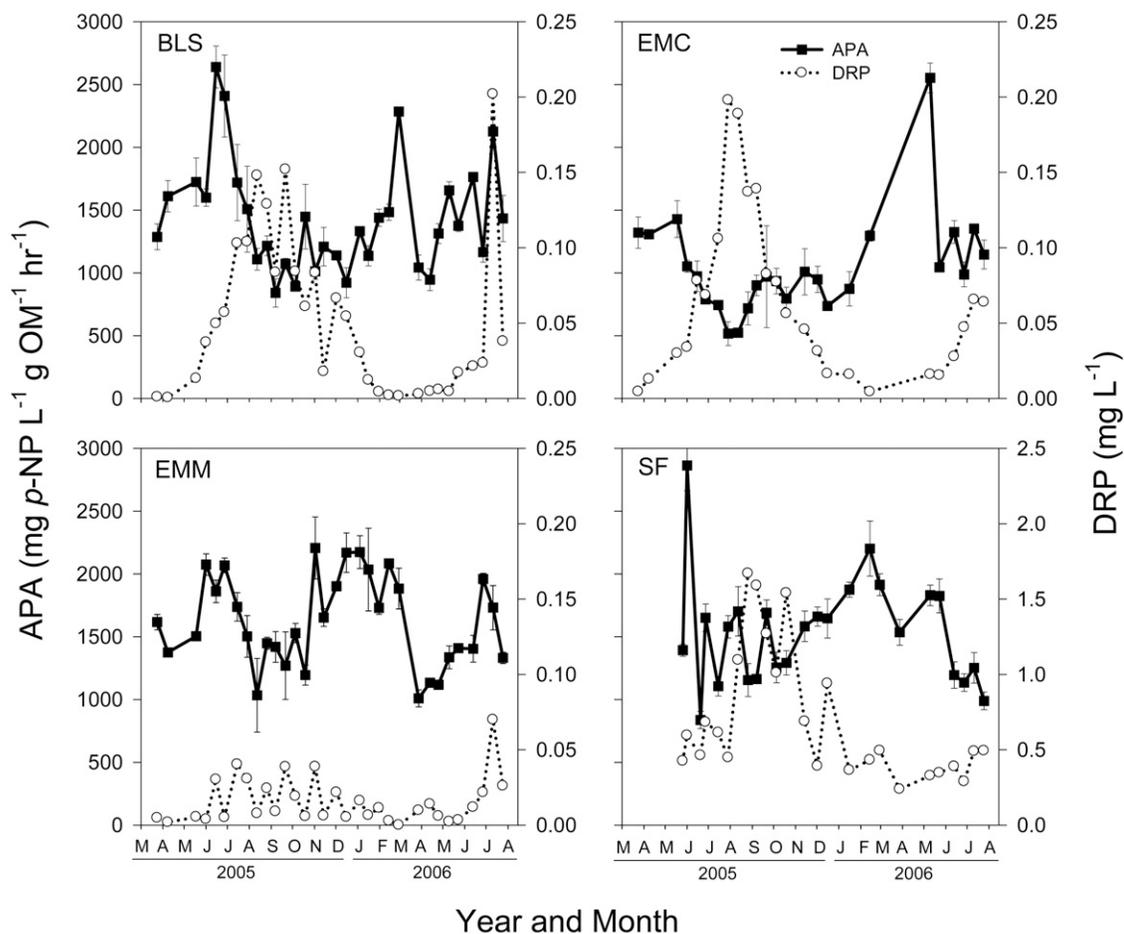


Fig. 6. Alkaline phosphatase activity (APA) in the sediments for the four east-central Illinois sites (with error bars for one standard deviation) from March 2005 through August 2006. Stream water dissolved reactive P (DRP) concentrations are plotted on the right axis.

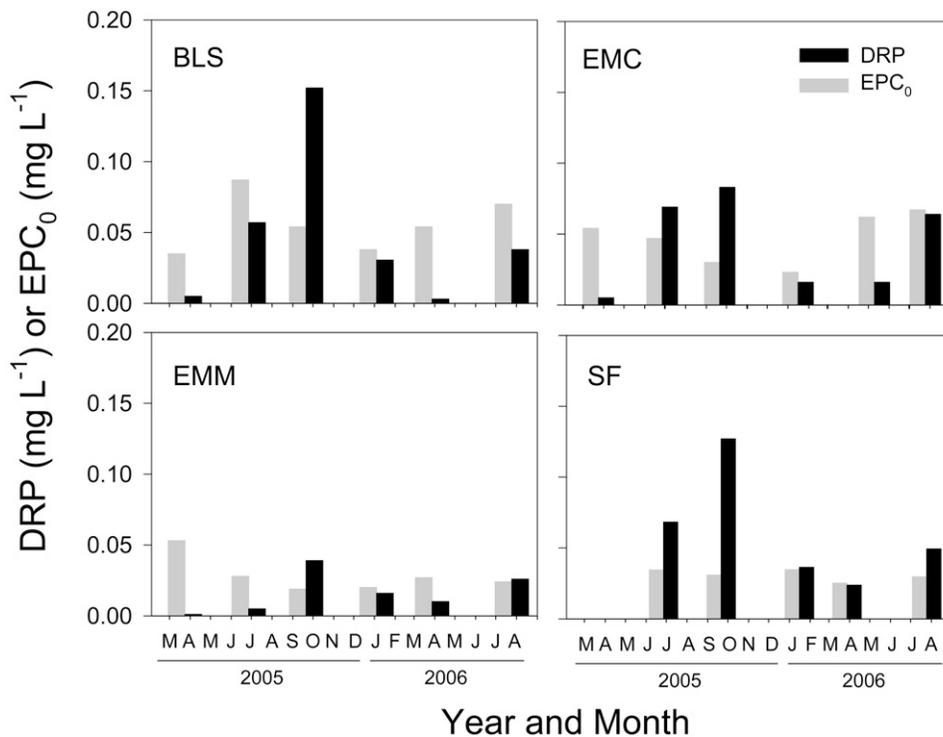


Fig. 7. Dissolved reactive P (DRP) and sediment equilibrium P concentrations at zero release or retention (EPC_0) for the four east-central Illinois sites from March 2005 through August 2006.

Table 4. Biotic contribution to dissolved reaction P (DRP) removal in sediments for four east-central Illinois sites. BLS, Black Slough; EMC, Embarras at Camargo, IL; EMM, Embarras at Meander; SF, Salt Fork in the Vermilion watershed.

Sampling date	Biotic contribution to total DRP removal (%)			
	BLS	EMC	EMM	SF
25 July 2006	28	34	20	11
30 Aug. 2006	29	42	20	43
9 Oct. 2006	54	43	38	25
Mean	37	40	26	26

The mean biotic contribution to total P uptake at BLS, EMC, EMM, and SF was 37, 40, 26, and 26%, respectively (Table 4). Black Slough had the greatest biotic contribution value of 54% measured on 9 Oct. 2006. Sediment organic matter content was weakly correlated ($r_s = 0.60$, $p = 0.0380$) with the biotic uptake. EMC, which had the highest mean organic matter content, also had the greatest mean biotic contribution to uptake.

We used repeated measurements of sediment APA as an indication of microbial processing of P in surface sediments. Although APA is a measure of P limitation and our sites were all relatively P-enriched, we chose to use this parameter as a means of examining temporal and between-site variability; both BLS and EMM sites had DRP concentrations near or below detection limit during spring and were almost consistently lower than EMC and SF (sometimes as much as an order of magnitude less as in the case of SF) throughout the year. Mean values of sediment APA were statistically different among the sites (Kruskal-Wallis test, $p < 0.0001$) and ranged from 1050 to 1620 $mg\ p\text{-NP}\ L^{-1}\ g\ Om^{-1}\ h^{-1}$ (Table 3). When not normalized for organic mat-

ter, APA was significantly correlated with organic matter content within the sediments ($r_s = 0.47$, $p < 0.0001$). A temporal pattern was clearly present at EMC (despite the lack of samples collected due to high Q during March and April 2006), less so at BLS and SF, and not present at all in EMM (Fig. 6). The APA pattern at EMC is the inverse of the stream water DRP concentration. All sites combined showed a weak negative correlation between the APA and DRP ($r_s = -0.19$, $p = 0.0003$). When each site was evaluated individually, only EMC had a significant inverse correlation ($r_s = -0.62$, $p < 0.0001$).

Discussion

In our study a major factor regulating the ability of sediment to sorb P from the water column and to accumulate large pools of reactive P (as measured by RSP) was particle size, although given the strength of our correlation coefficients other factors likely played a role. Most stream sediments that we sampled across Illinois were coarse textured, but the locations that were fine textured (and thus had greater organic matter) were able to more strongly sorb P from the water column (initial mass slopes near 1), with larger RSP values (as much as 232 $mg\ P\ kg^{-1}$). Other studies have documented a similar pattern, with EPC_0 values negatively correlated with sediment particle size or organic matter (Klotz, 1988, 1991; Haggard et al., 1999; McDowell and Sharpley, 2001; McDowell et al., 2003). The lack of correlation between RSP and stream water P concentrations, but presence of a correlation between RSP and sediment total P suggests that sediments exert control on stream water P concentrations when the stream water is low in P. However in most streams, RSP was a small percentage of sediment total

P (median RSP = 2.9% of sediment total P), suggesting that sorption of DRP from the stream water was not a dominant process leading to sediment P accumulation. During short- to medium-term periods, P release is likely to be a function of the bioavailable P pool (McDowell et al., 2003), which we suggest is represented by the RSP. Therefore, we conclude that particle size is an important factor in sediment accumulation, but that other processes and factors are also important.

We found large differences in EPC_0 estimated in DDW versus stream water. We believe this difference was mostly due to ionic concentration differences between stream water and DDW, which has previously been shown to affect P adsorption to sediments (Klotz, 1988, 1991). Our regression analysis indicated that EPC_0 in stream water was 45% of the concentration in DDW, so that the use of stream water in these hard water streams does greatly affect calculated value.

Haggard et al. (1999) hypothesized that the sediments from agriculturally-dominated central Oklahoma streams acted as a transient pool for P. This appears to be happening in some of the Illinois streams examined in this study. Based on EPC_0 values, it can be assumed that an increase in the pool of benthic sediment P occurs during the low-Q, high stream water P concentration period in late summer and early fall. We suggest this may be occurring in three sites in the Embarras watershed, and for other streams throughout Illinois where DRP was $>0.09 \text{ mg L}^{-1}$. In these streams, there would then be a subsequent release of P into the water column the remainder of the year until late summer or early fall conditions were reached again. Mainstone and Parr (2002) describe this as the general trend in sediments and evidence from our study and others (e.g., Chaubey et al., 2007) supports this notion.

Our results suggest that sediment P as assessed by equilibrium P concentrations across a wide range of streams throughout Illinois does reflect stream water concentrations, similar to relationships found in other studies (Klotz, 1988, 1991; Haggard et al., 1999, 2004, 2007). At low stream water DRP concentrations most sediments appear to have EPC_0 greater than the stream water DRP, suggesting these sediments would have the potential to desorb P and be a source of P to the streams. At higher concentrations ($>0.09 \text{ mg L}^{-1}$ DRP), the sediments have the potential to uptake DRP from the water column. At the intensive sites, EPC_0 values varied little during the year or in response to flow conditions, but DRP concentrations did vary greatly, leading to periods when sediments were a potential source of P (higher flow periods), and times when they were a potential sink (during low Q). Given the large loads of P in streams and rivers of Illinois (David and Gentry, 2000; Gentry et al., 2007), the release of P during a high flow period would seem unlikely to alter stream water loads. To investigate this further, we calculated the approximate size of the RSP and the readily exchangeable sediment P relative to annual DRP loads in the EMC site. We used the load data from Royer et al. (2006) and estimated the stream bed area by scaling up the streambed area from a similar, but smaller watershed in east-central Illinois (Schaller, 2003). To bracket the possible range that might be expected, we performed the calculations assuming the sediments were 5 cm thick and then again using a sediment thickness of 30 cm. In both cases we assumed

a bulk density of 1 g cm^{-3} . On an annual basis, RSP was equal to 2.3 to 13.6% of the DRP flux from EMC, given a sediment thickness of 5 and 30 cm, respectively. The readily exchangeable P in the sediment was $<1\%$ of the annual DRP flux from the watershed if sediments were 5 cm thick, and increased to approximately 2% if the sediments were 30 cm thick.

For streams with low P concentrations during low-Q periods, P desorption could add to stream P concentrations; however, RSP values suggest that this impact may be limited. The RSP values were relatively low (75th percentile was $27.2 \text{ mg P kg}^{-1}$), with many of the low DRP streams having RSP values at or near 0 mg P kg^{-1} (Table 2). We made a low-Q estimate of the size of the RSP and the readily exchangeable sediment P relative to low-Q DRP loads as described above, with the streambed area reduced by 20% to account for decreased stream width and length during low-Q periods (Schaller, 2003). For EMC, RSP was equal to 90% of the low-Q DRP load, and the readily exchangeable sediment P was equal to 11%, given a sediment depth of 5 cm. If sediments were 30 cm thick, RSP increased to $>500\%$ of the low-Q DRP load and the readily exchangeable sediment P to 70%. During low-Q periods, the sediments in this agricultural stream may serve as a source of DRP but our estimates do not support the notion that sediments may be a long-term P source capable of maintaining high stream water DRP even if anthropogenic inputs were significantly reduced. When sediments accumulate in agricultural streams, the streams are often subjected to dredging to remove the sediments. Such action would reduce the overall pool of sediment P available for possible release to the stream water, but could also reduce the ability of the stream bed to buffer inputs of reactive P from the landscape (Smith et al., 2006), at least over the short term. Management activities clearly can disrupt the natural sediment-water P dynamics in streams, but the exact nature of the disruption likely depends on the timing and intensity of the management activity, the characteristics of the stream, and the amount of external P loading to the stream.

The results from the SF site demonstrate the strong influence a WWTP can have on stream-sediment P dynamics. Stream water P concentrations were generally an order of magnitude greater in SF than the other three intensive sites due to the WWTP. The sediments in SF appeared to act as a P sink during most of the year, but the fate of that P is unknown, because there was no mass accumulation of P in the sediments based on total P concentrations (Table 3). An accumulation would be expected, as was found in the study by Thiebaut and Muller (2003) who showed a significant relationship between water column DRP and total P within the sediments. Data from sediments across the state showed only a weak relationship ($r_s = 0.21$, $p = 0.028$) between these variables. Salt Fork had little organic P and only slightly more inorganic P than EMM, a site of similar texture (Table 3). It is possible that there could be a relatively quick assimilation and then subsequent microbial mineralization of the P compounds, precluding a long-term accumulation.

We examined the biotic contribution to P uptake during late summer and early fall, when this process should have its maximum influence (Khoshmanesh et al., 1999). Haggard et al. (1999) examined three central Oklahoma streams with similar water chemistry

and physical sediment characteristics as the sites in east-central Illinois and reported an average biotic contribution of 38%, similar to the average of 32% found in the present study (Table 4). Evidence for end-product repression of alkaline phosphatase is well documented in terrestrial ecosystems (Spiers and McGill, 1979; Harrison, 1983; Kang and Freeman, 1999; Allison and Vitousek, 2005), but there are conflicting results on the occurrence within sediments. If end-product repression is occurring within the benthic sediments, APA would show an inverse relationship to DRP. Dissolved reactive P did reach low concentrations in two of the intensively sampled streams during spring months (Fig. 2), and we would expect greater APA during these same months. However, our data only slightly support this, given the observed pattern and weak correlation coefficients. The results from our study indicate only limited and weak occurrence of end-product repression in east-central Illinois stream sediments. We suggest that biotic uptake can influence stream-sediment P dynamics, but the magnitude of the influence is likely small for most of the year and not able to affect annual P flux from agricultural watersheds.

Conclusions

Using sediments collected from a wide range of streams across Illinois during a low-Q period and from evaluating temporal patterns at four intensive sites, we found that sorbed P in sediments reflected stream water DRP concentrations. The strength and character of this sorption was influenced by sediment particle size and related organic matter content, with finer textured, higher organic matter sediments more strongly retaining stream water DRP and accumulating larger reactive P pools. Biotic processing of DRP at the four intensive sites was an important process, but difficult to put into the context of overall sediment P retention processes. Microbial activity, as assayed by APA, was found to be consistently present, but only weakly related to stream P concentrations. Overall, we conclude that sediments in Illinois streams are a reflection of and partially affected by stream water P concentrations, but that the sediments seem unlikely to alter annual P loads in streams throughout Illinois, but may affect concentrations at low Q.

Many states, including Illinois, are currently developed nutrient criteria and standards for streams and rivers that focus on P. Our results suggest that if P inputs (either point or nonpoint source) are reduced, sediments are unlikely to provide long-term buffering of stream water P concentrations. However, in some systems there could be a time lag between reductions in external P loading and improvements in water quality, particularly during periods of low discharge when our results suggest sediments could serve as a P source. Lastly, we suggest that P standards for streams and rivers in Illinois may be most successful if developed with consideration of sediment dynamics, and activities that influence those dynamics, in addition to simple relationships between water column P and algal biomass.

Acknowledgments

Funding was provided by the State of Illinois through the Illinois Council on Food and Agricultural Research (C-FAR), Water

Quality Strategic Research Initiative. We thank Corey Mitchell, Karen Starks, Lowell Gentry, Allyson Morgan, Kate Von Holle, Tom Heatherly, Josh Burke, Tessa Marusarz, Emily Keane, Amber Herzel, and Linda Jacobson for field and laboratory assistance.

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