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Phosphorus sorption in drainage channel-floodplain systems in agricultural watersheds

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PHOSPHORUS SORPTION IN DRAINAGE CHANNEL-FLOODPLAIN SYSTEMS IN AGRICULTURAL WATERSHEDS

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ABSTRACT

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The two-stage channel is an in-stream conservation practice that creates inset floodplains in agricultural drainage channels and stabilizes streambanks. Inset floodplains are excavated adjacent to the channel, hydrologically reconnecting it to the main channel and tripling the reactive surface area during high flow events. It is uncertain what effect these channel designs have on complex phosphorus (P) dynamics in the stream and in the floodplain, both during baseflow and when channels are flooded. In order to evaluate these practices as a P management strategy, we took soil and water samples from streambed sediments and floodplain soils in 10 two-stage channels in central and northern Indiana during the summer of 2017. Soils were analyzed for their water-extractable P; oxalate-extractable P, Fe, Al; equilibrium P concentration (EPC_0) at zero net sorption; and a P sorption index. We also conducted a particle size analysis, determined moisture content of soils, and calculated loss on ignition to estimate organic matter content. We found that floodplain soils had more water-extractable P and a higher EPC_0 than streambed sediments, likely reflective of the elevated SRP concentrations experienced by floodplain soils during storm events. Floodplains also had greater P retention capacity, which was driven by organic matter and amorphous iron oxides providing sites for P binding. Differences between the two-stage channel design and the trapezoidal design were more modest. Streambed sediments were generally similar in the two systems, but inset floodplains had a greater ability to capture P in amorphous iron oxides than naturalized floodplains. As organic matter was the key driver of P retention capacity, differences recovery after the disturbance of construction may have masked differences. Overall, these results indicate that there are relatively minor changes in soil P dynamics after floodplain construction; however, the larger active surface area of the restored floodplains during storm events suggests that P buffering capacity may increase compared traditional trapezoidal channels.

CHAPTER 1. INTRODUCTION

Phosphorus (P) has been identified as the primary contributor to eutrophication in many freshwater bodies (Correll 1998; Davis et al. 2009), with a variety of sources contributing to large P loads, depending on the land use, geology, hydrology, and human development of the contributing watershed. Nonpoint sources of P, such as fertilizer and manure application on agricultural lands, are major contributors to eutrophication problems, particularly in the Western Lake Erie Basin (Chaffin et al. 2011; Kane et al. 2014; Scavia et al. 2014). For example, one study found that 89% of TP and 71% of SRP delivered to the western Lake Erie basin originated from non-point sources (Maccoux et al. 2016).

Phosphorus loads are transported to downstream waterbodies almost exclusively by a network of constructed drainage channels and subsurface tile drains in agricultural watersheds of the US Midwest. The system has been engineered over the past 150 years to lower the naturally high water table and increase crop yields (King et al. 2015). During high flow events, the drainage system acts as an efficient conduit of runoff and nutrient loads. However, when flows subside, and retention times increase, channels can also function as hot spots of biogeochemical activity in the landscape. This presents an opportunity for drainage channels to be modified to limit excess nutrients, such as P, from being transported downstream to sensitive water bodies.

Phosphorus cycling in drainage channels is driven by multiple processes including sediment sorption and desorption, precipitation and dissolution, and biological uptake and release (Reddy et al. 1999). Phosphate ions adsorb and desorb to amorphous iron (Fe) and aluminum (Al) oxides, humic-Fe(Al) complexes, and directly to organic matter (Gerke and Hermann 1992). In fluvial systems, these reactions are primarily dependent on contact time between water and sediment (Collins et al. 2016), but concentrations of the respective chemical species, redox conditions, pH, and temperature also plays a major role in sorption dynamics (Holtan et al. 1988). Precipitation and dissolution reactions typically involve calcium, but can also involve iron, aluminum, and manganese, and are highly dependent on pH. Biological activity regulates dissolved oxygen, redox potential, and water column mixing at the sediment-water interface. Additionally, microorganisms and plants directly assimilate P to satisfy a variety of cellular processes. However, in many fluvial systems, abiotic controls tend to dominate over biotic controls, especially when concentrations are high and biological uptake reaches saturation (McCallister and Logan 1978; Klotz 1985).

The complexities of abiotic and biotic drivers of P dynamics make fluvial systems difficult to study; thus, functional soil and water measurements are frequently used to characterize drainage channel sediments. These functional measurements allow for predictions about system behavior that would not otherwise be possible by examination of a single point in time. The equilibrium phosphorus concentration at zero net sorption (EPC_0) is one such measurement (Smith et al. 2006; Sharpley et al. 2007; Ahiablame et al. 2010; Liu et al. 2013). The EPC_0 of sediment or soil quantifies the soluble reactive phosphorus (SRP) concentration in the water column that causes no net movement of P to or from the solid phase (Beckett and White 1964; Taylor and Kunishi 1971). A second technique that is often used for characterizing P sorption characteristics is a P sorption isotherm (Barrow 1978). Phosphorus isotherms describe the relationship between the concentration of P in the solid and liquid phase at a constant temperature. Isotherms, however, are labor intensive to create, so a phosphorus sorption index (PSI) is frequently used to capture the essential characteristics of the isotherm (Bache and Williams 1971).

Phosphorus retention capacity is most frequently controlled by soil organic matter content, clay content, and amorphous Al and Fe oxides (Y E Sallade and Sims 1997; Axt and Walbridge 1999; Liu et al. 2013; Shore et al. 2016). Amorphous Al/Fe oxides and organic matter provide binding sites for P, while clay particles increase the specific surface area of the soil. By comparing the EPC_0 of drainage channel sediments to water column SRP concentrations, it has been shown that channels can act as both sinks (Smith et al. 2005; Ahiablame et al. 2010) and sources (Smith et al. 2005; Sharpley et al. 2007; Ahiablame et al. 2010) of P. Channel sediments may retain P during periods of elevated P concentrations, and may leach P when concentrations are low (Ahiablame et al. 2010), keeping the streambed in a state of dynamic equilibrium. The P sorption index has also been frequently used in statistical models to determine the driving factors of P retention capacity (Nguyen and Sukias 2002; Wang et al. 2012; Liu et al. 2013). In this way, these functional metrics provide a proxy for P retention in fluvial systems.

The two-stage channel design is a proposed P conservation practice that could enhance P retention from agricultural nonpoint sources. It has traditionally been used to stabilize streambanks through the construction of inset floodplains in trapezoidal channels draining agricultural lands (Powell et al. 2007a). Typically, agricultural drainage channels are deep and over-widened, have simplified morphology, and have a low hydraulic gradient. They are regularly dredged to remove accumulated sediments which accelerates channel evolution processes. This creates conditions for increased bank erosion during high flows leading to bank slumping and mass wasting of bank sediments (Landwehr and Rhoads 2003). When dredging does not occur, channel evolution processes allow the slumped banks and erosion/deposition processes in the channel to create stable naturalized floodplains with dense herbaceous vegetation (Rhoads and Massey 2012). Two-stage channel design accelerates this stabilization process by actively constructing inset floodplains next to the channel while leaving the baseflow channel intact. When floodplains become inundated during periods of high flow, water velocities decrease on the benches and particulate matter is allowed to settle out (Powell et al. 2007). The lower shear stresses decrease erosion and sediment transport, undercutting, and bank slumping during high flow events (Powell et al. 2007b).

Dense herbaceous vegetation on the floodplain benches further stabilizes channel banks and transforms these areas into biogeochemical hot spots. The two-stage channel has therefore been proposed as a conservation practice for reducing nutrient loss. During storm events, floodplain inundation triples the reactive surface area and allows for longer contact time between flood waters and floodplain soils.Nutrient processing rates depend on many factors such as accumulation of organic matter, increased arability of soil after compaction during construction, and establishment of robust microbial communities, all of which are a function of age (McMillan and Noe 2017). As two-stage channels age, we would expect them to also become more effective at nutrient removal, particularly processes fueled by biological activity. This has been shown for nitrate processing in similar two-stage agricultural channels (Mahl et al. 2015), as anoxic groundwater flows into floodplains rich with organic matter, leading to optimal conditions for nitrate removal via denitrification (Roley et al. 2012). However, little is known about how the aging of these systems might affect P retention.

It has been demonstrated that two-stage channels can reduce SRP load (Hodaj et al. 2017), and concentration (Davis et al. 2015; Mahl et al. 2015). However, results vary widely. Davis et al. 2015 showed significant P concentration reductions at only one of the four study sites, while Mahl et al. 2015 showed significant decreases in two of the five two-stage reaches. It was hypothesized that these reductions were from sorption to fine sediments and assimilatory biotic uptake. However, it is unclear what causes some channels to behave as sinks for P, while others do not. Additionally, Liu et al. 2013 evaluated the P sorption capacity dynamics of a two-stage channel in the Jinjing watershed of southeastern China. They found that vegetation type had a significant impact on soil P characteristics but could not statistically differentiate the two-stage and control reaches. These studies lay important foundational work for the effectiveness of the two-stage channel as a P conservation practice but underscore the need to better understand fundamental P dynamics in these systems.

We collected soil and water samples from ten two-stage sites in Indiana and Michigan during baseflow to investigate patterns of P retention and release in the streambed sediments and floodplain soils of restored and conventional channels. The first objective of the study was to quantify the differences in soil P characteristics between streambed sediments and floodplain soils. As streambed sediments are responsible for regulating P loads during baseflow, and floodplain soils are only activated during storm events, these changes allow us to make inferences about channel behavior during baseflow versus stormflow. The second objective was to characterize the effect of floodplain construction on soil P characteristics in the streambed and floodplain. We hypothesized that inset floodplains would have a higher P retention capacity, while streambed sediments will be unaffected by the conservation practice because construction activities are limited to the near-stream zone and do not directly disturb the channel itself. Lastly, our third objective was to investigate how any differences that emerged between the two-stage and traditional channel changed through time. We expected organic matter accumulation on floodplain benches to correlate with channel age, which would positively impact P retention and accumulation in floodplain soils.

CHAPTER 2. METHODS

2.1 Site Descriptions

Ten sites across central and northern Indiana were sampled once during base flow conditions during the growing season (June–August 2017) (Figure 1). Watershed land-uses were dominated by row crop agriculture in either a corn *(zea mays)* – soybean (*glycine max*) or corn – soybean – wheat (*triticum aestivum*) rotation. The climate is similar across sites, with a mean summer temperature of 21°C and mean winter temperature of -2°C. Average annual precipitation is approximately 1000 mm, and is evenly distributed throughout the year, with slightly more rainfall in the spring. Sites were selected across a range of sizes, ages, and geographic locations in order to capture a representative snapshot of existing two-stage channels (Figure 1). The youngest site was implemented 2 years prior to sampling, and the oldest site was implemented 13 years prior to sampling (Table 1). Sites ranged in discharge from 0 to 500 L s^{-1}, and from 5 to 80 cm in stream depth. All channels were either first or second order streams. Watershed areas were calculated using the USGS StreamStats tool, with watershed areas ranging from 0.40 to 25.50 km^2. Soils were generally silt loams, silty clay loams, or clay loams, had low slopes (0 to 2 percent), and were poorly drained (Table 1).

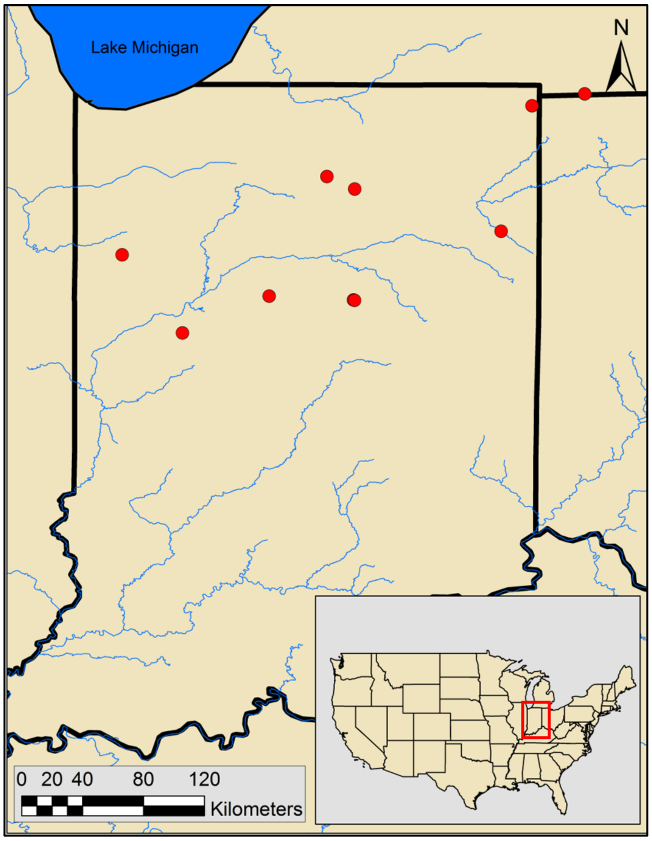

Figure 1: Site map for the ten sampling locations.

Table 1: Site characteristics table. For sites with significant inputs between the control and two-stage reaches, or with disconnected control and two-stage reaches, watershed area for the two-stage outlet is shown without parentheses, and the control outlet watershed is shown in parentheses.

Site Name	Glacial Region	Project Year	County	Latitude	Longitude	Dominant Watershed Soil Series	Hydrologic Soil Group	Drainage area (km^2)	CTL Bank State
Fish Creek	North Lake Moraine	2009	Steuben	41.640	-84.833	Del Rey silt loam - Fine, illitic, mesic Aeric Epiaqualfs	C/D	25.50	Intact
Ransbottom	North Lake Moraine	2009	Kosciusko	41.147	-85.881	Rensselaer loam - Fine-loamy, mixed, superactive, mesic Typic Argiaquolls	B/D	19.95 (0.24)	Intact
Crommer	North Lake Moraine	2004	Hillsdale (MI)	41.709	-84.522	Sloan silt loam - Fine-loamy, mixed, superactive, mesic Fluvaquentic Endoaquolls	B/D	10.30	Intact
Little Pipe	Central Till Plain	2012	Howard	40.490	-85.882	Pewamo silty clay loam - Fine, mixed, active, mesic Typic Argiaquolls	C/D	17.30	Slumped
Rice Bell	Central Till Plain	2011	Howard	40.515	-86.387	Sloan silt loam - Fine-loamy, mixed, superactive, mesic Fluvaquentic Endoaquolls	B/D	4.19	Slumped
Little Pipe 2	Central Till Plain	2015	Howard	40.493	-85.888	Pewamo silty clay loam - Fine, mixed, active, mesic Typic Argiaquolls	C/D	18.90	Slumped
TPAC	Central Till Plain	2012	Tippecanoe	40.298	-86.899	Sloan clay loam - Fine-loamy, mixed, superactive, mesic Fluvaquentic Endoaquolls	B/D	2.90	Slumped
Kirkpatrick	Central Till Plain	2013	Jasper	40.759	-87.255	Reddick clay loam - Fine-loamy, mixed, superactive, mesic Typic Endoaquolls	C/D	4.94 (18.52)	Intact
Shatto	North Lake Moraine	2007	Kosciusko	41.222	-86.045	Sebewa loam - Fine-loamy over sandy or sandy-skeletal, mixed, superactive, mesic Typic Argiaquolls	C/D	12.10 (9.68)	Slumped
Adams	North Lake Moraine	2010	Adams	40.898	-85.016	Whitaker silt loam - Fine-loamy, mixed, active, mesic Aeric Endoaqualfs	B/D	0.40 (0.21)	Intact

2.2 Field Sampling Procedure

At each site, two 100-meter stream reaches were established in a constructed inset floodplain and the naturalized floodplains in a paired conventional agricultural drainage channel. Care was taken to avoid any subsurface tile drain inputs or other major changes in land use (e.g., roads or dairy operations). Ideally channels with naturalized floodplains (hereafter referred to as "control") were located either upstream or down stream of two-stage reaches, but this was not always possible. In such instances, the nearest stream of similar order and land use was used as the control.

Stream water grab samples were first taken from the downstream and upstream ends of each reach and kept on ice until they could be filtered and analyzed. Next, four 1.5-cm diameter soil cores were taken from 5 evenly spaced transects (0, 25, 50, 75, and 100 meters) to a depth of 5 cm along each of the reaches in both the floodplain and streambed. For the control reaches, soil samples from naturalized floodplains were taken in place of the inset floodplain samples, but in some cases, intact banks were used. All five transects of samples (20 cores total) from the streambed of each reach were homogenized, and all five transects of samples from the floodplain or bank for each reach were homogenized. Each location would therefore have four samples: two-stage floodplain, two-stage streambed, control floodplain, and control streambed. All soils were kept on ice until they could be analyzed. Finally, discharge measurements were taken using a Sontek FlowTracker2 ADV and the current-meter method (Rantz 1982) at both the upstream and downstream ends of each reach.

2.3 Laboratory Analyses

Unless otherwise noted, all soil analyses described below were conducted in triplicate. To determine moisture and organic matter content, soils were dried at 60°C in a forced draft convection oven for 72 h. Moisture content (MC) was calculated as the difference between wet and dry soil mass divided by the wet soil mass. Samples were then combusted in a muffle furnace at 550°C for 4 h. Soil organic matter (OM) was estimated as the mass loss during combustion divided by the soil mass pre-combustion (Tuttle et al. 2014).

Field moist soils were extracted for 4 h in the dark with a 90% acetone 10% water solution, centrifuged, and the supernatant used for chlorophyll *a* (chl *a*) analysis on a Trilogy® Laboratory

Fluorometer (EPA method 445.0). For all other analyses, soils were air-dried at 60°C, ground, and passed through a 2-mm sieve. Soil particle size distribution was determined using laser diffraction particle size analysis on a Malvern® Mastersizer 3000 (Konert and Vandenberghe 1997). Briefly, approximately 3 g of soil were soaked overnight in 30 mL of 10% hexametaphosphate. The following day, solutions were shaken for 30 min before being analyzed. Particle size distributions were then simplified into sand, silt and clay fractions for each soil.

To determine water-extractable P (WEP), 1 g of dried, ground soils was extracted with 25 mL of a 0.02M KCl solution for 1 h on a shaker-table (Pierzynski 2000). Two drops of toluene were added to inhibit microbial activity. After shaking, the solutions were centrifuged at 5000 rpm for 10 min, filtered through a 0.45 um cellulose nitrate filter, and analyzed on a SEAL Analytical® AQ2 Nutrient Analyzer. The SRP concentration in the supernatant was then normalized by the mass of extracted soil.

The equilibrium phosphorus concentration at zero net sorption (EPC_0) was determined by extracting 1 g of dry soil with 20 mL of 0.02 M KCl solutions with varying amounts of added potassium phosphate to give final SRP concentrations of 0, 1, 2, 3, and 4 mg P L^{-1} (Taylor and Kunishi 1971). Two drops of toluene were added to inhibit microbial activity. These solutions were put on a shaker table for 24 h, then centrifuged at 5000 rpm for 10 min, filtered, and run on an AQ2 Nutrient Analyzer for SRP. The mass of sorbed P was then plotted against the initial SRP concentration in each solution. The x-intercept of the best fit line through these points is defined as the EPC_0 (Klotz 1985), which represents the SRP concentration in the water column that causes no net movement of P between the soil and the water column. The slope of this same line is reported as the linear adsorption coefficient K_d and can be interpreted as the affinity of the soil for P at low concentrations. For every 1 mg L^{-1} increase in SRP concentration, each kg of soil will uptake K_d mg of SRP. All R^2 values of the best fit lines for these analyses were greater than 0.93.

In order to evaluate the concentration of amorphous iron and aluminum oxides in the soil samples, we extracted 0.4 g of dry soil with 40 mL of 0.2M ammonium oxalate at pH 3 for 4 h in the dark (McKeague and Day 1966; Darke and Walbridge 1994). Centrifuged and filtered samples were then analyzed using a Perkin Elmer® Optimate 8300 ICP-OES for Fe, Al, and P. The degree of P saturation (DPS) can then be calculated using:

$$DPS = \frac{P_{ox}}{\alpha(Fe_{ox} + Al_{ox})}$$

where α is the maximal saturation factor for total sorption and was set at a value of 1 for this study. The α factor has been set at 0.5 for non-calcareous sandy soils (Lookman et al. 1995; De Smet et al. 1995; Maguire and Sims 2002) and has been set at 1 in studies characterizing diverse soil types (Kleinman and Sharpley 2002; Zhang et al. 2005). Although no DPS model has been established in Indiana, we use this index as a comparative measure between the sampling locations and sites. The DPS index is often closely related to P solubility, although the strength of this relationship depends on the soils being studied (Beauchemin and Simard 1999).

A single point P sorption index (PSI) was also calculated by extracting 1.0 g of dry soil with 20 mL of 0.02M KCl water amended with 11.4 mg of potassium phosphate monobasic to give a final SRP concentration of 130 mg P L^{-1} for 24 hours (Dunne et al. 2006; Hogan and Walbridge 2007). The resulting filtrate was then analyzed by ICP-OES. PSI was calculated as *x/log C* where *x* is the mass of P sorbed (mg P per 100 g of dry soil) and *C* is the final SRP concentration of the solution (µmol P L^{-1}). This index has been shown to be directly related to the maximum P sorption capacity of the soil, although this relationship differs by location (Y. E. Sallade and Sims 1997; Axt and Walbridge 1999; Dunne et al. 2006).

Finally, each stream sample was split into two aliquots. The first 200-ml aliquot was filtered through a 1.5-µm glass microfiber filter. The difference in dry (105°C) filter weight pre- and post-filtering was normalized by the filtered water volume to give the Total Suspended Solids (TSS) (APHA/AWWA/WEF 2012). A separate 15-ml aliquot was filtered through a 0.45-µm cellulose nitrate filter and analyzed for dissolved reactive phosphorus (Colorimetric molybdenum-blue method, Detection Limit = 0.01 mg P L^{-1}), nitrate/nitrite (Cadmium reduction method, Detection Limit = 0.25 mg N L^{-1}), and ammonium (Alkaline phenate method, Detection Limit = 0.02 mg N L^{-1}) on a SEAL Analytical® AQ2 Discrete Analyzer (APHA/AWWA/WEF 2012).

2.3 Statistical Analyses

All data was analyzed using R software version 3.4.3; multivariate analyses were assisted by the MASS package (Venables and D.Ripley 2002). Paired Wilcoxon signed-rank were used to test for differences in soil properties between two-stage and control reaches. All measurements were averaged across floodplain and stream samples before comparing the two-stage and control reaches. Spearman's rho was used to test for correlations between variables, and significance was determined using the t-distribution. Significant correlations were further tested using simple linear regressions and transformed when necessary to achieve normality. An F-distribution was used to test for significance of these relationships. An alpha value of 0.05 was used for all significance testing and adjusted using the Bonferroni correction for multiple comparisons when a series of statistical tests were completed. Variables in the text are reported as a mean ± one standard deviation.

We used a stepwise regression analysis on the SAS JMP software to identify the variables that best predict the PSI, EPC_0, and K_d of bank sediments. Parameters included in the algorithm include all measured soil P properties (WEP, P_{ox}, Fe_{ox}, Al_{ox}), environmental variables (OM, chl *a*, sand, silt, clay, water column SRP, NO_3^-, and NH_4^+), and site characteristics (water temperature, watershed area, stream width, and stream depth) (16 total parameters). Streambed sediments and bank soils were lumped together in the model, but a binomial Streambed-Bank variable was added to test if these distinctions had any effect on P isotherm characteristics. A second binomial variable to distinguish between two-stage and control designs was also included. AIC_c minimization was used as the criteria for adding new variables to the model. Parameter addition was stopped when new variables were no longer significant based on an F-test. The models have limited applicability for predictive purposes as the dataset was too small to remove a training or test subset against which to validate the model but are valuable in identifying the drivers of these soil P indices.

CHAPTER 3. RESULTS

3.1 Soil property changes between streambed sediments and bank soils

We found distinct differences in physical, biological, and chemical soil properties between streambed sediments and floodplain soils (Table 2). Silt fraction increased slightly from 50% to 56% between the streambed and banks (Wilcoxon signed-rank test, $p<0.001$). This increase came with a commensurate decrease in sand content but no change in clay content. Biologically, chl *a* was highly variable across all sites and stream locations (coefficient of variation (CV) = 0.89). Concentrations were 13% lower in the bank soils than the streambed, although this difference was only significant at the 90% confidence level (Wilcoxon signed-rank test, $p=0.076$). Soil organic matter (OM) was also 54% higher in the floodplain soils than in the streambed, increasing from 4.2% to 6.5% of dry mass (Table 2; Wilcoxon signed-rank test, $p<0.001$).

Table 2: Comparison of soil properties between all streambed sediments and all bank soils.

Soil Property	Streambed sediments	Floodplain soils	Percent change	Ranked-Sign Test Significance
Sand (%)	39.9	34.2	-15%	<0.001
Silt (%)	50.1	56.2	14%	<0.001
Clay (%)	9.93	9.62	-3%	0.869
OM (%)	4.24	6.51	54%	<0.001
Chl *a* (mg kg^{-1})	1.16	1.00	-13%	0.076
WEP (mg P kg^{-1})	0.68	1.46	115%	0.027
EPC_0 (mg P L^{-1})	-0.011	0.093	-	0.001
K_d (L kg^{-1})	15.4	15.9	3%	0.123
PSI (L kg^{-1})	258	338	31%	0.002
P_{ox} (mg P kg^{-1})	8.74	9.80	12%	0.154
Fe_{ox} (mg Fe kg^{-1})	58.7	53.2	-9%	0.154
Al_{ox} (mg Al kg^{-1})	26.2	30.8	17%	0.021
DPS (%)	10.3	11.7	13%	0.012

Floodplain soils had more P, but also a higher P retention capacity than streambed sediments. There was more than twice the amount water-extractable P (WEP) in the floodplain than the streambed (Table 2; Wilcoxon signed-rank test, $p<0.001$). This increase in WEP coincided with a 100 µg P L^{-1} increase in EPC_0 (Wilcoxon signed-rank test, $p=0.001$), making floodplain soils more likely to release P than streambed sediments at the same overlying SRP concentration.

There was also a 12% increase in oxalate-extractable P (P_{ox}) in the floodplain soils, although this difference was not significant (Wilcoxon signed-rank test, p=0.134). In addition to the higher WEP, EPC_0 and P_{ox} in floodplain soils, the PSI was 31% higher than streambed sediments (Wilcoxon signed-rank test, p=0.002), indicating a greater capacity to retain P in the floodplains.

3.2 Soil property changes between two-stage and trapezoidal channel designs

In contrast to the distinct difference between the streambed sediments and floodplain soils, differences between the two-stage and naturalized floodplains were modest. Physical and biological soil properties were similar between two-stage and control reaches in both the streambed and floodplain soils (Table 3). Particle size fractionation and moisture content were nearly indistinguishable between designs. Soil moisture content (MC) of bank soils was relatively consistent across all sites with a mean of 29% and a standard deviation of 8% (Wilcoxon signed-rank test, p=0.262). The two measured biological soil indicators, OM and chl *a*, were also similar between the two-stage and control designs. In particular, there was no difference in OM between the two-stage floodplain soils and the control bank soils, as was initially hypothesized.

Table 3: Summary of soil and water data collected at two-stage and control reaches – separated between streambed sediments and bank soils. Means are shown with 95% confidence intervals.

Location	Reach	Moisture Content	Organic Matter (%)	Chl *a* ($ug\ g^{-1}$)	Sand (%)	Silt (%)	Clay (%)
Streambed	Two-stage	-	3.9 ± 1.0	0.9 ± 0.3	40 ± 10	50 ± 7	10 ± 3
	Control	-	4.5 ± 1.6	1.4 ± 0.7	40 ± 10	50 ± 8	10 ± 4
Floodplain	Two-stage	31 ± 4 %	6.5 ± 0.9	1.1 ± 0.7	34 ± 11	56 ± 8	10 ± 4
	Control	28 ± 3 %	6.5 ± 0.9	0.9 ± 0.5	34 ± 11	56 ± 8	9 ± 4

Unlike the physical and biological soil properties, soil chemistry was significantly different between the two-stage and control. Streambed sediments in the two-stage channel had a lower tendency to release P at low water column SRP concentrations, as quantified by a lower EPC_0, less WEP, and a higher K_d. WEP in stream sediments was reduced from 0.84 to 0.52 mg P kg^{-1} (Figure 2). This represents a 40% reduction in readily-available P (Wilcoxon signed-rank test, p=0.027).

The lower streambed WEP corresponded with a 50 µg P L^{-1} lower EPC_0, although this difference was not statistically significant (Wilcoxon signed-rank test, p=0.432), along with a 9% increase in K_d (Wilcoxon signed-rank test, p=0.193). Streambed sediments had little to no change in P properties related to more recalcitrant P, including PSI, P_{ox}, Fe_{ox}, and Al_{ox} (Wilcoxon signed-rank test, p=0.695, 0.322, 0.846, and 0.375 respectively).

Floodplain soils followed similar patterns as the streambed sediments in WEP, EPC_0, and K_d. WEP was 30% lower, EPC_0 was 80 µg P L^{-1} lower, and K_d was 8% higher in the two-stage reaches, although none of these differences were statistically significant (Wilcoxon signed-rank test, p=0.375, 0.160, 0.193). In addition to changes in readily-available P, floodplain soils also had increases of 7%, 20%, 30%, and 6% over the naturalized floodplain soils of the control channel for PSI, P_{ox}, Fe_{ox}, and Al_{ox} (Wilcoxon signed-rank test, p=0.105, 0.037, 0.064, 0.432 respectively). P_{ox} was highly correlated with both Fe_{ox} and Al_{ox} in the bank soils (Spearman's rank correlation; ρ=0.81, p<0.001; ρ=0.86; p<0.001 respectively). This had the effect of keeping the degree of P saturation (DPS) relatively consistent at 11.7% across all reaches (CV=0.235), with no significant difference between channel designs (Wilcoxon signed-rank test, p=0.375).

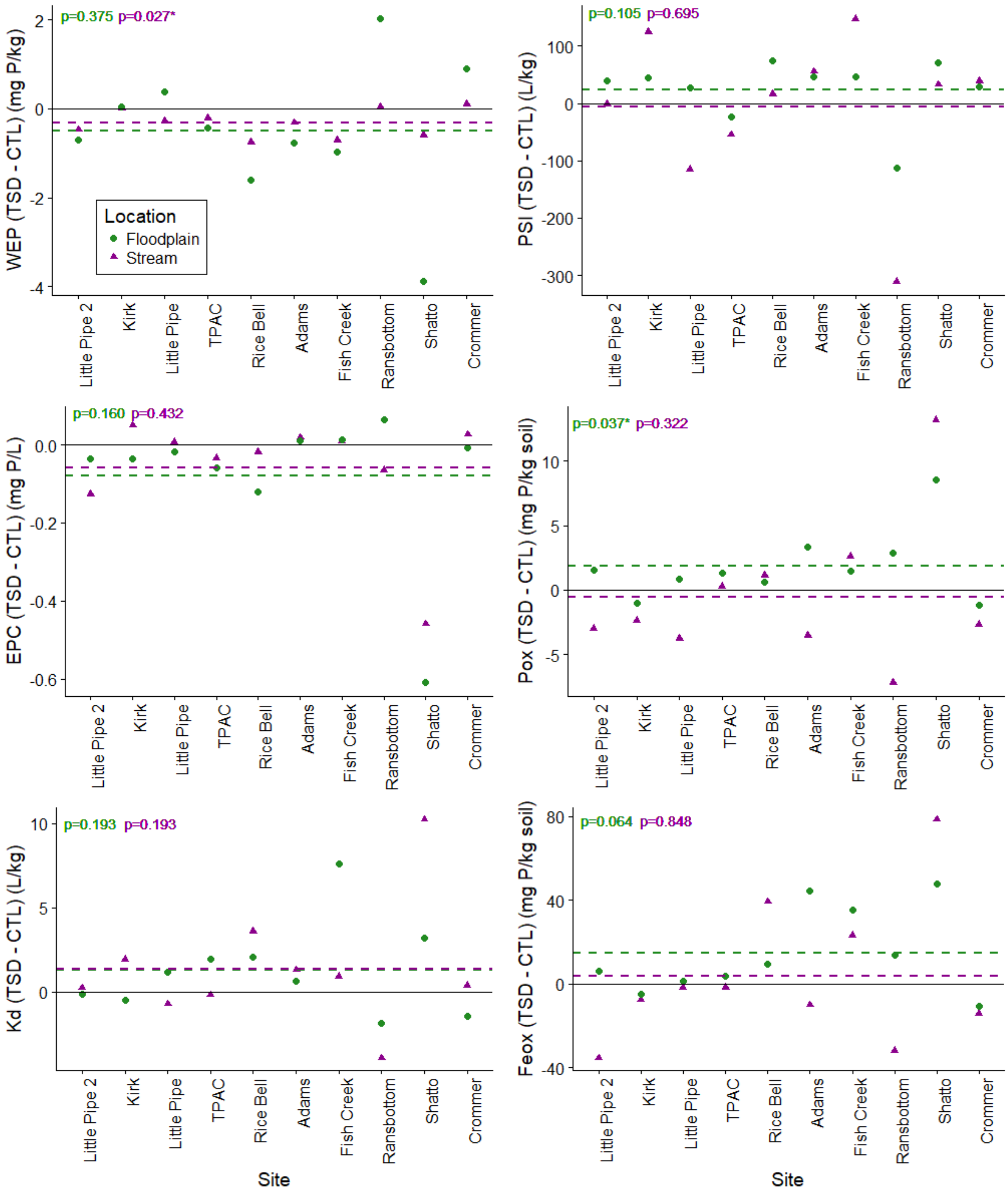

Figure 2: Water-extractable P, EPC_0, K_d, PSI, P_{ox}, and Fe_{ox}. Sites are ordered from newest to oldest from left to right, and the means of floodplain and streambed differences are shown as dotted lines. Differences between the two-stage and control samples were tested using a paired Wilcoxon signed-rank test, and p-values are shown in the top left corner of each plot. Results are noted with an asterisk if significant at an alpha value of 0.05.

In addition to comparing soil properties between the two-stage and control, we hypothesized that age would play a significant role in shaping these systems. Only two-stage floodplain soil organic matter was significantly correlated with age of the channel. We normalized floodplain OM to the control to account for among site variability. A simple linear regression with age revealed a significant positive relationship (Adj. R^2=0.37, p=0.037, Figure 3). The model parameters indicate that floodplain OM drops by 1.9 ± 0.9% when subsurface soils are exposed during two-stage channel construction (intercept = -0.0192). The two-stage benches then accumulate 0.30 ± 0.11% organic matter more than the unmodified channels each year after construction. The linear regression indicates that approximately 7 years after two-stage construction, the control banks and two-stage floodplains are expected to have the same OM. The same normalization was done for all other soil physical, biological, and chemical properties, but no significant relationships emerged.

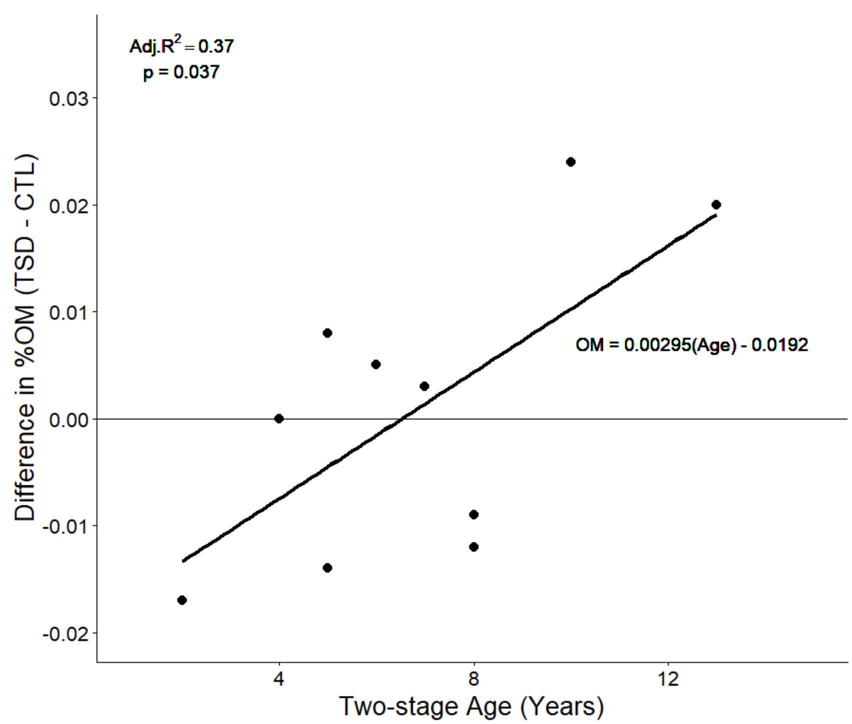

Figure 3: Difference between the organic matter content of control reach bank soils and two-stage floodplain soils plotted against the number of years since two-stage implementation. A simple linear regression is shown as a solid line.

3.3 Source-sink behavior of channels

SRP concentrations were generally low, but ecologically significant, across sites (0.03 ± 0.05 mg P L^{-1}), as would be expected during baseflow in the growing season. Out of the 20 reaches, 5 had a higher EPC_0 concentration than SRP concentration (sediments expected to function as a source), while 15 had a lower EPC_0 than SRP (sink function) (Figure 4). Sites tended to group together, with only a small influence of channel design on their sink/source distinction or strength. We quantified P source or sink strength by the linear distance between the point (SRP, EPC_0) and the 1:1 line (Figure 4). The sign of this distance is negative for sinks, and positive for sources. While the two-stage reaches were a 40 ± 96 µg P L^{-1} stronger sink than the control reaches based on this metric, the difference was not statistically significant (Wilcoxon signed-rank test, p=0.232). The Shatto control channel was an outlier and a strong source of P, therefore heavily skewing these means (Figure 4). The Adams channel was the strongest sink of P, but the control and two-stage reaches were relatively similar. These two sites also had the highest EPC_0 and stream water SRP concentrations of any location, respectively. Across all sites, the EPC_0 of floodplain soils was higher than that of the streambed sediments (Table 2). The number of predicted reaches serving as P sources therefore increased from 5 to 7 when comparing the water column SRP concentrations to the EPC_0 of floodplain soils.

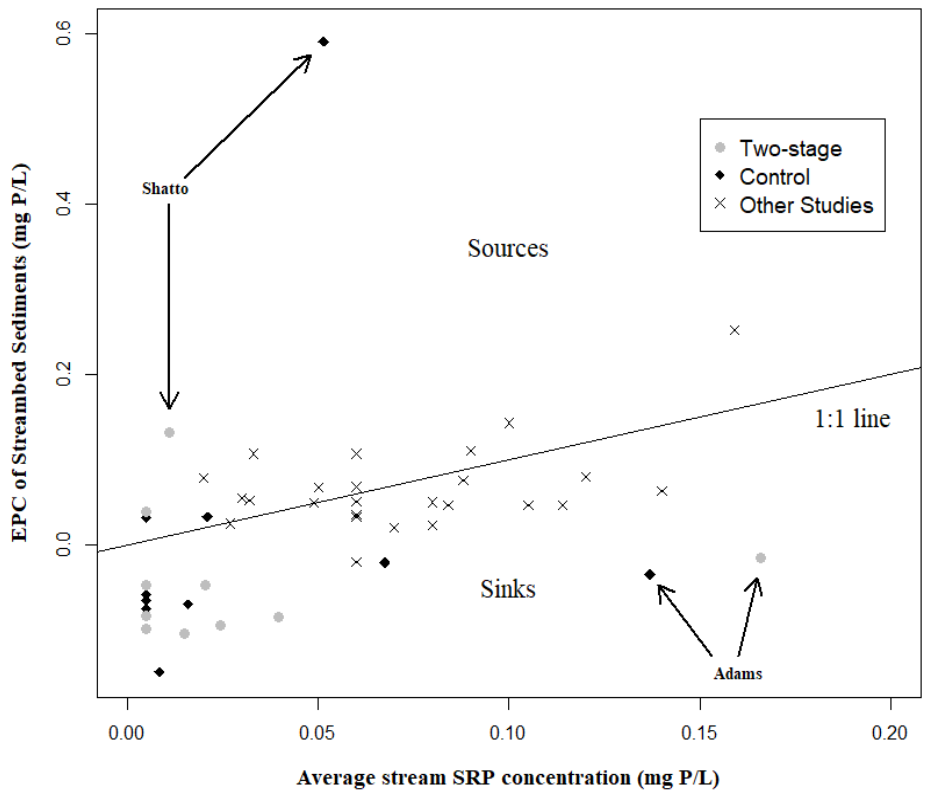

Figure 4: Average SRP concentration in stream water plotted against the EPC_0 of streambed sediments. Smith et al. (2005), Smith et al. (2006), Ahiablame et al. (2010) are shown with an x, while data from this study are shown as solid point. Points above the 1:1 line should theoretically function as sources of P, while points below the 1:1 line should function as sinks.

3.4 Identifying drivers of PSI, EPC_0, and K_d

We conducted three stepwise multiple regressions to elucidate the controls on PSI, EPC_0, and K_d. Site characteristics, soil properties, soil P pools, and two binomial stream-floodplain and two-stage-control variables were used as inputs to the algorithm. Results of these regressions show that soil OM was the best predictor of PSI, followed by the clay fraction and Fe_{ox} (Table 4). PSI was positively correlated with each of these parameters, and the model could account for 76% of the variability in PSI for both the streambed and banks. The only parameter needed in the EPC_0 model was WEP, which explained just over 80% of the variability. The linear adsorption coefficient (K_d) was best predicted by the clay fraction and Fe_{ox}, explaining 56% of the variability together. Notable parameters that did not appear in the models were the site characteristics, namely: stream width, stream depth, watershed area, or water temperature.

Table 4: Results of three stepwise regression analyses for PSI, EPC_0, and Kd. Model parameters are listed in the order they entered the model.

Variable	**Model**	**Adj. R^2**	**P-value**
PSI	$= 3830(OM) + 15.0(Clay) + 3.02(Fe_{ox}) - 207$	0.76	0.002
EPC_0	$= 0.162(WEP) - 0.144$	0.80	<0.001
K_d	$= 0.262(Clay) + 0.0461(Fe_{ox})$	0.56	<0.001

CHAPTER 4. DISCUSSION

4.1 Streambed and floodplain source-sink dynamics

Nearly two-thirds of P loads are transported during storm events, making these critical moments for nutrient capture (Pionke et al. 1999; Sharpley et al. 2008). To better understand how the increase in reactive surface area associated with the two-stage design will affect P dynamics, we used several functional soil P properties. They help link fundamental soil characteristics to expected P fluxes in the channel, which allow us to make predictions about drainage channels' behavior. Furthermore, comparing soil P properties between the streambed sediments and floodplain soils leads to inferences about channel behavior during baseflow and stormflow. When making these comparisons, streambed sediments are more representative of P retention during baseflow, while streambanks are only activated during stormflow.

In general, streambed sediments contained less P than floodplain soils. WEP and EPC_0 were both significantly lower in streambed sediments. Both the WEP in the floodplain soils (1.46 mg P kg^{-1}) and streambed sediments (0.68 mg P kg^{-1}) were significantly smaller than that found by Dunne et al. 2007 (7.6–18.7 mg P kg^{-1}) in drainage channels in Florida, but within the same range of Nguyen et al. 2002 (0.20–9.08 mg P kg^{-1}) reported in New Zealand. We assert that the changes in WEP and EPC_0 are likely reflective of the different SRP concentrations in surface and/or groundwater that the streambed and banks are exposed to. It is well-established that in-stream SRP concentrations in agricultural watersheds increase during storm events (Carpenter et al. 1998; Hart et al. 2004; Gentry et al. 2007). Floodplain soils, both in the two-stage floodplains and naturalized floodplains in conventional channels, are exposed to these elevated concentrations. The equilibrium relationship between floodplain soils and water column SRP during storms shifts up the isotherm relative to what would be expected at baseflow. SRP concentrations are typically elevated for only a short duration during storm events, and exhibit complex hysteretic behavior (Williams et al. 2018). It is therefore likely that bench inundation would persist longer than the rise and fall of SRP concentrations, potentially making floodplains both a sink and source of P within a single storm event. Conversely, lower SRP concentrations at baseflow shift the equilibrium between stream sediments and surface water downwards.

The differences between EPC_0 in streambed sediments compared to floodplain soils is further underscored by their source-sink behavior. When comparing baseflow SRP concentrations to the EPC_0 of streambed sediments, we showed that 15 of the 20 sites should be acting as sinks for P (Figure 4). Other studies of drainage channels in Indiana have found similar splits between the number of sources (11) and sinks (14) (Smith et al. 2005; Smith et al. 2006; Ahiablame et al. 2010).The mean EPC_0 of streambed sediments (-0.011 mg P L^{-1}) were among the lowest reported in Indiana (Smith et al. 2005; Smith et al. 2006; Ahiablame et al. 2010). In contrast, the mean EPC_0 of floodplain soils (0.093 mg P L^{-1}) was within the expected range for drainage channels in Indiana. If we make a similar source-sink comparison between SRP and the EPC_0 of floodplain soils, the number of predicted sink sites drops to 13 due to higher EPC_0 in the bank soils. While this suggests that floodplains could in fact be acting as a source of P to the steam during storms, EPC_0 is most useful when compared to actual in-stream concentrations over short (storm events) and long (seasonal) timescales (Sharpley et al. 2007). SRP concentrations have been shown to vary widely in headwater streams in agricultural watersheds (King, Williams, and Fausey 2015; Hodaj et al. 2017). Both source and sink behavior may therefore be possible, depending on storm timing and size. EPC_0 of floodplain soils could be an important metric for predicting P retention based on water quality monitoring efforts already underway in the Midwest.

In addition to having more loosely-sorbed P, floodplain soils had a higher P retention capacity than streambed sediments, as estimated by PSI. Measured values of PSI in our study sites ranged from 113–634 L kg^{-1}, which was within the 50–5819 L kg^{-1} range found by Sallade and Sims (1997) in Delaware, and slightly above the 32–330 L kg^{-1} reported by Dunne et al. (2006). Both Dunne et al. (2006) and Axt and Walbridge (1999) also found that PSI was a function of landscape position. However, the 31% increase we found from streambed to banks was smaller than the 75% increase from streambed to wetland soils reported by Dunne et al. (2006).

Our regression analysis showed that PSI was best predicted by OM, clay content, and Fe_{ox} (Table 4). Iron oxides and clay particles have long been recognized as significant contributors to P sorption (Agbenin and Tiessen 1994; Reddy et al. 1998; Smith et al. 2005; Zhuan-xi et al. 2009; Wang et al. 2012). However, while clay content and Fe_{ox} were slightly lower in the bank soils (3% and 9% decrease, respectively), OM was more than 50% higher, which suggests that it is a stronger driver of the observed PSI increase between floodplains and streambed sediments.

Other studies have found similar relationships between PSI and OM both in terrestrial soils and aquatic sediments (Sanyal et al. 1993; Y E Sallade and Sims 1997; Axt and Walbridge 1999; Zhuan-xi et al. 2009). It is well-established that OM provides sites for P sorption both directly and indirectly through humic-metal complexes (White and Thomas 1981; Gerke and Hermann 1992; Guardado et al. 2007; Gerke 2010). In particular, Al and Fe complexed by humic acids have 5 times the sorption capacity of Fe and Al in amorphous oxides, and 50 times the sorption capacity of crystalline Al and Fe on a molar basis (Torrent et al. 1990; Gerke and Hermann 1992). Our data indicate that OM is also a significant contributor to P sorption capacity in constructed inset floodplains.

While the increase in P sorption capacity may indicate a greater ability to buffer P loads during storm events, there was no similar increase in K_d between the banks and streambed to coincide with the increase in OM. PSI and K_d are reflective of the capacity for soils to adsorb P at high and low SRP concentrations, respectively. The inclusion of OM in the PSI model, but not in the K_d model may indicate that OM is important for providing sorption sites only at high SRP concentrations. The high binding energy of much of the OM fraction may prevent significant P sorption before concentrations are high. In the environmentally-relevant ranges that K_d was measured (0–4 mg P L^{-1}), amorphous iron oxides, as estimated by Fe_{ox}, were a much better predictor of P buffering capacity. These findings are similar to those of Zhang and Huang 2007, who showed that iron oxides were only correlated with K_d when exchangeable-P pools were low. At high concentrations, iron oxides became saturated, and no longer had sorption sites available to further remove SRP from the Florida Bay. Our findings indicate that while OM provided the majority of total sorption sites, P is preferentially binding to iron oxides, particularly at SRP concentrations typical of drainage water in the Midwest (<1 mg L^{-1}). This implies that underlying soil type may be the most important parameter for the retention of P in floodplain soils. If iron compounds are not already present in the subsurface, then the efficiency of the channel as a sink for P may be reduced. Soil test results during the early stages of a project could help identify those sites most well-suited for P management via two-stage channels and other management practices as these controlling factors would also be applicable to other soil-based practices (e.g., grassed waterways).

4.2 How does the two-stage design affect P dynamics?

While the two-stage design had little effect on physical and biological soil properties, differences in chemical soil properties emerged. We observed lower EPC_0 and WEP in the streambed sediments of two-stage channels, which are both indicative of stronger sink behavior. Two-stage channels generally narrow as they age, increasing water velocities in the main channel (Powell et al. 2007). At our sites, two-stage reaches had higher water velocities, which may have flushed out loosely-sorbed P more quickly than a traditional channel, thereby lowering EPC_0 and WEP. However, we also observed minimal changes in isotherm properties, K_d and PSI, which implies that the sediments have similar affinity for P between the control and two-stage channel.

There were also changes in two-stage channels in the floodplain soils. Similar to stream sediments, constructed floodplain soils had a lower EPC_0 and less WEP than the control, indicating that two-stage floodplains are less likely to contribute SRP to the stream channel when activated. These changes coincided with an increase in PSI and K_d. Although statistically insignificant, the 7% and 8% increases coupled with a tripling in reactive area during storm events could lead to significantly more P capture than a traditional channel. These changes were driven primarily by a 30% increase in Fe_{ox} in the floodplains. While our study did not directly measure the mechanisms driving these changes, we hypothesize that more frequent wetting of banks soils in a two-stage channel may allow for rapid cycling of oxic and anoxic conditions. Fe oxides are reduced when soils are flooded, dissolving them into solution. When soils again become oxic, Fe oxides do not reform with the same crystallinity, and becomes disordered (Darke and Walbridge 2000). Similarly, when subjected to experimental cycles of wetting and drying, soils had significantly more amorphous Fe oxides than unflooded cores (Darke 1997; Kinsman-Costello et al. 2016) which has been suggested to increase with the periodicity and frequency of flooding (Kuo and Mikkelsen 1979). The imperfections in the Fe oxide lattice structure create additional P sorption sites on the mineral surface. If a two-stage channel has more or deeper redox cycles, this may lead to an increase in amorphous iron compounds. It is clear that these changes are effective at increasing P retention as the two-stage floodplains also capture 20% more P_{ox} than the trapezoidal banks. All else equal, if the active area of the entire stream-floodplain system is tripled in the two-stage design and the P captured on iron oxides increases by 20% in the top 5 cm, then we can approximate an increase in overall system capacity by a factor of more than 3.5 per length of channel. While this estimation does not allow us to calculate total P retention, it does highlight the potential that constructed inset floodplains have for adsorbing P to iron oxides.

4.3 Two-stage development through time

We found that OM was a significant driver of P sorption capacity (Table 4). OM content of floodplains ranged from 4.45–9.13%. This is within the range of OM contents found by Mahl et al. 2015 (3.5–11%) at other two-stage sites. However, there was no increase in OM between the control channel and two-stage floodplains, as was initially hypothesized. Based on the regression analysis between OM and two-stage age, we postulate that age may have been the confounding factor in detecting these changes (Figure 3). Regression model parameters indicate that soil OM decreases by 2% when a two-stage is constructed, and OM accumulates 0.3% more than the control soils each year afterwards. The decrease when two-stage channels are constructed can be attributed to exposure of subsurface soils as inset floodplains are excavated beside the channel. The faster OM accumulation on floodplain soils is likely caused by a combination of carbon inputs associated with greater hydrologic connectivity (McMillan and Noe 2017) and slower OM mineralization caused by extended periods of inundation (Tate 1979).

If we divide the decrease in OM content during construction by the rate of OM accumulation, we find that the two-stage channel is predicted to have the same OM content as its control counterpart about 7 years after construction. We saw no leveling-off of OM in our data, so it is unclear how long this trend would continue. However, we expect that the floodplains will reach a steady state where OM inputs and outputs are similar. The point where OM stabilizes will be controlled by a variety of factors including OM inputs and bench height. Lower benches will be inundated more frequently, and therefore will be under anoxic conditions for longer periods of time, further slowing OM breakdown. While OM dynamics in wetlands are dependent on autochthonous carbon inputs, a significant portion of carbon budgets in floodplain systems comes from allochthonous carbon inputs (Hoffmann et al. 2009). Consequently, restored wetlands can develop for more than 50 years before significant OM accumulation can be detected (Ballantine and Schneider 2009). This dataset potentially indicates that the allochthonous carbon inputs characteristic of fluvial systems allow for faster system recovery than a constructed wetland.

With only 10 data points in our regression analysis, the relationship between age and OM is far from conclusive, but it suggests that the time scale over which we evaluate the success of these projects needs to be re-examined. Despite the reinforcing trends of greater OM input and slower OM breakdown, two-stage channels may take more than a decade of development before significant changes in OM and P retention capacity can be detected. Most monitoring efforts are targeted at the 2-5-year time frame, because that is the funding and personnel availability. These results imply that monitoring efforts need to be maintained over even longer periods of time to better capture the development trajectory of these systems. To still be economically feasible, samples might need to be taken less frequently or focused on a smaller subset of sites.

CHAPTER 5. CONCLUSIONS

We found distinct changes in physical, biological, and chemical soil properties between streambed sediments and bank soils, highlighting the different chemical and hydrologic conditions seen by the respective areas of the channel. Both constructed and naturalized floodplain soils stored significantly more P than streambed sediments, which corresponded to a high capacity for P retention, corresponding to higher SRP concentrations that come with surface runoff. Streambed sediments had no change in P retention capacity between the two, but a small increase in P retention capacity was observed in the inset floodplain soils. Combined with larger wetted areas during storm events, two-stage channels may significantly increase P capture, particularly by amorphous iron oxides.

Organic matter was also a key driver of P retention capacity as evidenced by multiple regression analysis, which will likely have a stronger control as both naturalized and constructed floodplains age. Modeling results showed that OM build-up on floodplain soils takes about 7 years before it has recovered to pre-construction levels. Furthermore, the well-documented correlation between organic matter and P sorption capacity suggests that P retention follows a similar trajectory. These systems may therefore take longer to recover from disturbance than previously thought. As the mean age of two-stage channels in this study was close to 7 years, differences in soil P properties may have yet to emerge.

The P soil properties measured in this study are primarily focused on P dynamics over the daily to monthly time scale, but long-term P retention is also important from a management perspective. The only long-term sinks of P in the channel-floodplain system are storage of P in recalcitrant organic and inorganic compounds in soils, and deposition of particulate P on floodplain benches. While this study found modest differences in P dynamics between the two-stage and traditional designs, the larger wetted area of the two-stage channel during storm events implies greater exchange of water between biochemically active regions in the riparian area and the stream. Given that the potential for P uptake is similar on a mass-basis between the designs, the two-stage would be expected to act as both a stronger sink and source when active. The two-stage channel has potential to buffer high loads that are expected during storms but may shift to a source when concentrations subside.

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