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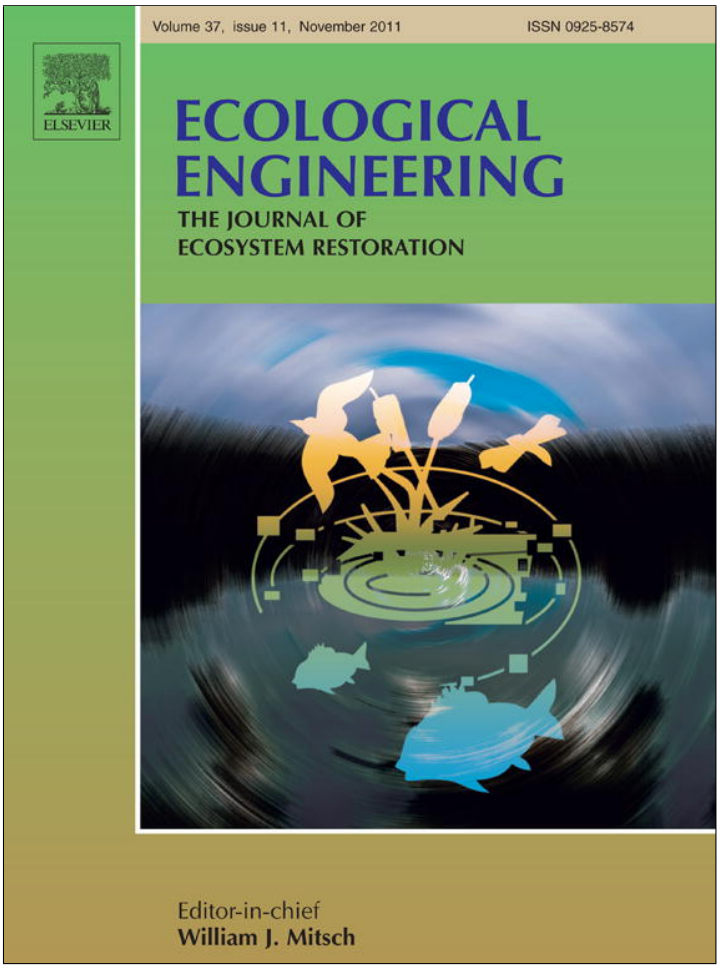

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Short communication

Phosphorus dynamics within agricultural drainage ditches in the lower Mississippi Alluvial Valley

Robert Kröger[a,*], Matthew T. Moore[b]

[a] Department of Wildlife, Fisheries and Aquaculture, Mississippi State University, PO Box 9690, MS 39759, USA
[b] USDA-Agricultural Research Service National Sedimentation Laboratory, Water Quality and Ecology Research Unit, PO Box 1157, Oxford, MS 38655, USA

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ABSTRACT

Excessive phosphorus loading from fertilizers in agriculture results in enriched runoff and downstream aquatic system eutrophication. This study evaluated phosphorus dynamics in agricultural drainage ditches across eight sites within the Lower Mississippi Alluvial Valley (LMAV). The objective of the study was to examine the capacity of drainage ditches across the LMAV to sorb P. Spatially and temporally, all drainage ditch sediments had very low immediately bioavailable phosphorus (P_w), and a very low degree of phosphorus saturation (DPS < 20%) throughout the LMAV. Phosphorus binding energy (K) (0.34–0.60 L/mg) and P sorption maxima (17.8–26.6 L/mg) were low, with very little variation in space and time. Using these metrics, drainage ditches sampled within the LMAV could be described as P sinks, capable of sorbing varying degrees of P seasonally as a result to changes in the Fe-P pool. Sorption, however, will likely be low due to low P sorption maxima and low binding energies. These results will help in P management within primary aquatic systems (such as drainage ditches) within the agricultural landscape and enhance P mitigation strategies at the source, prior to runoff reaching downstream aquatic systems.
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1. Introduction

Phosphorus (P) loading into aquatic systems, especially those that are P limited, can result in eutrophication and a loss of aquatic ecosystem integrity (Sharpley, 1980; Sharpley et al., 1992). Typically, excessive P loading is derived from agriculture, excessive fertilizer applications and elevated P soil concentrations. In the Mid-South (Mississippi, Arkansas and Tennessee), agricultural runoff is surface driven, with runoff channelized to surface drainage ditches that direct flow to downstream systems. It is thus vital to understand how drainage ditch sediments interact and contribute to P dynamics in agriculture and to downstream aquatic ecosystems.

In freshwater aquatic systems, P is considered as a limiting nutrient (Adler et al., 1994, 1996; Alexander et al., 2008). Phosphorus is also typically the limiting nutrient in agricultural systems and is amended through fertilizer applications. Global P applications increased from 813 million tons in 1913 to 17 billion tons in 1980 (Hart et al., 2004), with waning current fertilizer sales attributed to increased economic constraints. Seasonal patterns of rainfall, varying fertilization strategies, and water table fluctuations result in variable P concentrations in runoff. Therefore, varying influences may affect P concentrations and loads on drainage ditches as primary aquatic systems receiving runoff.

Phosphorus occurs in drainage ditches in the Mid-South as a result of two processes: (1) high natural P concentrations in agricultural and drainage ditch sediments and (2) surface runoff carrying P rich sediments that are deposited in the drainage ditch. Phosphorus undergoes multiple reactions in the sediments and at the sediment–water interface based on varying biogeochemical parameters (Palmer-Felgate et al., 2011). Dissolved inorganic P in the water column can be bound or sorbed to particulate molecules through sorption of Fe and Al or precipitation of Ca. Bioavailable forms of P include Fe and Al-P, which can become readily available if redox and pH conditions change. Non-labile P or forms of recalcitrant and organic P are those P forms that will not desorb under reduced biogeochemical conditions to become ortho-phosphate. Drainage sediments could have the capacity to be both P sinks and sources depending on saturation capacity, soil type, and biogeochemical conditions (Qian et al., 2011). There have been numerous studies describing P in runoff (Gentry et al., 2007; Hart et al., 2004; Kleinman et al., 2007; McDowell and McGregor, 1980; McDowell et al., 1989; Vadas et al., 2008; Yates and Prasher, 2009). There have been fewer studies that have examined P in adjacent drainage ditches (Kröger et al., 2008; Moore et al., 2010; Needelman et al., 2007; Nguyen and Sukias, 2002; Sharpley et al., 2007; Vaughan et al., 2007). Vaughan et al. (2007) noted a high standard devia-

* Corresponding author. Tel.: +1 662 325 4731; fax: +1 662 325 8976.
E-mail address: rkroger@cfr.msstate.edu (R. Kröger).

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Fig. 1. Drainage ditch locations within the Lower Mississippi Alluvial Valley. Eight sites were sampled quarterly in 2008. All sites were in row-crop agriculture of corn, cotton, rice or soybeans.

tion for oxalate P across and within individual ditches. There is, however, little information on how drainage ditch sediments operate as either sinks or sources for P dynamics, and more especially in the Lower Mississippi Alluvial Valley (LMAV).

Managers of agriculture require information whether surface drainage ditches associated with row-crop agriculture in LMAV are sinks or sources of P to downstream aquatic ecosystems. Answers are required for effective management of agricultural runoff, effective management of surface drainage ditches, and for the protection of downstream aquatic ecosystems. This study examined the capacity of drainage ditches across the LMAV to sorb P. This study also investigated temporal changes in saturation capacity, P dynamics and overall P reduction capacity to produce better management recommendations for drainage ditch systems.

2. Materials and methods

2.1. Study locations and experimental design

Eight study locations throughout the LMAV, comprised of three ditches per location were selected for water and sediment sampling (Fig. 1). All eight study locations were cropped in either corn, cotton, soybeans or rice, which are the predominant agricultural crops in the LMAV. Sediments and water were collected on four quarterly sampling events throughout 2008. Within each ditch, three sediment samples were taken longitudinally along the fall of the drainage ditch. This provided a total of 261 drainage sediments. Sediment samples were taken from the upper 15 cm of each soil profile in the middle of drainage channel. Sediment and water samples were labeled accordingly, and were transported on ice from the field to the USDA—Agricultural Research Service, National Sedimentation Laboratory in Oxford MS for nutrient analysis. An aliquot of 100 mL of water sample was filtered for dissolved inorganic P (DIP) analysis, while 100 mL of unfiltered water was digested for total inorganic P (TIP) (Murphy and Riley, 1962). Sediments were air-dried in a greenhouse to a constant weight, and shaken through a 2 mm sieve. Particle size analysis on ground sediment occurred using the hydrometer method of Bouyoucos (1962). Soil pH was measured in a 1:1 mixture of soil:dilute salt solution (0.01 M $CaCl_2$–calcium chloride) using a Oakton handheld pH electrode. Soil moisture was determined by the difference in weight before and after drying 5.0 g of field moist drainage ditch sediment at 105 °C in a gravity convection oven.

2.2. Phosphorus digestions

Acid ammonium oxalate extraction (Vaughan et al., 2007) extracts both non-crystalline/amorphous and poorly crystalline Fe and Al from analyzed sediments. The extraction also yields a P_{ox} which is P associated with non-occluded and occluded Fe and Al (Maguire and Sims, 2002). Each sediment was air-dried, coarse material removed through a 2 mm soil sieve, and approximately 1.0 g ± 0.01 of sediment placed in labeled centrifuge tubes for extraction. A 40 mL solution of 0.2 M ammonium oxalate $(NH_4)_2C_2O_4.H_2O$ (28.3 g in 1 L deionized (D.I.) water = 0.2 M solution) and 0.2 M oxalate acid $H_2C_2O_4.H_2O$ (25.2 g in 1 L D.I. water = 0.2 M solution) with a pH of 3 (Maguire and Sims, 2002; Pautler and Sims, 2000; Vaughan et al., 2007) was added to each centrifuge tube for a consistent 1:40 (v/v) soil/solution ratio. Iron and Al analysis occurred on an Elementar Atomic Adsorption, following typical atomic adsorption procedures. Samples were diluted 1:4 (v/v) using 2000 mg/L NaCl to suppress interferences. Oxalate P analysis was performed using an ICP-MS (Agilent Series). Samples were diluted 1:50 (v/v) with D.I. water and appropriate standard curves created to bracket the samples. Run protocol defined a five level standard curve, a check standard inputted into the run after every 20th sample, and a blank run after every check standard. All P analyses resulted in concentration ranges in mg/L. Concentrations were multiplied by volume of reagents used for the respective analysis, and divided by the initial weight of soil within the digestion to produce mg/g of element per dry weight.

Phosphorus sorption maxima (S_{max}), as well as phosphorus binding energy (K), were determined by saturating 5 g (dry weight basis) with four standard P concentrations (5, 10, 25 and 100 mg/L), as well as running a control for water extractable P (P_w). Phosphorus standards were 50 mL of respective P addition in a centrifuge tube, minus any sediment addition. Sediment samples were placed in polyethylene, 50 mL centrifuge tubes and incorporated with 50 mL $CaCl_2$ solution spiked with assigned concentrations of $KH_2PO_4^{3-}$. All tubes were shaken in the dark on a reciprocating Eberbach shaker for 16 h, centrifuged at 2500 rpm, filtered through 0.45 μm Whatman nitrate cellulose filter, and the supernatant analyzed for DIP using molybdenum-blue colorimetry (Murphy and Riley, 1962). Standard curves were regressed with concentration at 99% confidence, and absorbance of samples read at 880 nm on a Thermo Scientific Genesys 10 spectrophotometer. Phosphorus sorption (PS) was the calculated difference between the added P

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concentration (P_o) and the final P concentration at equilibrium (PD) (assumed after 16 h of shaking):

$$PS = \frac{(P_o \times V) - (PD \times V)}{M}$$

where V is the volume of liquid (L) added to the chambers, and M the mass by dry weight of sample (kg). Phosphorus sorption parameters were estimated using Langmuir isotherms as follows:

$$\frac{PD}{PS} = \frac{1}{KS_{max}} + \frac{PD}{S_{max}}$$

By plotting PD/PS versus PS, S_{max} can be determined from the slope ($1/S_{max}$) and K (P binding energy) from the intercept ($1/KS_{max}$).

Degree of phosphorus saturation (DPS) was calculated as an index of ditch sediment potential to release P into water column. There are two suggested critical DPS values: 40% (Sallade and Sims, 1997) (drainage ditch sediments) and 25% (Breeuwsma et al., 1995) (soils). Sediments with values greater than the critical values were suggested to have a higher susceptibility to P losses than those with lower DPS values. Degree of P saturation is determined as the percentage of P retention as sediment extractable P (Borling et al., 2004). Degree of P saturation is calculated using the following equation post ammonium oxalate extraction (Maguire and Sims, 2002):

$$DPS_{ox} = \left(\frac{P_{ox}}{0.5[Al_{ox} + Fe_{ox}]}\right) \times 100$$

2.3. Statistical analyses

Site data were tested for normality using a Shapiro–Wilks goodness of fit test. Data were log- or arcsine transformed to fit normality assumptions for ANOVA, and comparisons made between seasons, and sites. Pearson linear correlations were made between respective P parameters and P concentrations. Alpha was set at 0.05 for all tests.

3. Results

Particle size analysis of all ditch sediments indicated high silt percentages as compared to sand and clay components. Ditch sediment was typically acidic (pH range: 4.3–6.1) (Table 1). Oxford location sediments were the most acidic (loess hill site), with all other locations in the 5–6.1 pH range. Sediment moisture contents were low, <20% overall, for all seasons, confirming the lack of clay particles in the sediments retaining moisture. Drainage ditch width (<1–10.5 m) and length (160–440 m) varied within and among sites.

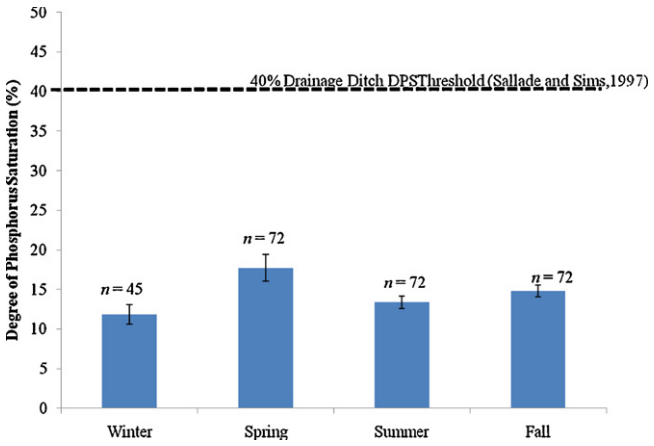

Fig. 2. Degree of phosphorus saturation for drainage ditch sediments across seasons. Note small standard deviations between sites within each sampling event. Critical threshold was suggested from Sallade and Sims (1997).

There were significant differences between Al_{ox} and Fe_{ox} concentrations in all drainage ditch sediments. Fe-oxalate concentrations ranged between 4 and 7 mg Fe/g while Al_{ox} concentrations were consistently below 1 mg Al/g. Fe-oxalate concentrations changed significantly with season ($F = 2.34$; $p = 0.01$) with higher Fe concentrations in winter and fall, and decreased through summer and spring. P-oxalate concentrations ranged between 0.34 and 0.44 mg P/g. These concentrations were an order of magnitude higher than immediately bioavailable P (P_w) for all ditch sediments (Table 1). P_w increased in most drainage ditch locations from winter to fall ($r^2 = 0.78$; $p = 0.001$), with significant differences among locations. Although there were no seasonal differences in P_w ($F = 0.56$; $p = 0.6$), there were statistically significant differences in available P_{ox} ($F = 3.5$; $p = 0.01$), which were substantiated and correlated with changes in Fe_{ox}. A Pearson's linear correlation between P_w and P_{ox}, highlighted a significant ($p = 0.01$) positive linear trend ($r^2 = 0.259$), though variable. The DPS of all ditch sediments across all seasons (Fig. 2) had <18% DPS threshold. There were significant seasonal differences in DPS between drainage ditch sediments ($F = 6.5$; $p = 0.001$), with the highest DPS value occurring in spring samples, concurrent with most fertilizer applications, and the lowest DPS value occurring in winter, a time where runoff P concentrations are theoretically at their lowest. Mean P sorption maxima (S_{max}) (Fig. 3) ranged 17.8–26.6 mg P/kg, and P binding energies (K) (Fig. 3) ranged between 0.34 and 0.60 L/mg for all drainage ditch sediments. Sorption maxima and binding energies showed very little variation among locations, or between seasons within locations (standard deviation for all sites: <0.6 S_{max}; <0.08 K).

Table 1
Physicochemical characteristics of drainage ditch sediments within sites throughout the Lower Mississippi Alluvial Valley. Characteristics of pH, soil moisture, Fe_{ox}, Al_{ox}, P_{ox} and P_w are means (±S.D.) across all quarterly sampling periods. Seasonal drainage ditch characteristics are means (±S.D.) for each season.

Site	% Silt	pH	Soil moisture (%)	Fe_{ox} (mg/g)	Al_{ox} (mg/g)	P_{ox} (mg/g)	P_w (mg/g)
Oxford	87 ± 5	4.3 ± 0.27	22 ± 5.1	5.1 ± 1.7	0.29 ± 0.33	0.42 ± 0.28	0.012 ± 0.008
Memphis	85 ± 5	5.4 ± 0.54	17 ± 5.2	5.2 ± 2.1	0.25 ± 0.26	0.51 ± 0.26	0.022 ± 0.01
Jonesboro	97 ± 1	5.5 ± 0.33	13 ± 3.7	2.3 ± 0.6	0.35 ± 0.37	0.10 ± 0.02	0.004 ± 0.003
Success	96 ± 1	5.8 ± 0.40	17 ± 4.6	5.9 ± 2.3	0.29 ± 0.29	0.26 ± 0.06	0.015 ± 0.005
Stoneville	94 ± 2	5.3 ± 0.45	19 ± 5.9	6.1 ± 2.1	0.49 ± 0.52	0.46 ± 0.17	0.024 ± 0.009
Portageville	90 ± 4	6.0 ± 0.36	19 ± 6.0	6.7 ± 1.8	0.24 ± 0.05	0.61 ± 0.09	0.033 ± 0.01
Judd Hill	53 ± 10	6.0 ± 0.38	9 ± 6.2	2.9 ± 1.1	0.12 ± 0.05	0.30 ± 0.12	0.032 ± 0.01
Tallahatchie County	96 ± 1	5.2 ± 0.32	15 ± 8.5	7.9 ± 1.8	0.27 ± 0.06	0.48 ± 0.07	0.028 ± 0.01
Winter		5.2 ± 0.04	19 ± 1.4	6.0 ± 2.9	0.90 ± 0.34	0.42 ± 0.33	0.019 ± 0.01
Spring		5.5 ± 0.03	15 ± 1.4	4.8 ± 2.4	0.18 ± 0.08	0.40 ± 0.19	0.017 ± 0.007
Summer		5.6 ± 0.03	18 ± 1.9	4.9 ± 2.3	0.15 ± 0.06	0.33 ± 0.16	0.021 ± 0.01
Fall		5.4 ± 0.03	18 ± 1.9	5.4 ± 2.3	0.17 ± 0.08	0.41 ± 0.21	0.023 ± 0.01

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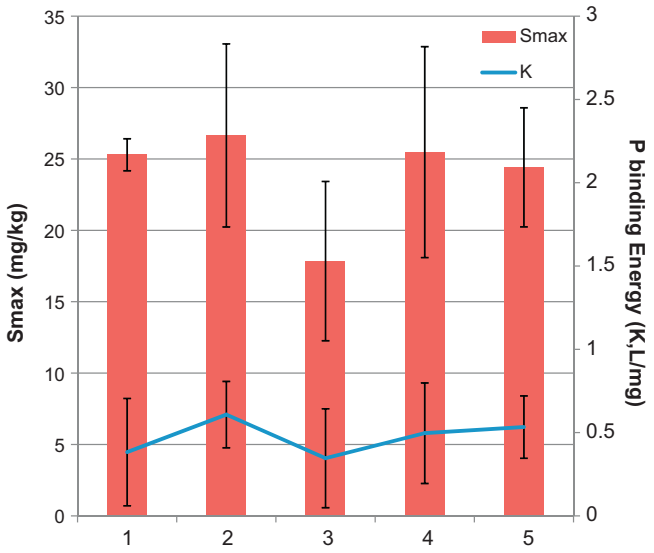

Fig. 3. P sorption maxima (S_{max}; mg/kg) derived from Langmuir isotherms, and phosphorus binding energy (K, L/mg) for all ditch sediments, per season in the Lower Mississippi Alluvial Valley.

4. Discussion

Multiple factors that influence whether ditch soils act as a source or sink include physico-chemical characteristics (Fe, Al, and pH), concentration of P in runoff, flooding frequency and inundation affecting soil redox, flow, and ditch size. Dunne et al. (2007) highlighted the lack of information of P storage and dynamics in agricultural drainage ditches. Across all drainage ditches sampled within the LMAV, silt percentages were greater than 80% (except for Judd Hill). These percentages were not surprising as these systems have sediment deposited that is moving off the agricultural landscape through runoff. The lack of clay particles in the sediments will decrease the surface area and sites for P sorption and decrease the ability of drainage ditch sediments sampled within the LMAV to sorb P in runoff and from the water column. Ditch sediments were acidic, typically below 5.6, suggesting that these sediments have the potential for P sorption through hydroxide association (Reddy and Delaune, 2008). Reddy and Delaune (2008) highlight that acidic sediments and soils have a greater affinity for phosphate anion adsorption. Under acidic conditions, available Al-OH groups gain protons ($Al(OH)_2^+$), providing a positive charge and increasing potential adsorption affinity with the orthophosphate anion. Sharpley et al. (2007) showed that sediments from ditches draining agricultural areas maintain a high dissolved P concentration in flowing water (0.374 mg P/L). The current study had similar reactive P concentrations in the overlying water column, with dissolved reactive P ranging between 0.08 and 1.3 mg P/L (0.44 ± 0.2). Sediment oxalate extractable Fe content (4–7 mg Fe/g) was significantly higher than oxalate-extractable Al content (<1 mg Al/g) indicating that amorphous and non-crystalline Fe would play a pivotal role in P adsorption and desorption in these drainage ditches, as influenced by inundation frequency and duration and coupled redox conditions of the sediments. The DPS for LMAV ditch sediments (<18%) was substantially lower than the critical level suggested for drainage ditch sediments (40%) (Sallade and Sims, 1997), and for soils (25%) (Breeuwsma et al., 1995). All drainage ditch sediments, through all seasons, fell below both critical thresholds, supporting the conclusion that drainage ditch sediments in the LMAV were P sinks. There were statistically significant differences in DPS between seasons ($F = 6.5$; $p = 0.001$), with the highest DPS (17.7%) occurring in spring. This increase is hypothesized as a result of increased occurrence of reactive P in runoff from fertilizer activities and post application runoff events elevating P concentrations in these drainage systems.

Studies that have examined P sorption maxima and binding energies in sediments report large ranges in both variables. Sorption maxima data in the current study had very low variability and showed no statistical difference ($p < 0.05$) between locations and between seasons. The S_{max} range (18–27 mg P/kg) for ditch sediments within the LMAV was very much lower than those reported for soils in agriculture in China (122–293 mg P/kg) (Zhuan-Xi et al., 2009), Korea (28–821 mg P/kg) (Ji-Hyock et al., 2006) and U.S. sediments (196–1821 mg P/kg) (Gale et al., 1994). Similarly, P binding energy ranges (0.34–0.60 L/mg) were lower than most reported studies in China (1.64–8.65 L/mg) (Zhuan-Xi et al., 2009), U.S. (0.412–1.85 L/mg) (Smith et al., 2005) and Korea (0.36–1.51 L/mg) (Ji-Hyock et al., 2006). Low sorption maxima as well as low binding energies suggests that drainage ditch sediments have a low capacity for P sorption. It can be hypothesized that the lack of clay particles, which are important sites for cation exchange capacity, as well as the low Al-concentrations in the sediments, yield low P site availability for adsorption and thus lowers the sorption maxima and binding energy.

Water extractable P was examined as a potential source of P for eutrophication from drainage ditch sediments. Water extractable P has been suggested as a potential indicator for aquatic systems and highlights the propensity for sediment to be a source for immediately dissolved reactive P. Water extractable P was very low for all drainage ditch sediments, and declined with season. Similar to work by Kleinman et al. (2007), it is difficult to establish whether observed declines in P_w were due to desorption through time or associated changes in sediment geochemistry and P pools (i.e. labile–non-labile).

5. Conclusion

These results have highlighted that drainage ditch sediments associated with agriculture have the capacity for being P sinks; however, sorption will be limited by the P sorption maxima and binding energies of the sediments. However, they also had low potential of contributing P to downstream environments, as DPS values fell under both 40% and 25% critical thresholds. If these systems are manipulated by inundation, the low concentrations of Fe and Al in sediments, decreases the potential of these sediments to desorb P to the overlying water column through changes in sediment redox and low concentrations of bioavailable P with inundation.

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