

SOURCES OF PHOSPHOROUS LOADING IN KANSAS STREAMS

by

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Abstract

Phosphorus (P), an essential nutrient for plant growth and animal needs, has been identified as an ubiquitous water quality impairment in the United States. In Kansas, a major agricultural state, P loading to the surface waters is a top priority because of the critical role of P enrichment in eutrophication processes and resultant water quality degradation. The objective of this study was to quantify the P sorption and desorption of both stream sediments and upland soils in two Kansas watersheds with contrasting degrees of animal agriculture; Upper West Emma Creek (UWEC) and Red Rock Creek (RRC) watersheds. In-stream sediments were collected from banks, pools, riffles and depositional features. Soils were sampled from wheat, row crop, pasture, and manure-amended fields. Stream water samples were taken under baseflow and storm flow conditions. Our analyses of sediments and soils included equilibrium P concentration at zero net P sorption (EPC_0), maximum adsorption capacity (P_{max}), anion exchange extractable P (P_{lab}) and degree of P saturation (DPS). Water samples were analyzed for dissolved reactive phosphorous (DRP). Bank erosion pins were installed in order to estimate bank erosion rates in both watersheds. Results showed that in-stream sediments do not have much more sorption capacity remaining indicated by low P_{max} and high DPS. A comparison between mean P_{lab} of stream sediments ($8.8 \text{ mg P kg}^{-1} \text{ soil}$) versus field soils ($61.2 \text{ mg P kg}^{-1} \text{ soil}$) reflected that they represent a relatively minor long-term P supply. Of the stream sediments, bank soils had the highest P_{lab} concentrations ($24.8 \text{ mg P kg}^{-1} \text{ soil}$) and would be the largest in-stream P source. Manure-amended fields had the highest P_{lab} ($118.6 \text{ mg P kg}^{-1} \text{ soil}$) due to continued inputs of manure-based P; therefore, representing a large available P pool. Bank erosion contributed about 41% and 11% of the total sediment load in UWEC and RRC respectively. Sediments loads indicated that RRC has more upland sediment inputs than UWEC.

Moreover, DRP during storm flow was higher at RRC than UWEC, indicating higher P inputs in RRC from upland soils. Finally, in order to minimize P inputs to the stream system, bank stabilization should be addressed in UWEC and upland best management practices should be implemented in RRC.

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List of Abbreviations

Al _{ox} :	Oxalate Extractable Aluminum.
DepS:	Depositional Surface.
DepSub:	Depositional Subsurface.
DP:	Dissolved Phosphorous.
DPS:	Degree of Phosphorous Saturation.
DRP:	Dissolved Reactive Phosphorous.
EPC ₀ :	Equilibrium at Zero Net Phosphorous Sorption.
Fe _{ox} :	Oxalate Extractable Iron.
ICP:	Inductively Coupled Plasma Spectroscopy.
Loc:	Location.
P:	Phosphorus.
PB:	Pool Bed.
P _{lab} :	Anion Exchange Extractable P.
P _{max} :	Maximum Adsorption Capacity.
P _{ox} :	Oxalate Extractable Phosphorous.
PP:	Particulate Phosphorous.
P _w :	Water Extractable Phosphorous.
RB:	Riffle Bed.
RRC:	Red Rock Creek.
Tclay:	Total Clay.
Tsand:	Total Sand.
Tsilt:	Total Silt.
UWEC:	Upper West Emma Creek.

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Dedication

I would like to dedicate this thesis to my beloved husband Juan and my family in Medellin, Colombia. Without their support, this thesis would have not been possible.

CHAPTER 1 - Introduction

Phosphorous Fate and Transport at the Watershed Scale: Literature Review

Nature of the Problem

Phosphorus (P), an essential nutrient for plant growth and animal needs, has been identified as an ubiquitous water quality impairment in the US. In Kansas, a mainly agricultural state, P is applied to agricultural soils in order to assure high yielding crops and economic sustainability. Historically, P has been applied beyond crop requirements leading to P enrichment in soils (Carpenter, 1998). The high soil P concentrations increase the potential risk of P loss in runoff from agricultural fields to surface water (Sharpley et al., 1993). Phosphorus plays a critical role in nutrient enrichment of water bodies, leading to dense growth of biomass (i.e., eutrophication). During biomass decomposition processes there is a decrease in dissolved oxygen leading in to water quality degradation. Therefore, it is in the best interest of sustainable agricultural production to understand all factors that affect P inputs to surface waters. Although best management practices are generally focused on controlling P losses at field scales, many physical, chemical, and biological processes influence the eventual P loading to down-stream water bodies. Thus, in order to fully comprehend P fate and transport at the watershed scale, it is important first to understand phosphorus status in soil, P transport mechanisms to water surfaces, in-stream mechanisms of P uptake-release, and other key characteristics of stream systems, such as channel morphology, that may also alter P uptake and release in-stream systems (Withers and Jarvie, 2008).

Phosphorous Status in Soil

There are several forms of P and multiple pathways by which P may be taken up by plants or leave the site as P runoff or leaching (Figure 1.1). Native P in soils originates from the weathering of soil minerals and other more stable geological materials (Pierzynski et al., 2005). Once P is solubilized in soils by the chemical and physical processes of weathering, it can be accumulated by plants. Phosphorus is taken up by plants from the soil solution mostly as orthophosphate (e.g., HPO_4^{2-} or H_2PO_4^-). Phosphorus exists in soils in inorganic and organic forms. In unweathered soils, P exists primarily as calcium phosphates (e.g., apatite) while in highly weathered soils P exists primarily as iron or aluminum phosphates. Phosphorus in soil solution can become unavailable through precipitation, which happens if plant available inorganic P reacts with dissolved iron, aluminum, manganese (in acid soils), or calcium (in alkaline soils) to form phosphate minerals. Phosphorus can be also bound to Al and Fe oxides, which are commonly present in highly weathered soils. Phosphorus sorbed to soil particles may become part of the soil solution through desorption processes. Finally, P in soil solution can be converted to organic P through microbial conversion or immobilization. This microbial P can become plant available over time as the microbes die through the process of mineralization. Phosphorus can also be accumulated by plants and recycled back into the soil as plants die.

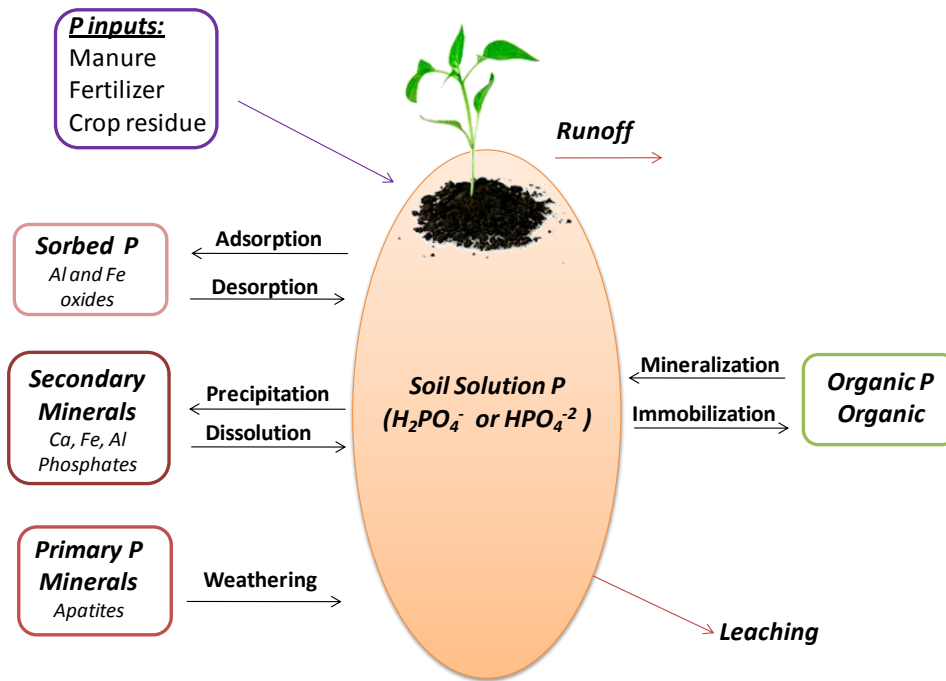


Figure 1.1 The soil P cycle: P forms and conversion processes. Adapted from Pierzynski et al. (2005)

Phosphorus can also become part of the soil solution when is added from inorganic or organic sources. As solid phase P forms cannot replenish the soil solution rapidly enough to satisfy plant needs, continued fertilizer application is needed. High application rates of fertilizers will increase P availability for plant growth; however, it will potentially cause more phosphate to be lost to water running over the soil surface or leaching through the soil. If fertilizer applications are managed properly, P additions in combination with appropriate rates of other fertilizers can reduce runoff and soil erosion by increasing crop growth. However, if P is added in a manner that exceeds plant needs, the risk of P loss to surface water can increase.

Even though P applications may be managed, there is still considerable risk of P transport from the landscape to the surface water. Therefore, it is important to understand the main transport mechanisms of P from the landscape to surface water: soil erosion and surface runoff.

Phosphorous Transport from the Landscape to Surface Water

Phosphorus may be transported to the surface water mainly by soil erosion and surface runoff (Figure 1.2). During rainfall, soil particles interact with the rainwater mobilizing and transporting P in the dissolved (DP) and particulate P (PP) forms to the water course. Generally, P runoff from agricultural lands consists of 75 to 90 % PP (Sharpley et al., 1993). Sources of PP may include soil particles, fertilizers, livestock manure, and plant material (Haygarth and Jarvis, 1999).

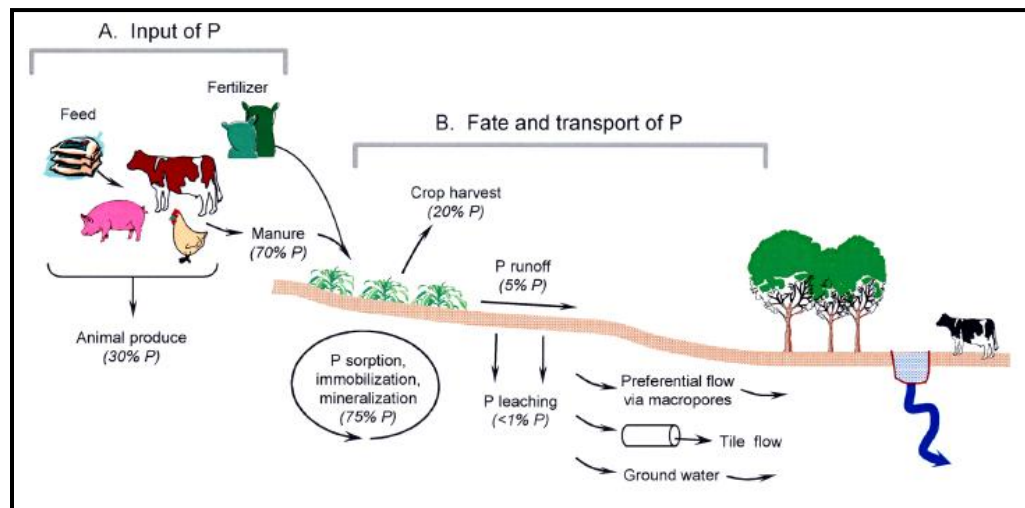


Figure 1.2 Factors affecting input, fate and transport of P in agricultural fields and stream systems. Source: Shigaki, F., A. Sharpley, and L. Prochnow. 2006. Animal-based agriculture, phosphorus management and water quality in Brazil: Options for the future. *Scientia Agricola*. 63:194-209.

Soil erosion from upland fields is mostly influenced by rainfall (e.g., storm size), irrigation, and land management practices (e.g., till, no till) (Sharpley et al., 1993). Several studies have shown that agricultural land use can influence water chemistry in ground and surface waters in the Ozark Highlands (Haggard et al., 2007; Haggard et al., 2003; Petersen, 1999)

Withers and Hodgkinson (2009) evaluated the effect of farming practices on phosphorus fate and transport. Farming operations contribute significantly to the annual P load when they are carried out simultaneously over a large proportion of the watershed area. Additionally, high P loads to stream water coincided with high rainfall and high moisture conditions of the field soils. Other studies have found that manure application can export dissolved P into the stream water and typical P concentrations in surface runoff from manure applied fields can be over 10 mg L⁻¹ (Withers et al., 2003).

Phosphorus losses as a function of flow type (i.e., storm flow and baseflow) and storm size has been also quantified for a mixed-land use watershed (Sharpley et al., 2008). Storm flow contributed only a third of the watershed discharge yet contributed 65% of dissolved reactive P (DRP) and 80% of total P (TP) exported. Additionally, throughout the 10-yr period, most of the P exported during baseflow and storm flow was particulate P (79% and 54%, respectively). Finally, it was concluded that that P release from soil and/or area of the watershed producing runoff increases as storm size increases as well.

Stream bank erosion also contributes a significant percentage of the P and sediment load in streams (Zaimes et al., 2008). Sekely (2002) suggested that streambank erosion in a Minnesota watershed contributed 30-45% of the sediment load to the stream system. And in the Midwestern region, it has been estimated that bank erosion contributes between 30% to 40% of the sediment for the East Nishnabotna and Des Moines Rivers in Iowa (Odgaard, 1987), and up to 50% in two Illinois streams (Trimble, 1984).

In-Stream Mechanisms of P Uptake

The P buffering capacity of stream systems is a function of biochemical and physical processes (Withers and Jarvie, 2008). Thus, as P is transported in the downstream direction,

biotic as well as abiotic factors contribute to its assimilation. Phosphorus assimilation will depend on the form of P entering the stream system, its reactivity, and the water residence time. Reddy et al. (1996) estimated that the P assimilation capacity of the Otter creek was around 5% of the total P load. House (2003) reported retention rates between 10 and 30% under a range of flow conditions. Jarvie et al. (2002) recorded up to 60% net retention in the Upper River Kennet. Phosphorous retention is highly variable and depends on stream environment, ecology, and management. The physical-chemical processes are sorption/desorption reactions, mineral precipitation and dissolution, and advection and diffusion (Haggard et al., 2007; House, 2003; Reddy, 1999). The biological controls in stream systems include periphyton, phytoplankton, microorganisms and macrophytes (Withers and Jarvie, 2008).

As P adsorption/desorption reactions play a major role in the P retention and cycling at the watershed scale, this thesis is focused on P adsorption and desorption behavior of stream sediments and field soils once they are in contact with the stream water.

P Sorption/Desorption Behavior as a Function of Sediment Chemistry and EPC_0

It is well known that stream sediments have the ability to adsorb dissolved P from the water column or release P to the surface water depending on the chemical composition of the sediment and equilibrium P concentration at zero net P sorption (EPC_0). Among the most important sediment characteristics that influence P adsorption from the water column are sediment particle size distribution (Haggard et al., 1999; Klotz, 1988), organic matter (Stone et al., 2004), water-extractable P forms (McDowell et al., 2002), divalent cation presence (Klotz, 1991; Klotz, 1988), and amorphous and poorly crystalline forms of oxalate extractable Fe and Al (Novak, 2006). Sediments with high clay content are able to adsorb more P, conversely, sediments with high sand content are able to adsorb less P. Amorphous Fe- and Al-oxides are

clay-sized minerals that tend to have highly reactive surfaces, and therefore, high P adsorption capacities.

Similarly, soil organic matter content also plays an important role in P adsorption. The presence of organic compounds promotes the formation of orthophosphate complexes onto the surface of the sediment; therefore, increasing the P adsorption capacity. Furthermore, divalent cations may also enhance P adsorption capacity of stream sediments due to an increase in the accessibility of positive charged edges of clay minerals (Havlin and Tisdale, 2005)

McDowell et al. (2001) found that P release from in-stream sediments was well correlated to Mehlich soluble Al and organic matter content of the stream sediments. Novak (2006) found that amorphous and poorly crystalline forms of Fe and Al (as measured by oxalate extractable Al and Fe) were statistically correlated with maximum P adsorption capacity values in soils and sediments. In addition to the sediment chemical characteristics, the EPC_0 also plays an important role during adsorption/desorption reactions. The EPC_0 of a sediment is often used to evaluate whether the sediments will act as a P source or sink to the flowing water (Froelich, 1988). In situations where stream sediments have a low EPC_0 , the sediments will adsorb P from stream water thereby reducing P concentrations in the stream water (Haggard et al., 2005; McDowell et al., 2003). However, sediments with high EPC_0 can release accumulated P back to the water column during periods of low or reduced P input (Haggard et al., 2005; Hoffmann et al., 1996). If sediment EPC_0 is approximately equal to the stream water dissolved P concentration, then sediments and the water column are in apparent equilibrium.

Several studies have found strong positive relationships between sediment EPC_0 and stream water dissolved P concentrations (Klotz, 1988; McDowell et al., 2003) indicating that stream sediments can have a controlling influence on the dissolved P concentrations in stream

water and therefore also have a controlling influence on down-stream water quality. An evaluation of stream sediment EPC_0 could indicate the potential dissolved P equilibrium for stream water. Furthermore, the EPC_0 of different stream sediments (e.g., stream bed, bank, and depositional features) may all be different, resulting in continual P flux from one sediment pool to another. These factors may have contributed to lack of correlation between stream sediment EPC_0 and stream water dissolved P concentrations for some studies (Haggard et al., 1999; Smith and Smith, 2005). This lack of correlations suggests that other factors could be controlling dissolved P concentrations in the stream (Haggard et al., 1999).

Influence of Stream Morphology in P Uptake Capacity

Stream hydrology and geomorphology controls the residence time of water within the channel, the flow velocity; and therefore, the contact time of the water-sediment interaction (Withers and Jarvie, 2008). During periods of slow flow, stream water interacts more with the stream sediments, thus increasing the nutrient retention capacity of the stream system. Additionally, zones of transport storage such as pools, channel beds, and floodplain areas are expected to increase nutrient retention capacity due to an increase of the water residence time within the reach (Withers and Jarvie, 2008).

Thesis Objectives

Even though P transport mechanisms at the watershed scale have been broadly investigated, most of the studies are focused on just P from upland soils or P interactions in stream systems. As of now, a broad comparison at the watershed scale of stream sediments, upland soils and surface water has not been made. Therefore, this research is aimed at quantifying sources and sinks of P at both landscape and stream systems and comparing those with the stream water quality. Another important contribution of this thesis project is the

rigorous stream sediment classification performed. This classification was based on the geomorphologic feature from which the sediment was sampled; therefore, giving us a better understanding of how each sediment type may contribute on the P buffering capacity of stream systems. Consequently, this thesis investigates the effects of soil, sediment, management, and stream geomorphology on P loading to surface waters in two Kansas watersheds through 5 interrelated objectives:

1. To quantify P concentration and availability in stream sediments sampled from different stream channel features and its potential for release and transport in stream water.
2. To estimate stream bank erosion.
3. To quantify P concentrations in field soils under different management practices and its potential for release and transport in surface runoff.
4. To compare P sorption and release characteristics of stream sediments and field soils to P concentrations in stream water.

Thesis Organization

This thesis is aimed at investigating the sources and sinks of dissolved and sediment-bound P in two Kansas watersheds with contrasting degrees of animal agriculture. Therefore, chapter 1 is focused on the literature review of P fate and transport at the watershed scale, chapter 2 is focused on the Upper West Emma Creek watershed, chapter 3 is focused on the Red Rock Creek watershed (RRC), chapter 4 compares both watersheds investigating major effects of animal agriculture on P loading to surface waters. Finally, chapter 5 intends to conclude about P sources and sinks at the two watersheds and how management practices should be addressed in order to improve the water quality of our Kansas stream systems.

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CHAPTER 2 - A Case Study of Phosphorous Sinks and Sources in Upper West Emma Creek Watershed

Introduction

Numerous hydrologic, geochemical, and upland processes govern the distribution, transport, and fate of dissolved and sediment-bound phosphorus (P) at the watershed scale. Phosphorus from upland soils enters stream channels via runoff; thereby increasing P concentrations in stream water. Biological and chemical transformations affect the availability of P to the stream biota. Retention and transport of sediments and nutrients (e.g., P) are among the major roles of stream channels. During transport, whether it is baseflow or storm flow, stream sediments buffer dissolved P concentrations while interacting with the water column (Haggard et al., 2005; McDowell et al., 2003). Thus, depending on the sediment equilibrium P concentration at zero net P sorption (EPC_0), the sediment will have the ability to adsorb or release phosphorus from or to the water column (Haggard et al., 2007). This equilibrium may be affected by the geology and morphology of the stream system. The geology of the stream determines the mineralogy and geochemistry of the stream sediments and the base line water chemistry of the stream sediments. For example, stream systems where bedrock weathers to produce clay, or fine silt, which are rich in Fe and Al hydroxides, are expected to generate sediments with high adsorption capacity (Withers and Jarvie, 2008). Several studies have linked Fe and Al concentrations with the P uptake capacity of sediments (Khalid et al, 1977; Richardson, 1985; Gale et al., 1994). Besides clay and silt content, stream geology may also control sediment chemical and physical characteristics, such as particle size distribution, organic matter, water extractable P forms, and divalent cation concentrations. Several studies have found that the aforementioned sediment properties are among the most important factors influencing the ability

of stream sediments to adsorb or desorb dissolved P (DRP) from or to the water column (Haggard, 2007).

Channel morphology also exerts an influence on sediment P uptake capacity because it controls the residence time of water within the reach, the flow velocity, and the contact time between the stream water and in-stream sediments (Withers and Jarvie, 2008). Based on the Rosgen system of channel classification, channel type is a function of channel slope, bed material, and channel dimensions (Leopold, 1994). As channel systems are dynamic landforms subject to rapid change due to storm flow events, it is possible to observe changes in channel shape and stream flow. Those changes are intimately associated with stream bank erosion and relocation of the channel features well known as banks, pools, riffles, and bars.

Upland agricultural activities might also affect stream water quality because P at the land surface may be released and transported to the water surface via runoff. Phosphorus movement in the landscape is a complex function of rainfall, land use, and soil management practices (Sharpley et al., 1993; Sharpley et al., 2008). Several studies have shown that agricultural land use (e.g., pasture) can influence water chemistry in ground and surface waters in the Ozark Highlands (Haggard et al., 2007; Haggard et al., 2003; Petersen, 1999). Withers and Hodgkinson (2009) found that farming practices significantly contributed to the annual P load when they were carried out in parallel over a large proportion of the watershed area.

In Kansas, a major agricultural state, P loading to surface waters is a top priority because of the critical role of P enrichment in the eutrophication processes and resultant water quality degradation. Thus, in order to evaluate potential sources and sinks of P at the watershed scale the Upper West Emma Creek watershed was selected and P sinks and sources were studied through the following objectives:

1. To quantify P in stream sediments originating from different stream features and its potential for release and transport in stream water.
2. To estimate stream bank erosion.
3. To quantify P in field soils under different management practices and its potential for release and transport in surface runoff.
4. To compare P sorption and release characteristics of stream sediments and field soils to P concentrations in stream water.

Materials and Methods

Study Site Description

Upper West Emma Creek (UWEC) is a sub-watershed of the Little Arkansas River. It is located in central Kansas within McPherson and Marion counties (Figure 2.1). The primary use of the watershed land area (124 km²) is cropland (90%), of which wheat (49%), corn (6%), soybeans (11%), sorghum (22%), and alfalfa (2%) are major crops. Grassland comprises 6%, followed by urban area with 2%, and forest with 2% of the total watershed area. Manure amended fields account for less than 1% of the total area of the watershed. Livestock production is concentrated in one dairy, one kennel and nine small, seasonal beef cattle operations. The primary soil series within the watershed are Ladysmith silty clay loam (Fine, smectitic, mesic Udertic Argiustolls), Farnum loam (Fine-loamy, mixed, superactive, mesic Pachic Argiustolls), and Goessel silty clay (Fine, smectitic, mesic Typic Haplusterts). Stream bed sediments (i.e., riffle bed and pool bed) are mostly sandy with a total sand composition between 87 to 98% and total silt between 2-13%.

Six stream reaches with different animal activity, upland cropping system, and flood plain contact were selected along the main channel (Figure 2.1 and Figure 2.2).

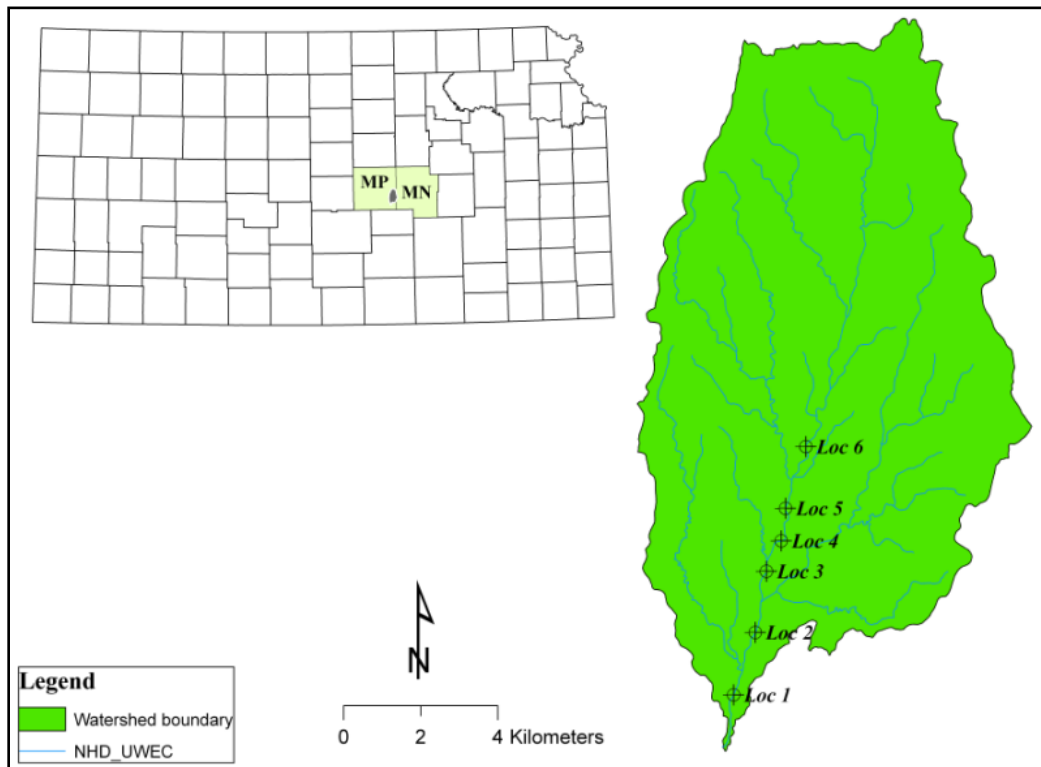


Figure 2.1 Stream-reach locations for sediment collection in Upper West Emma Creek watershed. Loc 1, Loc 2, Loc 3, Loc 4, Loc 5, and Loc 6 refers to location 1, 2, 3, 4, 5 and 6, respectively.

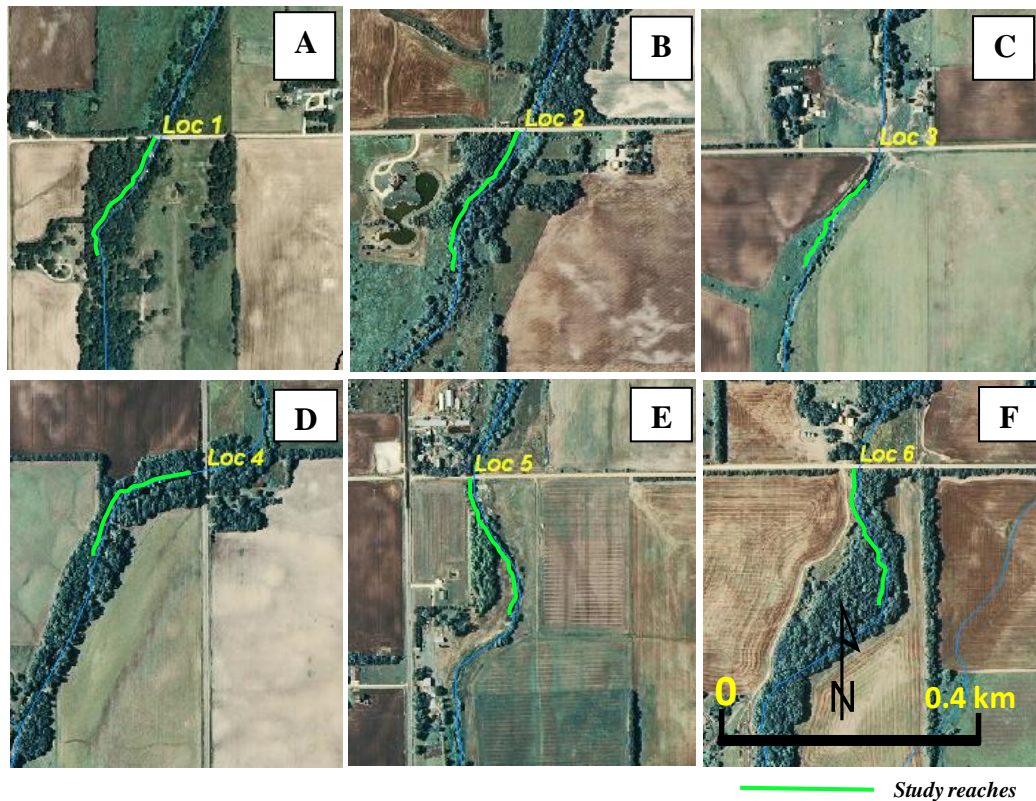


Figure 2.2 Aerial photograph of each of the six study reaches at Upper West Emma Creek Watershed. (A) Location 1 (Loc 1), (B) location 2 (Loc 2), (C) location 3 (Loc 3), (D) location 4 (Loc 4), (E) location 5 (Loc 5), and (F) location 6 (Loc 6).

No animal activity was observed at locations 1, 2, 4 and 6. However, there were sheep at location 3 and sheep and cattle at location 5. Animals at location 3 had direct access to the stream where animals at location 5 were isolated from the stream due to vegetation and high banks. Location 1, 2, 4, and 6 were bounded by trees and native vegetation on both sides. Location 3 was enclosed by pasture land on the left and a cultivated field on the right side of the stream when looking at the downstream direction (Table 2.1).

Table 2.1 Characteristics of each stream location at Upper West Emma Creek Watershed.

Stream location	Drainage Area km²	Livestock activity	Riparian Vegetation
Location 1	19	No presence	Forest
Location 2	16	No presence	Forest
Location 3	11	Sheep	Pasture
Location 4	10	No presence	Forest
Location 5	10	Sheep and cattle	Pasture
Location 6	6	No presence	Forest

Field Methods

Sediment Sampling

A total of 96 sediment samples were collected during summer 2007 and summer 2008. Each summer, at each stream location, two depositional features, two banks, one riffle bed, and one pool bed were selected for sampling (Figure 2.3). Sediments from depositional features were sampled at the surface (0-1 cm) (DepS) and subsurface (1-5 cm) (DepSub). A composite sample made of 10 subsamples was collected for each depositional feature. Subsurface samples were collected at the same point as surface sampling. The 10 sub-samples were randomly taken trying to cover all the area of the depositional feature. Composite samples were collected from bank features by removing 10 sediment samples from 0 to 5 cm deep on the bank face with an aluminum shovel. The 10 sub-samples were randomly taken between 0 and 10 cm above the water surface during base flow along a distance of 1 m of the bank. Every effort was made to assure representative sample collection from the 0 to 5-cm depth. Sediments from benthic zones such as pool beds (PB) and riffle beds (RB) were collected with a 2-L plastic container attached to a long handle. Once the benthic zone was selected, a random cross sectional line was selected to take the benthic sample. The plastic container was dragged across the length of the cross sectional line until the plastic container was full of sediment. The subsamples were thoroughly

mixed following sample collection and placed on ice. Samples were passed first through an 8-mm sieve to remove pebbles and roots. Finally, samples were passed through a 2-mm sieve, mixed, stored moist at 4° C and analyzed within 7 days.

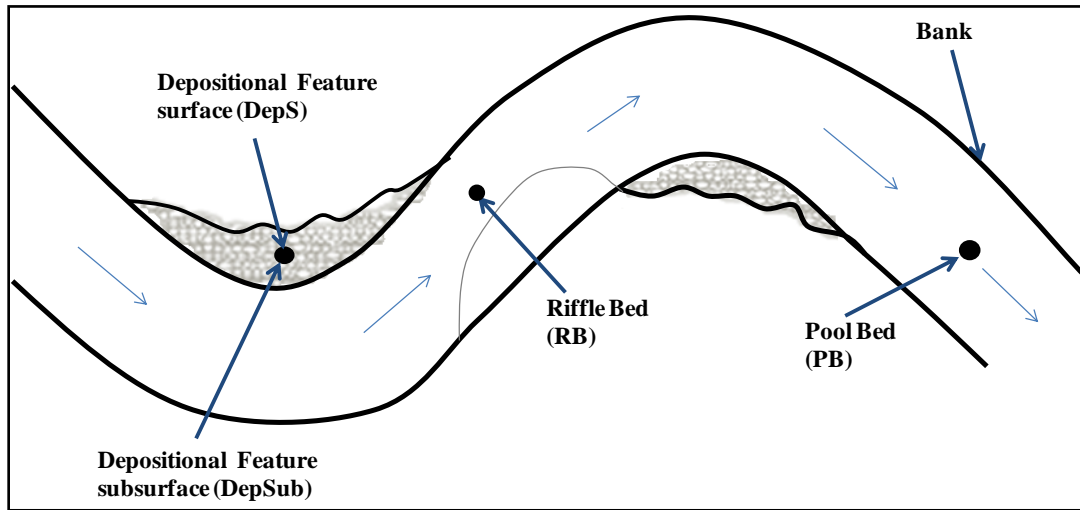


Figure 2.3 Stream sediment classification depending on sediment geomorphic location.

Extra bank profile samples were collected in order to more accurately estimate P related parameters for the entire bank profile. An extra eight bank features were selected randomly along the main channel. Composite samples were collected at 3 to 4 heights in a similar manner as previously described. Banks less than 60 cm were sampled at the top of the bank (0 cm), at the mid-point (23 cm from the top), and at the bottom of the bank (53 cm from the top). Banks greater than 60 cm high were sampled at the top (0 cm), at 1/3 (40 cm from the top) and 2/3 (76 cm from the top) and at the water surface (107 cm from the top) the. Samples were transported and processed as was previously described for bank samples.

Soil Sampling

Soil samples were collected from 32 fields representing the major land uses and soil types of the watershed (Figure 2.4). Soil sample collection was performed during summer 2008. Each field was walked through in a zigzag pattern. A single composite sample was collected from each field, consisting of approximately 80 sub-samples randomly taken throughout the field from 0-5 cm deep. The subsamples were thoroughly mixed after collection and placed on ice. Once returned to the lab, moist samples were passed through an 8-mm sieve to remove crop residues and roots. Finally, samples were passed through a 2-mm sieve, mixed, stored moist at 4° C, and analyzed within 7 days.

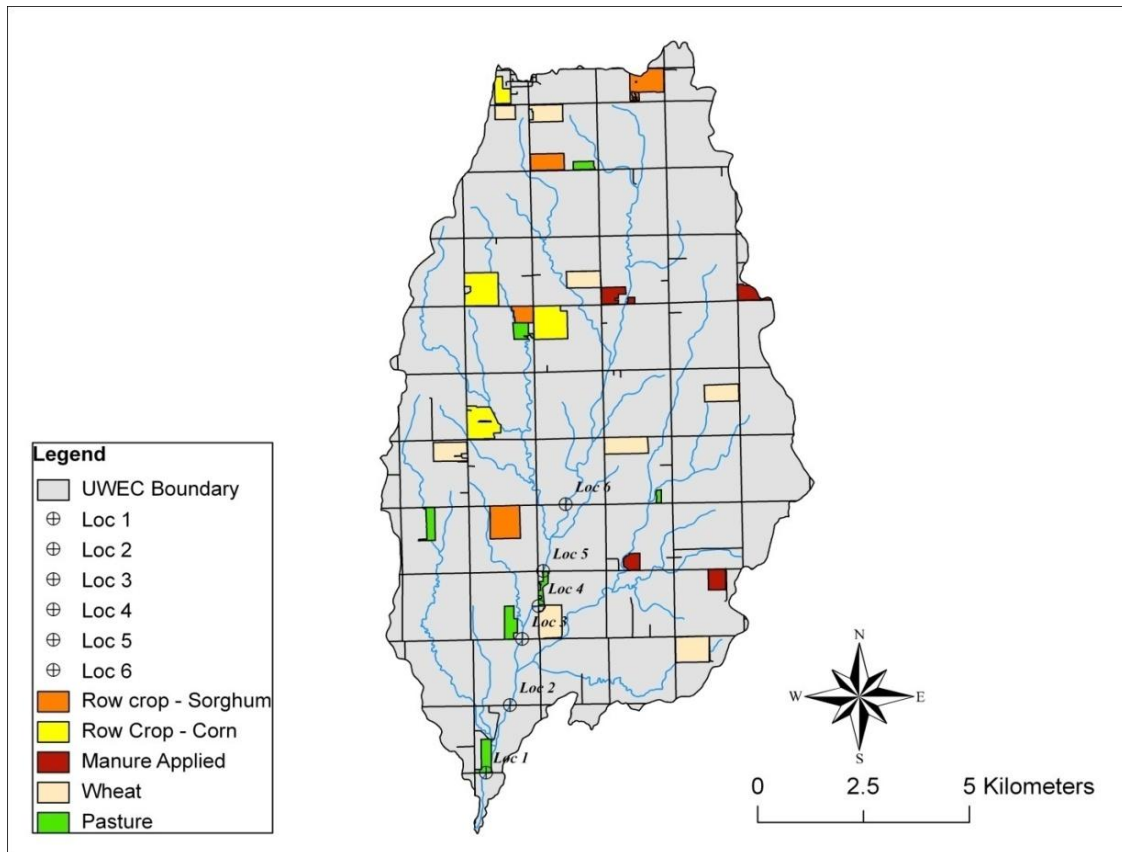


Figure 2.4 Soil sampling locations for wheat, row crop, manure applied, and pasture fields in the Upper West Emma Creek watershed. Loc refers to stream-reach location.

Water Sampling

Portable water samplers (ISCO model 6700) were installed at locations 1, 4 and 6 to measure water depth and collect storm flow samples over the course of the growing season. Stream discharge was estimated as a function of water depth with the slope-area method, which is a commonly used technique for indirect estimation of discharge by using Manning's equation (Gordon, 2004). The automatic samplers were programmed to collect several discrete water samples over the storm hydrograph. Finally, a composite sample of 1 L was prepared after each storm flow from 10 discrete samples collected over the hydrograph. The volume of each sub-sample was calculated by using the Equation 2.1.

$$S_i = \frac{t_i * q_i}{\sum t_i * q_i} * V_c \quad \text{Equation 2.1}$$

Where S_i is the volume of sub-sample i added to the final composite (mL), t_i is the time window between collection of two consecutive samples (s), q_i is flow at which each sample was taken ($\text{m}^3 \text{ s}^{-1}$), and V_c is the final volume of the composite sample (mL), which was 1000 mL. Storm flow samples were removed from the water sampler within 24 h of the peak hydrograph and returned to the lab for processing and analysis. Stream flow at each location was separated into storm flow and baseflow using the Web-based Hydrograph Analysis Tool (WHAT) which uses the local minimum method (Lim et al., 2005). Baseflow water quality was characterized with bi-weekly grab-samples collected at each of the study reaches from January 2008 through August 2009. Grab water samples were also taken at the moment of the sediment collection at each location, filtered immediately with a 0.45 μm filter, stored at 4° C and analyzed for dissolved reactive P (DRP) within 7 days.

Stream Channel Characterization

Cross sectional surveys were performed during summer 2008 and spring 2009 at the locations where ISCO samplers were installed (i.e., Location 1, 4 and 6). The cross sectional survey was performed in order to identify cross sectional changes along the main channel during one year period and to calculate the flow rating curves needed for computing stream flow based on water depth as measured by the ISCO samplers. The cross sectional surveys were developed in stream zones of active flood plain or bankfull discharge in order to have a reasonably clear view of geomorphic features at each of these three locations. Additionally, at each of these three locations, one bank feature was selected to estimate bank erosion rates.

One bank feature was carefully selected as a representative bank at locations 1, 4, and 6. Bank erosion was estimated by horizontally inserting 1.2-m steel pins into the face of the representative banks at 0.61 and 1.22 m above the stream bed (Figure 2.5) in June 2008. Pins were inserted flush with the bank surface. The length of the pin exposed was measured during May 2009 and used to estimate the volume of sediment eroded from banks within each reach according to equation 2.2

$$E_r = P_r * E_r * L_r \qquad \text{Equation 2.2}$$

where E_r is the estimated volume (m^3) of soil eroded from banks in stream reach r , P_r is the average pin exposure (m) measured for from the bank pins inserted in the representative bank of reach r , h_r is the height (m) of the representative bank of stream reach r , and L_r is the length (m) of stream reach r . The length of the stream reach was measured with a hand-held tape measure and the beginning and ending points were selected such that the length of each stream reach extended over all features sampled at the stream location.

The mass of eroded bank sediment was calculated by multiplying the volume of eroded sediments by the bulk density of the bank soils. Because the Farnum loam soil series is the primary soil along the main stream in UWEC, a typical bulk density for the Farnum loam profile (1.2 Mg m^{-3}) was assumed for the bank sediments (USDA-NRCS, 2009). Erosion rates for each stream reach were determined by dividing the mass of eroded sediment by the length of the reach.

It was assumed that bank erosion rates determined at locations 1, 4, and 6 were representative of UWEC bank erosion extending from location 6 down to location 1. Therefore, bank erosion for the entire stream length (from location 1 to 6) was estimated as the average of bank erosion rates for reaches 1, 4 and 6 multiplied by the distance from location 1 to location 6 (Equation 2.3).

$$\text{Total sediment (Mg)} = \text{Erosion rate (Mg m}^{-1}\text{)} * \text{stream length (m)} \quad \text{Equation 2.3}$$

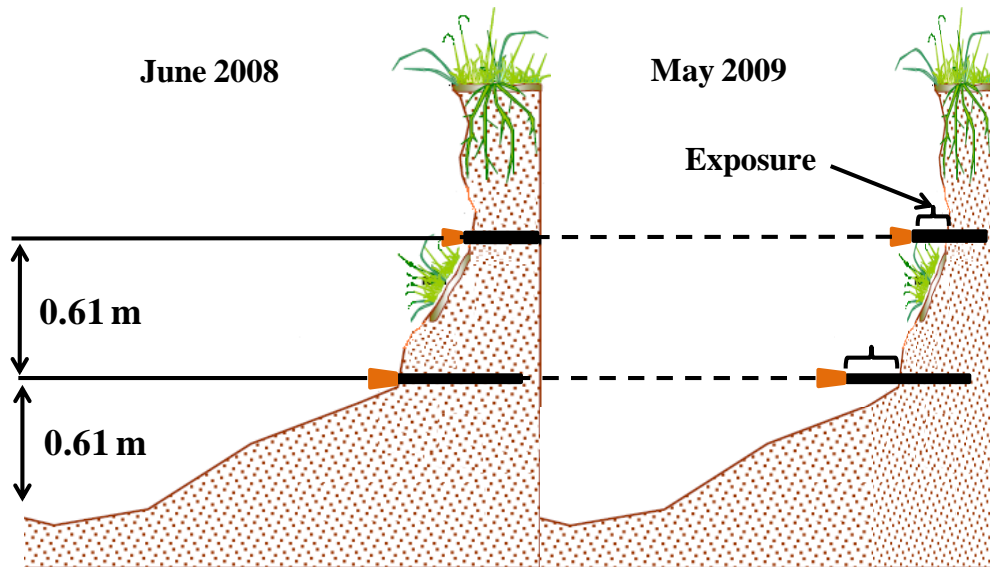


Figure 2.5 Bank pin placement and measurement methods for determination of bank erosion rates Bank study set up. Adapted from Rosgen (2008).

Laboratory Methods

Sediment, Soil and Stream Water Analysis

A subsample of each moist sediment was oven-dried (105°C) to determine gravimetric moisture content. Water extractable P (P_w) was determined on moist samples by shaking the equivalent of 2 g dry wt. sediment with 20 mL of DI water for 1 h followed by centrifugation at 10,000 rpm (14480 rcf) for 10 minutes. Finally, the supernatant was extracted with a plastic syringe with a stainless steel needle and filtered with a 0.45 μm syringe filter. The filtered solution was analyzed in a Lachat using 75.5 cm sample loop and standards from 0.025 to 2.0 mg P L^{-1} (Lachat Quick Chem method 10-115-01-1-A, Lachat Instruments, 2000). Poorly crystalline Al, Fe, and associated P were quantified as oxalate extractable Al (Al_{ox}), Fe (Fe_{ox}), and P (P_{ox}), determined by ammonium-oxalate extraction in the dark (Schwertmann, 1964). Thirty mL of extracting solution was added to 0.75 g (dry wt. equivalent) of moist soil and shaken on the reciprocating shaker at low speed in darkness for 2 h at room temperature. After shaking, the suspension was centrifuged at 10,000 rpm (14480 rcf) for 10 min. Supernatant was filtered using Whatman #42 filter paper and the extract was analyzed for Al, Fe and P via Inductively Coupled Plasma (ICP) spectrometry. These three oxalate extractable ions were used to calculate the degree of P saturation (DPS) of the soil sample. The DPS can be calculated from Equation 2.4 Where P_{ox} , Al_{ox} and Fe_{ox} are in mmol kg^{-1} .

$$DPS = \frac{P_{ox}}{Al_{ox} + Fe_{ox}} \times 100 \quad \text{Equation 2.4}$$

Phosphorus adsorption was studied by shaking moist sediments (1 g dry wt.) with 25 mL of a background electrolyte solution containing graduated concentrations of P (as KH_2PO_4) (0, 0.02, 0.1, 0.2, 0.5, 1, 2, 3, 6, 10, 20 and 30 mg P L^{-1}) during 24 h. The electrolyte solution was

prepared with a concentration of 0.002 M CaCl₂, 0.003 M NaCl, and 0.0004 M MgSO₄ to simulate ambient stream water ionic strength. Following the 24 h equilibration, samples were then centrifuged at 10,000 rpm (14480 rcf) for 10 minutes, filtered (0.45 µm syringe filter) and analyzed for P.

The Langmuir model (Equation 2.5) has been broadly used to describe P sorption to stream sediments (Haggard et al., 2005; McDowell et al., 2003).

$$q = \frac{P_{max} * k_l * C_{eq}}{(1 + k_l * C_{eq})} \quad \text{Equation 2.5}$$

Where P_{max} represents the maximum adsorption capacity and k_L the P binding energy. The adsorption isotherm data were fit to the Langmuir equation using an excel spreadsheet developed by Bolster (2008). Fitting parameters P_{max} and k_L were used to estimate the maximum P adsorption capacity and P binding energy, respectively. The EPC_0 was determined as the y-intercept of the regression of initial solution P concentration on mass of P adsorbed for P concentrations of 0, 0.02, 0.1, 0.2, and 0.5 mg P L⁻¹. Phosphorus desorption rate was quantified by sequential P extractions with anion exchange membranes obtained from BDH Laboratory Supply (BDH Product # 55164 2S). Anion exchange extraction followed the methods of Saggari et al. (1990), where anion exchange membranes were prepared prior to each extraction by shaking with 0.5 M NaHCO₃ adjusted to pH 8 for 30 min, repeated twice, then rinsed with distilled water by shaking for 5 minutes, repeated three times. Sequential extraction was performed by shaking 2 g dry weight equivalent of moist soil with 30 mL of distilled water and one anion exchange membrane strip (14.82 cm² surface area) for 72 hrs. The anion exchange membrane strip was replaced at 1, 2, 4, 10, 24, and 48 h of shaking. Phosphorus adsorbed on

membranes was eluted by shaking each membrane in 30 mL of 0.5 M NaCl for 1 h. Finally, the NaCl solution was analyzed for molybdate reactive P. Phosphorus desorption rate (P_{rel}) was determined by fitting desorption data to the Elovich equation (Chien and Clayton, 1980; McDowell et al., 2003). The differential form of the Elovich equation is

$$\frac{dq}{dt} = \alpha e^{(-\beta q)} \quad \text{Equation 2.6}$$

Where q is the amount of phosphate released or sorbed in time (t) and α and β are constants. The integrated form of Equation 2.3, which was fit to desorption data with non-linear regression, is

$$q = \frac{1}{\beta} \ln (1 + \alpha\beta t) \quad \text{Equation 2.7}$$

The constant α can be regarded as the initial P release rate because dq/dt approaches α as q approaches 0 (Equation 2.6), therefore, α was used as the best estimate of P_{rel} .

Total desorbable P, or labile P (P_{lab}), was determined as the total quantity of P desorbed during the 72 h anion exchange extraction, where preliminary research has shown near maximum P desorption at 72 h. Total carbon (T_{carbon}) of sediment samples was determined by dry combustion and particle size distribution Total sand (T_{sand}), Total clay (T_{clay}) and Total silt (T_{silt}) was determined by the pipette method (Gee and Bauder, 1986). All water samples were analyzed for molybdate reactive dissolved P, total dissolved P, and total P using standard methods (Maher and Woo, 1998). Select water samples were further analyzed for dissolved NO_3-N , NH_4-N , Ca, Mg, K, Na, Fe, and Al, EC, and pH, thereby characterizing the general chemical composition of the water. Phosphorus concentration in all water samples, P_{lab} , and P_w

extracts were determined colorimetric with an automated flow-injection analyzer (Lachat Quick Chem method 10-115-01-1-A, Lachat Instruments, 2000).

Data Analysis Comparison

Each data set (i.e., sediment and field data) was analyzed independently. The stream sediment data set was evaluated using analysis of variance by using SAS Proc Mixed protocol (SAS Institute Inc., 2004). Feature, location, and feature by location interaction were considered fixed effects. Year of sample collection (i.e., 2007 and 2008) was considered as a random variable because it did not have significant effect on any of the P related parameters of the stream sediments. Additionally, a test of slice effects was used to test the location effect for each feature and the feature effect at each location.

An independent analysis of variance was also performed for the field data set by using SAS Proc Mixed protocol. For this model the class variable was cropping system (i.e., manure applied, wheat no till, wheat till, and row crops). Subsequently, both sediment and field data sets were combined and analyzed again as a whole data set by using the SAS Proc Mixed protocol. In this case, the class variable was source which included all stream sediments types (i.e., Bank, RB, PB, DepS and DepSub) and cropping systems (i.e., manure applied, wheat no till, wheat till, and row crops). In this analysis the variable year was excluded because fields were not sampled at two different years. Thus, both years of sediments data were considered as replicates. Correlation coefficients, means and standard errors were also determined with SAS v 9.1.

Finally, water quality data (i.e., baseflow, storm flow and grab samples) was compared with the EPC_0 of soil and sediments by applying the unequal variances protocol for independent samples (Steel et al., 1980). The calculation was performed in Microsoft excel v. 2007.

Results and Discussion

Stream Location Effect on Sediments Phosphorous Chemistry

An analysis of variance (ANOVA) was developed to evaluate overall variations of P chemistry for sediments taken at different features and locations at Upper West Emma Creek watershed. The EPC_0 was the only variable significantly affected ($p < 0.001$) by stream location. Furthermore, there was a feature by location interaction for EPC_0 (Table 2.2).

Table 2.2 Significance of main effects and interactions from type III tests of fixed effects in the analysis of variance (ANOVA) for chemical and physical characteristics of stream sediment samples taken from pool bed, riffle bed, depositional surface, depositional subsurface, and bank features (Feature effect) at six reach segments (location effect) in Upper West Emma Creek. Asterisks indicate the level of significance from F-tests, where *, **, and * indicate $p < 0.05$, 0.01 and 0.001 respectively and ns = not significant.**

Analytical parameter †	Units	Effect		
		Stream Location	Channel feature	Feature by Location
EPC_0	$mg L^{-1}$	***	ns	*
P_{lab}	$mg kg^{-1}$	ns	***	ns
P_{rel}	$mg kg^{-1} h^{-1}$	ns	*	ns
P_{max}	$mg kg^{-1}$	ns	***	ns
k_L	$L mg^{-1}$	ns	*	ns
Fe_{ox}	$mg kg^{-1}$	ns	***	ns
P_{ox}	$mg kg^{-1}$	ns	***	ns
Al_{ox}	$mg kg^{-1}$	ns	***	ns
DPS	%	ns	***	*
P_w	$mg kg^{-1}$	ns	ns	ns
Tsand	%	ns	***	ns
Tsilt	%	ns	***	ns
Tclay	%	ns	***	ns
Tnitro	%	ns	***	ns
Tcarbon	%	ns	***	ns

† EPC_0 refers to the Equilibrium P concentration at zero net P adsorption, P_{lab} refers to Labile P, P_{rel} refers to rate of initial P release, P_{max} represent P maximum adsorption capacity and k_L represent the P binding energy from the Langmuir equation, Fe_{ox} , Al_{ox} and P_{ox} refers to oxalate extractable ions, DPS refers to degree of P saturation, P_w refers to water extractable P, and Tsand, Tsilt, Tclay, Tnitro, and Tcarbon refers to total sand, silt, clay, nitrogen and carbon, respectively.

Based on the tests of slice effects, EPC_0 of sediments from bank features ($p < 0.01$), depositional feature surface sediments ($p < 0.0001$), and depositional feature subsurface sediments ($p < 0.01$) were significantly different between stream locations (Figure 2.6). Conversely, EPC_0 values for pool bed and riffle bed sediments did not change significantly between locations.

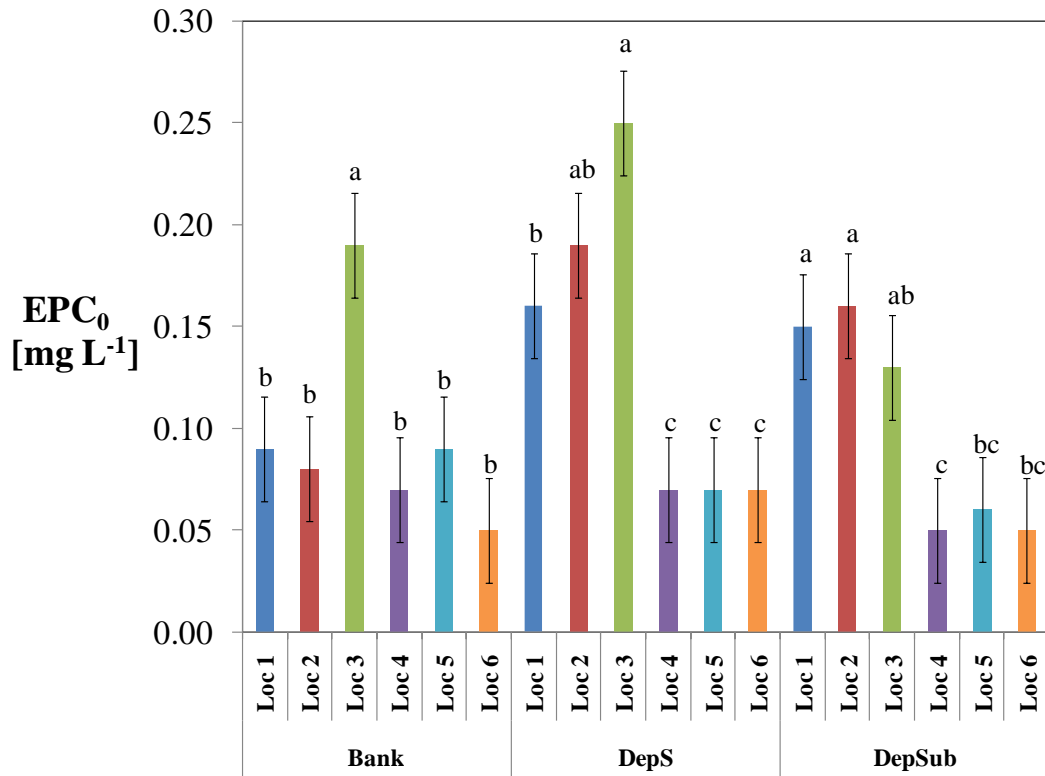


Figure 2.6 Location effects on the equilibrium P concentration at zero net P sorption (EPC_0) for sediments collected at bank, depositional surface (DepS), and depositional subsurface (DepSub) features. Different letters above bars denote significant differences between locations within the same feature ($p < 0.05$). Loc refers to stream-reach location.

Furthermore, it is observed (Table 2.2) that stream location did not affect chemical parameters such as P_{lab} , P_{max} and Al_{ox} , Fe_{ox} , and P_{ox} . Sediments particle size characterization, Tnitro and Tcarbon results reflected that physical as well as chemical characteristics of the sediment remained constant along the main channel. The EPC_0 of sediments increased at location 3 ($p < 0.05$) and may be attributed to the access of animals to the stream at that location; however,

the nature of our experimental design does not allow us to conclusively state that the animal access caused the increase in the EPC_0 .

This supposition is supported by findings from other studies that reported that more P was present in stream sediments from dairy farmed reaches than sheep-farmed reaches (McDaniel et al., 2009). Moreover, based on findings by Petersen (1999), nutrient concentrations in streams are higher in areas with greater agricultural land use than in forested areas which resulted in an increase in algal growth in streams. At the same time, many others studies have positively related sediment EPC_0 with stream water DRP concentrations (Klotz, 1988; McDaniel et al., 2009; McDowell et al., 2003) indicating that land use can have a controlling influence on the dissolved P concentrations and therefore also have a controlling influence on stream sediment EPC_0 .

A closer look at the EPC_0 values of sediments from bank, DepS, and DepSub as a function of the stream location allows identification of sediments that may be acting as a source or sink of P (Figure 2.7). EPC_0 of DepS sediments at location 3 has a similar value of the DRP in the stream water ($p > 0.05$); therefore, they may be acting as a source of P. Also, EPC_0 of bank and DepSub features are within 25% of the stream water DRP concentration at loc 3; therefore, if stream water DRP concentrations decrease, these sediments will be a source of P to the surface water.

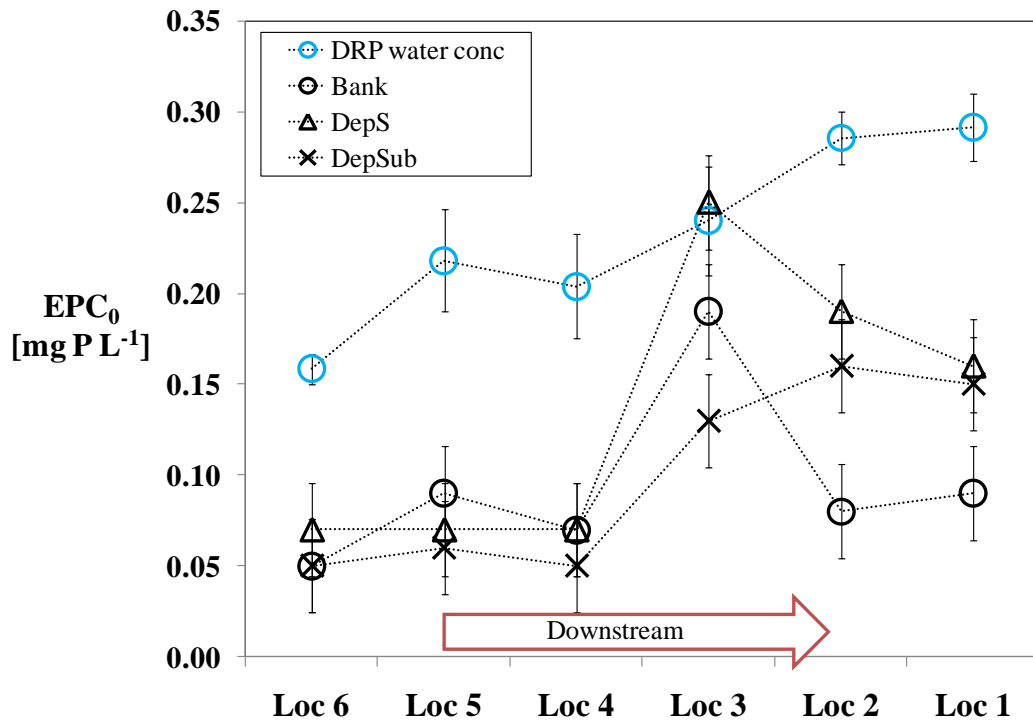


Figure 2.7 Equilibrium P concentration at zero net P sorption (EPC_0) for bank, deposition surface (DepS) and subsurface (DepSub) as a function of stream-reach location (Loc). Vertical bars represent the standard deviation of samples collected at the same location. DRP refers to the dissolve reactive P concentration in stream water at the time of sediment collection.

Stream Sediments Characterization as a Function of Geomorphology Location

Significant differences for P_{lab} ($p < 0.001$), P_{max} ($p < 0.001$), T_{carbon} ($p < 0.0001$), T_{clay} ($p < 0.001$), T_{sand} ($p < 0.001$), and T_{silt} ($p < 0.001$) were found between the sediments taken from the different stream features (Table 2.2). Bank sediments contained the highest clay and silt content (Table 2.3). Sediments from stream beds (RB and PB) and depositional features were over 90% sand (Table 2.3).

Table 2.3 Chemical and physical parameters of stream sediments taken from bank, pool bed (PB), riffle bed (RB), depositional surface (DepS), and depositional subsurface (DepSub) features in Upper West Emma Creek.

Analytical parameter †	Units	Stream features				
		Bank	PB	RB	DepS	DepSub
P _{lab}	mg kg ⁻¹	34.6 a	13.1 b	7.3 b	10.1 b	7.2 b
P _{max}	mg kg ⁻¹	158.6 a	46.0 b	18.4 b	24.9 b	19.8 b
k _L	L mg ⁻¹	0.34 bc	0.44 ab	0.38 ab	0.36 ab	0.51 a
Fe _{ox}	mg kg ⁻¹	670 a	252 b	92 c	116 c	138 c
P _{ox}	mg kg ⁻¹	97 a	40 b	19 c	19 c	20 c
Al _{ox}	mg kg ⁻¹	320 a	96 b	50 b	56 b	56 b
DPS	%	26 c	35 ba	39 a	33 b	34 b
P _w	mg kg ⁻¹	2.8 a	1.3 a	1.5 a	1.9 a	2.0 a
Tsand	%	56.6 b	93.3 a	97.2 a	96.3 a	97.3 a
Tsilt	%	26.3 a	5.1 b	2.4 b	3.1 b	2.2 b
Tclay	%	17.1 a	1.6 b	0.4 b	0.6 b	0.6 b
Tnitro	%	0.10 a	0.02 b	0.00 b	0.01 b	0.00 b
Tcarbon	%	1.2 a	0.3 b	0.1 b	0.1 b	0.1 b

† P_{lab} refers to Labile P, P_{max} represent P maximum adsorption capacity, k_L represent the P binding energy, Fe_{ox}, Al_{ox} and P_{ox} refers to oxalate extractable ions, DPS refers to degree of P saturation, P_w refers to water extractable P, and Tsand, Tsilt, Tclay, Tnitro, and Tcarbon refers to total sand, silt, clay, nitrogen and carbon, respectively.

A significant correlation ($r^2 = 0.62$ and $P < 0.001$) was found between P_{max} and Tclay for all sediment types (Figure 2.8). Similarly, P_{max} and Tcarbon were strongly correlated ($r^2 = 0.76$ and $P < 0.001$). This suggests that the P buffering capacity of sediments increases as fine material and organic content increase.

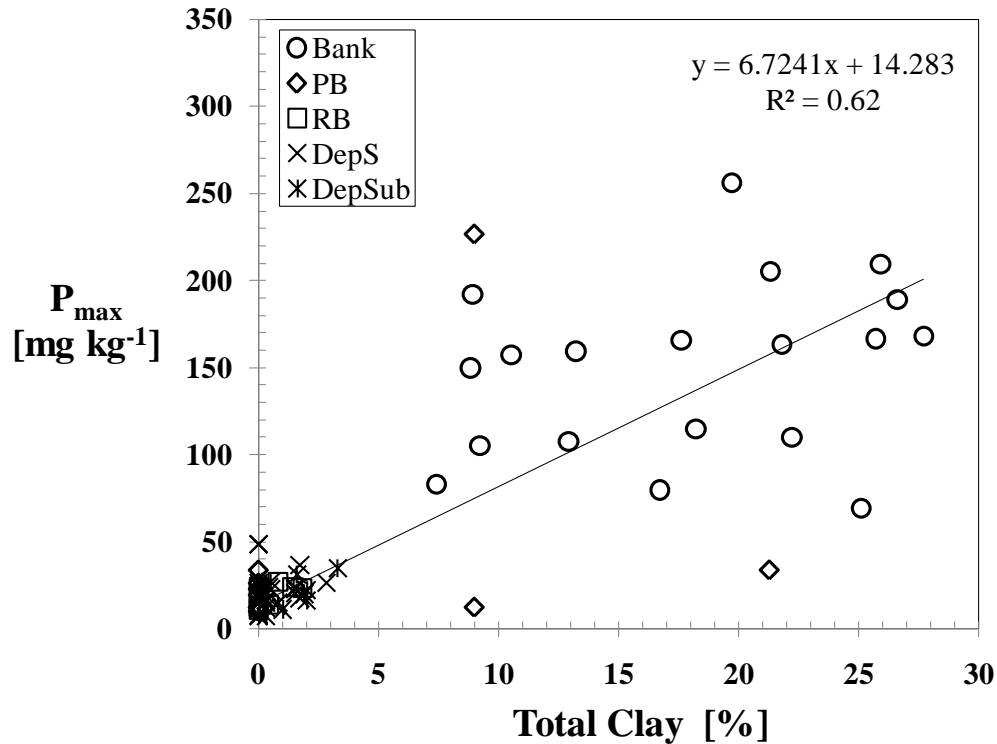


Figure 2.8 Relationship between Adsorption capacity (P_{\max}) and clay content (Tclay) of stream sediments sampled at bank, pool beds (PB), riffle beds (RB), depositional feature surface (DepS) and depositional features subsurface (DepSub).

Previous works have also linked amorphous and poorly crystalline forms of Al_{ox} and Fe_{ox} with P_{\max} values in soils and sediments (Gale, 1994; Khalid, 1977; Richardson, 1985). A highly significant ($r^2=0.82$ and $P<0.001$) linear relationship was found between P_{\max} and Fe_{ox} and between P_{\max} and Al_{ox} ions ($r^2=0.77$ and $P<0.001$) (Figure 2.9).

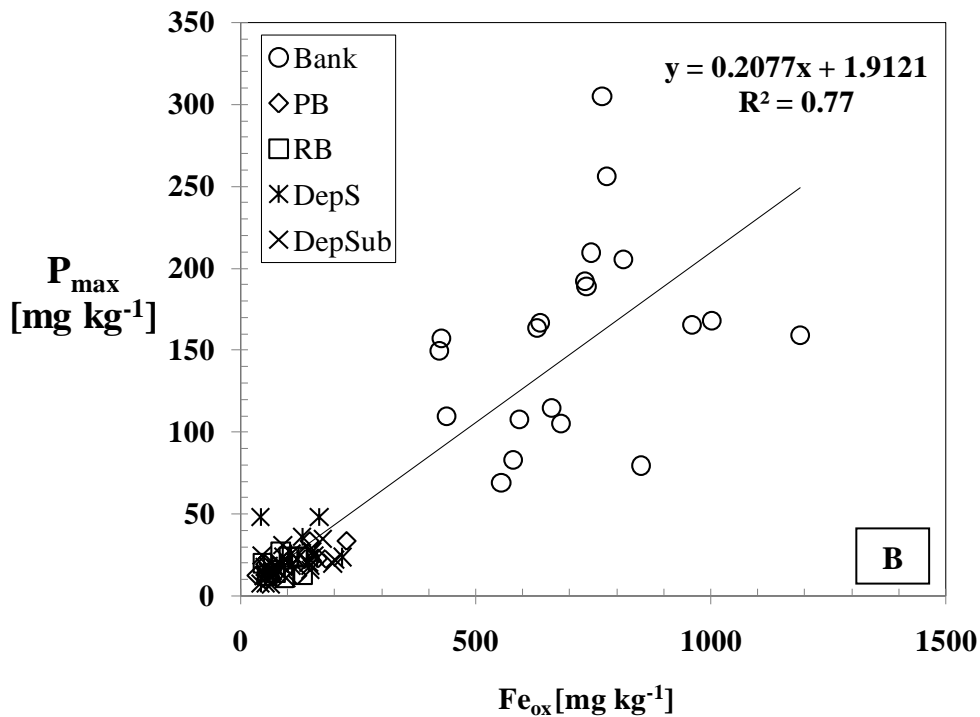
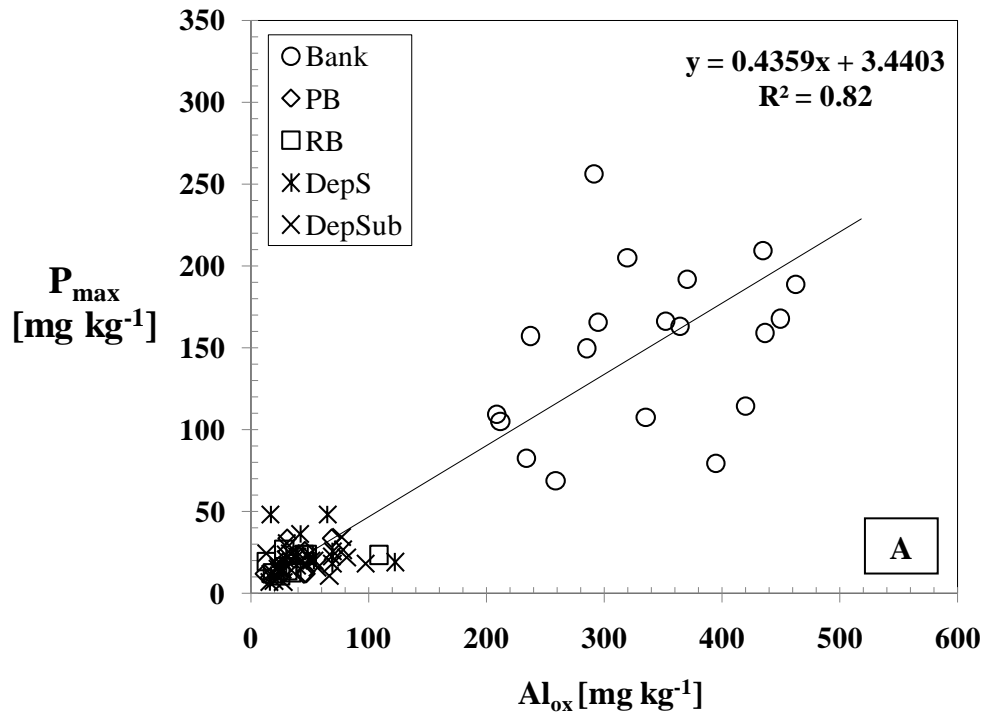


Figure 2.9 (A) Relation between maximum adsorption capacity (P_{\max}) and oxalate extractable Al (Al_{ox}) and (B) relation between P_{\max} and oxalate extractable Fe (Fe_{ox}) content of stream sediments sampled at bank, pool beds (PB), riffle beds (RB), depositional feature surface (DepS) and depositional features subsurface (DepSub).

Thus, T_{carbon}, Fe_{ox}, and Al_{ox} which are largely contained within the clay-sized particle fraction are good predictors of sediment P uptake and buffering capacity of the stream sediments. This is mainly because minerals such as alumino-silicates (e.g., clays) and metal oxides and hydroxides (e.g., Fe and Al) have greater specific surface area for P adsorption (Withers and Jarvie, 2008).

Sediment DPS was used to indicate phosphorus saturation status at the surface of the sediment. Even though, bank sediments had the highest mean values for P_{lab}, P_w and P_{ox}, they had the lowest DPS. This indicates that bank sediments may still have potential for P uptake and therefore have an important buffering role in aquatic ecosystems.

After 30 h, the P desorbed was approximately constant for sandy sediments (PB, RB, DepS, and DepSub) (Figure 2.10). However, bank sediments continued to desorb P up to 72 h. Thus, bank sediments presented very high labile P when compared with labile P of sandy sediments (Table 2.3). Phosphorus release rate (P_{rel}) was not significantly different between stream sediments (Table 2.2).

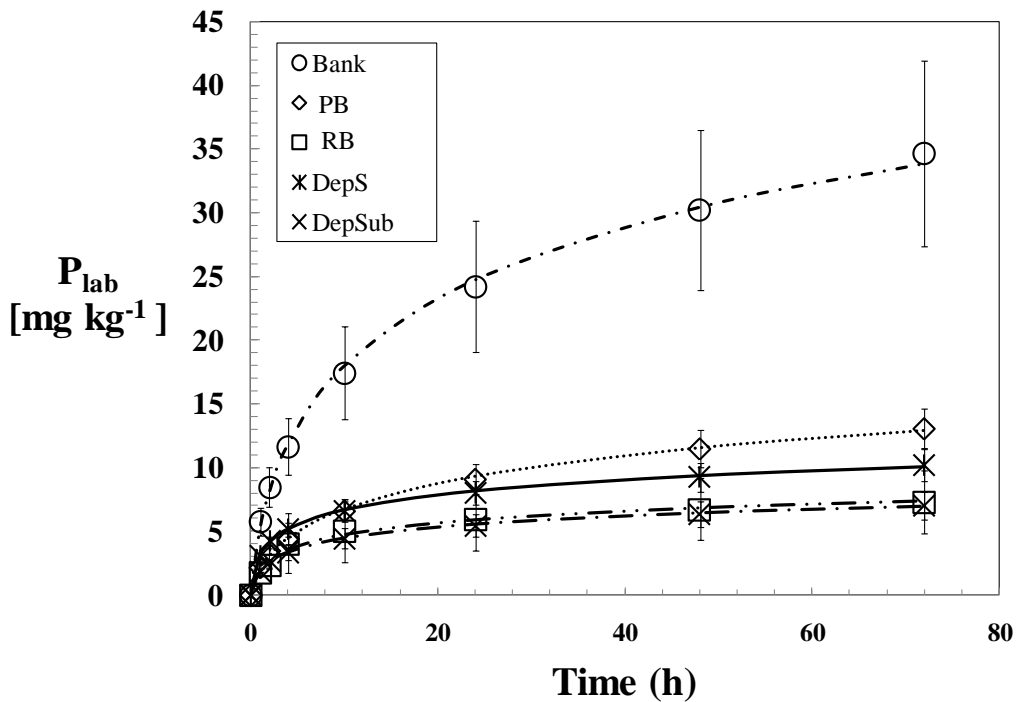


Figure 2.10 Phosphorus desorption as a function of time for sediments collected from Bank, pool beds (PB), riffle beds (RB), depositional surface (DepS) and depositional subsurface (DepSub) features. Vertical bars represent the standard deviation and dashed lines represent fitting of the Elovich model.

Cross Sectional Changes and Erosion Potential along the Main Channel

Cross sectional profiles at locations 1, 4, and 6 changed during the 2008-2009 period (Figure 2.11). Pool beds from location 1 and 4 appear to have scoured as indicated by the downward movement of the cross sectional profile while location 6 migrated laterally to the left of the pool bed. A preliminary study conducted by Keane and Sass (2009) (Unpublished data) in the same system reflected fluctuations in the pattern, profile and dimensions of the channel, therefore, they concluded that UWEC channel is an unstable system and relatively high sediment movement.

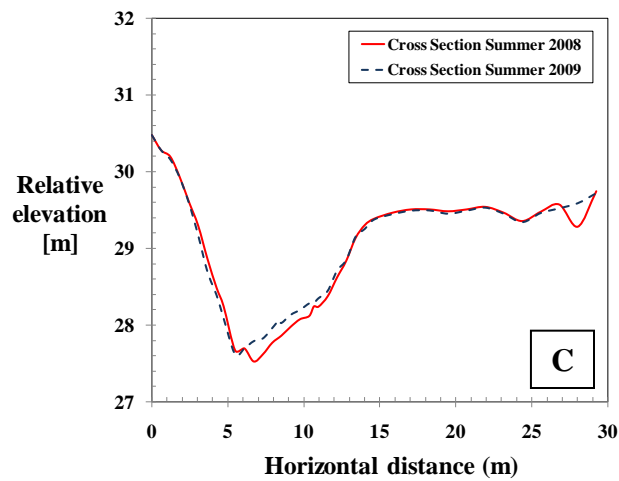
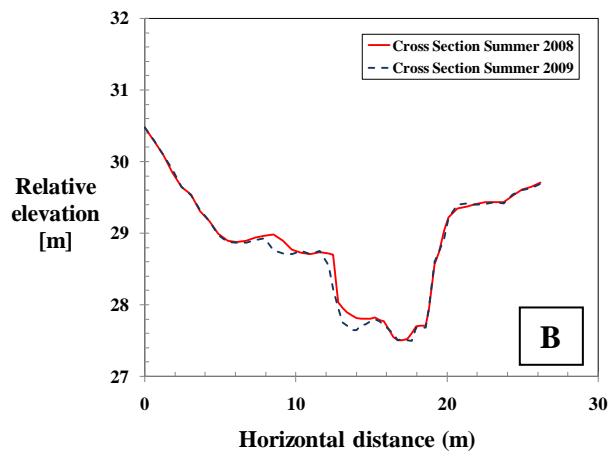
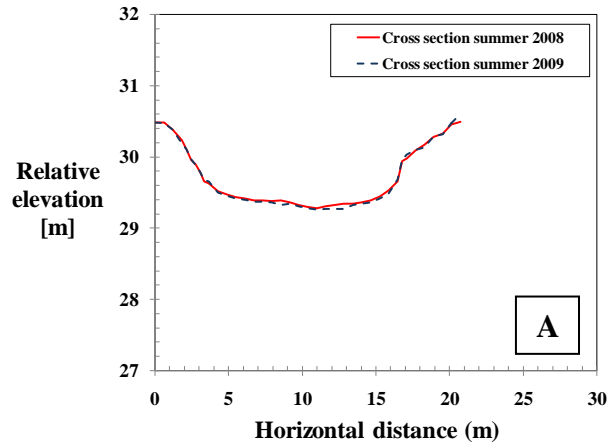


Figure 2.11 Change in cross sectional profile for three sampling locations on Upper West Emma Creek: (A) Location 1, (B) Location 4 and (C) location 6. Note: Elevation measurements are relative to an arbitrarily selected benchmark at each location for which elevation was assumed to be 30.48 m.

Based on data from the bank pin measurements, average pin exposure was 0.008 m, 0.012 m, and 0.087 m at location 1, location 4, and location 6, respectively (Table 2.4). It was estimated that 170 Mg of sediments were eroded from bank features at location 1, location 4, and location 6 during the study period (Table 2.5).

Table 2.4 Bank pin exposure at location 1, location 4 and location 6.

	Pin exposure		
	Location 1	Location 4	Location 6
	m		
Bank Pin at 0.61 m	0.006	0.012	0.071
Bank pin at 1.22 m	0.010	0.011	0.104
Average	0.008	0.012	0.087

Table 2.5 Bank erosion estimation at location 1, location 4, and location 6

Location	Pin exposure [m]	Bank height [m]	Stream length [m]	Bank erosion [m ³ / stream reach]	Sediment mass [Mg/ stream reach]
Location 1	0.008	1.4	543	5.9	7
Location 4	0.012	1.9	814	18.1	22
Location 6	0.087	2.0	691	117.6	141
Total				141.5	170

A total suspended sediment load of 1536 Mg and a total of 5.16 Mg of DRP were exported from the watershed at location 1 from June 2008 through May 2009 (Barnes et al., 2009 - Unpublished data). Therefore, by assuming a constant erosion rate of 0.083 Mg m⁻¹ at third and fourth order streams of the watershed which have a total length of 7.6 km, bank erosion of third and fourth order streams contributed with around 630 Mg of sediments to the stream system from June 2008 to May 2009.

Therefore, during the monitory period around 41% of the suspended sediment load in UWEC comes from erosion of the bank features located at third and fourth order streams. Additionally, based on the average P_{lab} (28 ± 4 mg P kg^{-1}) through the bank profile (Table 2.6), bank erosion in this section of the stream channel contributed with around 17 ± 3 kg of DRP to the stream system from June 2008 to May 2009. This represents 0.33% of the total DRP load reported at location 1. This calculation was based on the assumption that all of the P_{lab} was desorbed from the sediment during transport.

Table 2.6 Average of P_w , P_{ox} , P_{lab} through the bank profile.

Bank location	P parameters		
	P_w	P_{ox}	P_{lab}
	mg/ kg		
Water level	1.0	72	24
Middle level	2.0	91	24
Top level	4.6	114	35
Average through the bank profile	2.5	93	27
Stde[†]	0.6	11	4

[†] Refers to the standard deviation of the all 24 bank samples collected (8 bank features at three different levels). P_w refers to water extractable P, P_{ox} refers to oxalate extractable P, and P_{lab} refers to Labile P.

Upland Soil P Chemistry and Characterization

The EPC_0 from manure amended fields was markedly higher ($EPC_0=3.2$ mg P L^{-1}) than the other field soils (Table 2.7). Manure amended fields also contained the highest P availability ($P_{lab}=128$ mg P kg^{-1} soil) followed by wheat no till fields. Management practice (till vs no till) did not have a significant effect in P availability in wheat fields ($p>0.05$ for wheat till vs wheat no till).

Table 2.7 Phosphorous related parameters of upland soils from different cropping systems. Different letters denote significant differences between different cropping systems ($p < 0.05$). Pair wise comparisons were performed for those variables where cropping system resulted in a significant difference.

Cropping system	Analytical parameters [†]									
	EPC₀	P_{lab}	P_{rel}	P_{max}	k_l	Fe_{ox}	P_{ox}	Al_{ox}	DPS	P_w
	mg L ⁻¹	mg kg ⁻¹	mg kg ⁻¹ h ⁻¹	mg kg ⁻¹	L mg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	%	mg kg ⁻¹
Manure amended	3.18 a	127.8 a	97.1 a	209 a	0.16	943	338 a	735 a	52.5 a	19.9 a
Pasture	0.21 b	20.8 b	6.0 a	113 b	0.15	812	109 b	439 b	25.2 b	3.0 b
Wheat no till	0.41 b	66.9 ab	27.3 a	246 a	0.12	1001	122 b	418 b	23.2 b	8.1 ab
Wheat till	0.14 b	33.9 b	10.3 c	205 a	0.19	783	73 b	342 b	17.8 b	3.6 b
Row crops	0.10 b	48.4 b	85.2 a	229 a	0.23	960	179 b	866 a	23.2 b	3.0 b
p-value F^{††}	0.001	0.023	0.020	0.003	0.242	0.560	0.003	<0.0001	0.012	0.011

[†] EPC₀ refers to the Equilibrium P concentration at zero net P adsorption, P_{lab} refers to Labile P, P_{rel} refers to rate of initial P release, P_{max} represent P maximum adsorption capacity from the Langmuir equation, Fe_{ox}, Al_{ox} and P_{ox} refers to oxalate extractable ions, DPS refers to degree of P saturation, and P_w refers to water extractable P.

^{††} p-values for the test cropping system effect from the ANOVA for each analytical parameter.

However, P_{\max} for wheat no till was greater than P_{\max} for wheat till. On the other hand, manure applied fields have the highest saturation status (DPS=52.5%) because of the continuous manure applications. Soil pH was also consistently higher (Table 2.8) in the manure amended fields which may be also attributed to the manure applications.

Table 2.8 Analysis of particle size, total nitrogen, total carbon and soil pH of upland soil from different cropping systems in Upper West Emma Creek Watershed. Different letters denote significant differences between different cropping systems ($p < 0.05$).

Cropping system	Analytical parameters [†]					
	Tsand	Tsilt	Tclay	Tnitro	Tcarbon	pH
	% —————					
Manure amended	35.5 a	39.6	24.9 b	0.17 ab	2.0	6.4 a
Pasture	53.2 a	30.7	16.1 c	0.23 a	2.6	5.9 ab
Wheat no till	22.4 b	49.3	28.3 a	0.12 b	1.5	5.6 bc
Wheat till	41.7 a	36.1	22.2 b	0.10 b	1.3	5.2 c
Row crops	27.5 b	42.3	30.2 a	0.13 b	1.6	5.3 c
p-value F^{††}	0.046	0.133	0.030	0.024	0.068	0.001

[†] Tsand, Tsilt, Tclay, Tnitro, and Tcarbon refer to total sand, silt, clay, nitrogen and carbon, respectively.

^{††} p-values for the test cropping system effect from the ANOVA for each analytical parameter.

Comparisons between Stream Sediments and Upland Soils

As mentioned previously, EPC_0 was similar between stream sediments, with an average of about 0.1 mg L^{-1} . Although some field soils had a much greater EPC_0 , there was high variability and the means were not different from the stream sediments with the exception of manure amended soils that had the highest EPC_0 of all fields and stream features (Figure 2.12).

When comparing P desorption of stream sediments versus field soils, stream sediments had relatively low P_{lab} , and therefore, do not represent a large long-term P supply (Figure 2.13). Of the stream sediments, the bank soils have the highest P concentrations and would be the largest in-stream P source for this watershed.

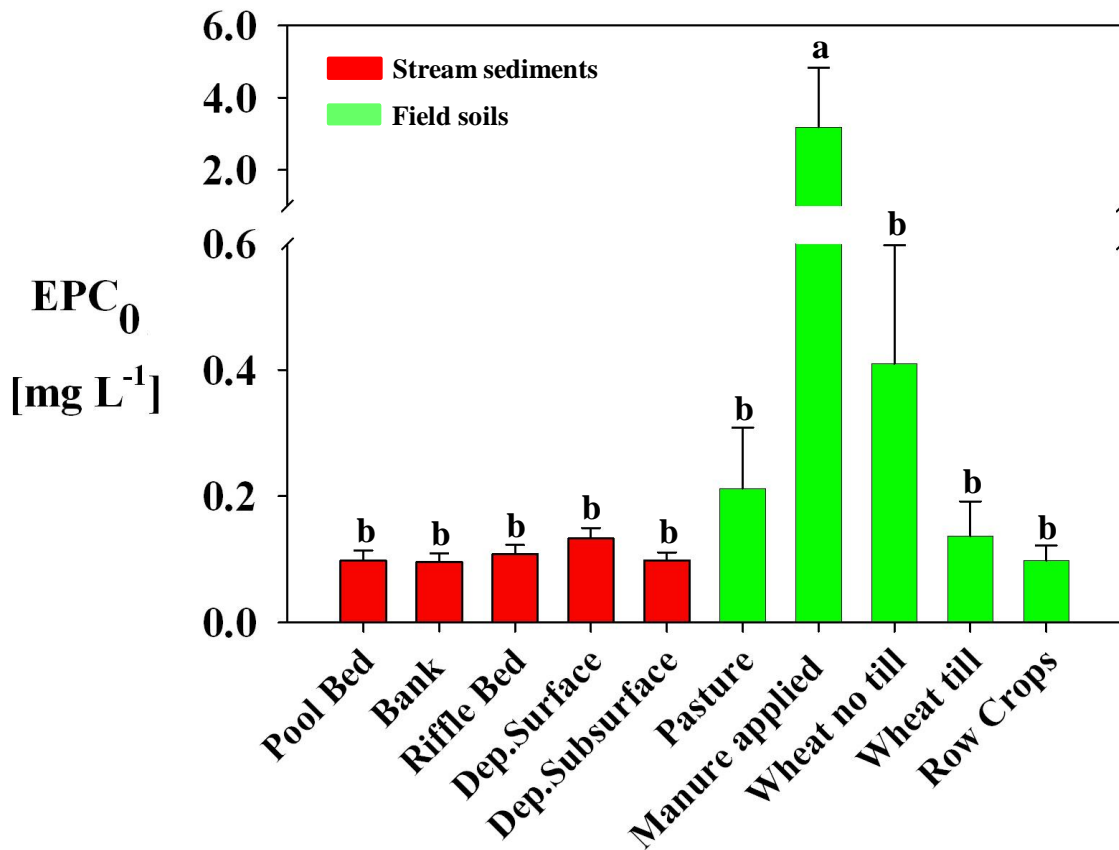


Figure 2.12 A comparison of the equilibrium P concentration at zero net sorption (EPC₀) of stream sediments and Field soils in the Upper West Emma Creek watershed. Different letters above bars denote significant differences between in-stream sediments and field soils ($p < 0.05$). Vertical bars represent the standard deviation of sediment and soil samples collected at each category.

Manure amended fields had the highest P_{lab} due to continued inputs of manure-based P; therefore, they represent a large available P pool. Finally, this may lead to an increase of P runoff from agricultural soils.

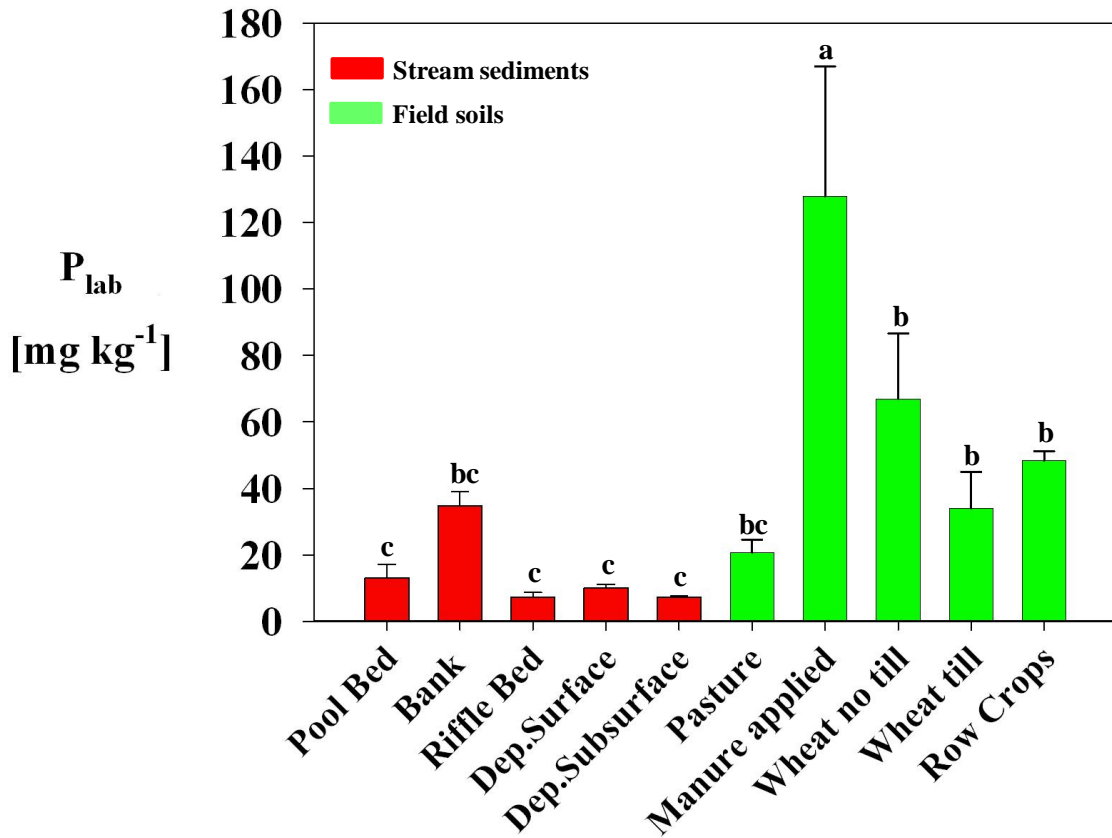


Figure 2.13 A comparison of labile P (P_{lab}) of stream sediments and field soils. Different letters above bars denote significant differences between in-stream sediments and field soils ($p < 0.05$). Vertical bars represent the standard deviation of sediment and soil samples collected at each category

Stream sediments had overall low P buffering capacities, indicated by low P_{max} , and high DPS (Figure 2.14). Of the stream sediments, bank sediments had the highest adsorption capacity with a slightly lower DPS than sandy sediments (PB, RB, DepS, and DepSub). Manure amended fields had a high adsorption capacity, however, they are over 50% saturated.

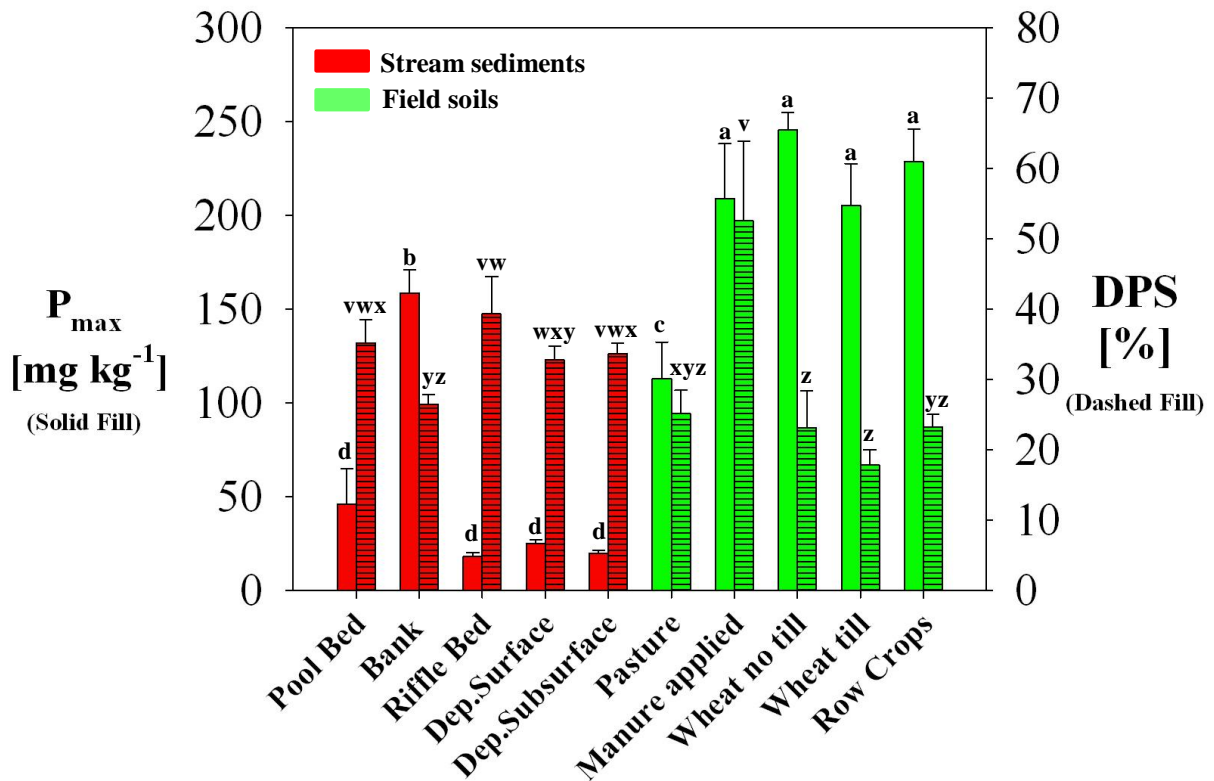


Figure 2.14 Maximum adsorption capacity (P_{max}) and degree of P saturation (DPS) of stream sediments and field soils. Different letters above bars denote significant differences between in-stream sediments and field soils ($p < 0.05$). Vertical bars represent the standard deviation of sediment and soil samples collected at each category

Comparisons between EPC_0 Values from Soils and Sediments and P Concentration in the Stream Water

Stream sediments interact with stream water through complex chemical, biological, and hydrologic processes. The end result of these processes modifies both the stream water and the sediment characteristics. In situations where stream sediments have low EPC_0 , the sediments will adsorb P from stream water; thereby, reducing P concentrations in the stream system (Haggard et al., 2005; McDowell et al., 2003). Water analysis from January 2008 through August 2009

showed an average DRP concentration of 0.14 mg L^{-1} during baseflow, and 0.25 mg P L^{-1} during storm flow.

Figure 2.15 shows the range of EPC_0 of stream sediments and field soils and DRP concentrations in stream water during baseflow and storm flow conditions. It was found that the DRP concentrations in stream water were consistently higher during storm flow than during baseflow ($p < 0.05$). Additionally, the mean EPC_0 of stream sediments is slightly less than the mean DRP during baseflow ($p < 0.05$); therefore, the sediments may act as a P sink under current conditions. However, due to the high DPS and low P_{max} , the sediments would not be a substantial P sink. On the other hand, field soils had a large range in EPC_0 , and therefore, no significant difference ($p > 0.05$) was detected when compared with DRP during storm flow. However, it is expected that some of the amended fields in which EPC_0 exceed the DRP in the stream water will release P to the stream system. Additionally, the EPC_0 of soils from some of the fields receiving conventional fertilizer were still in excess of the DRP of stream water, indicating that these soils may also represent an important P source in the watershed.

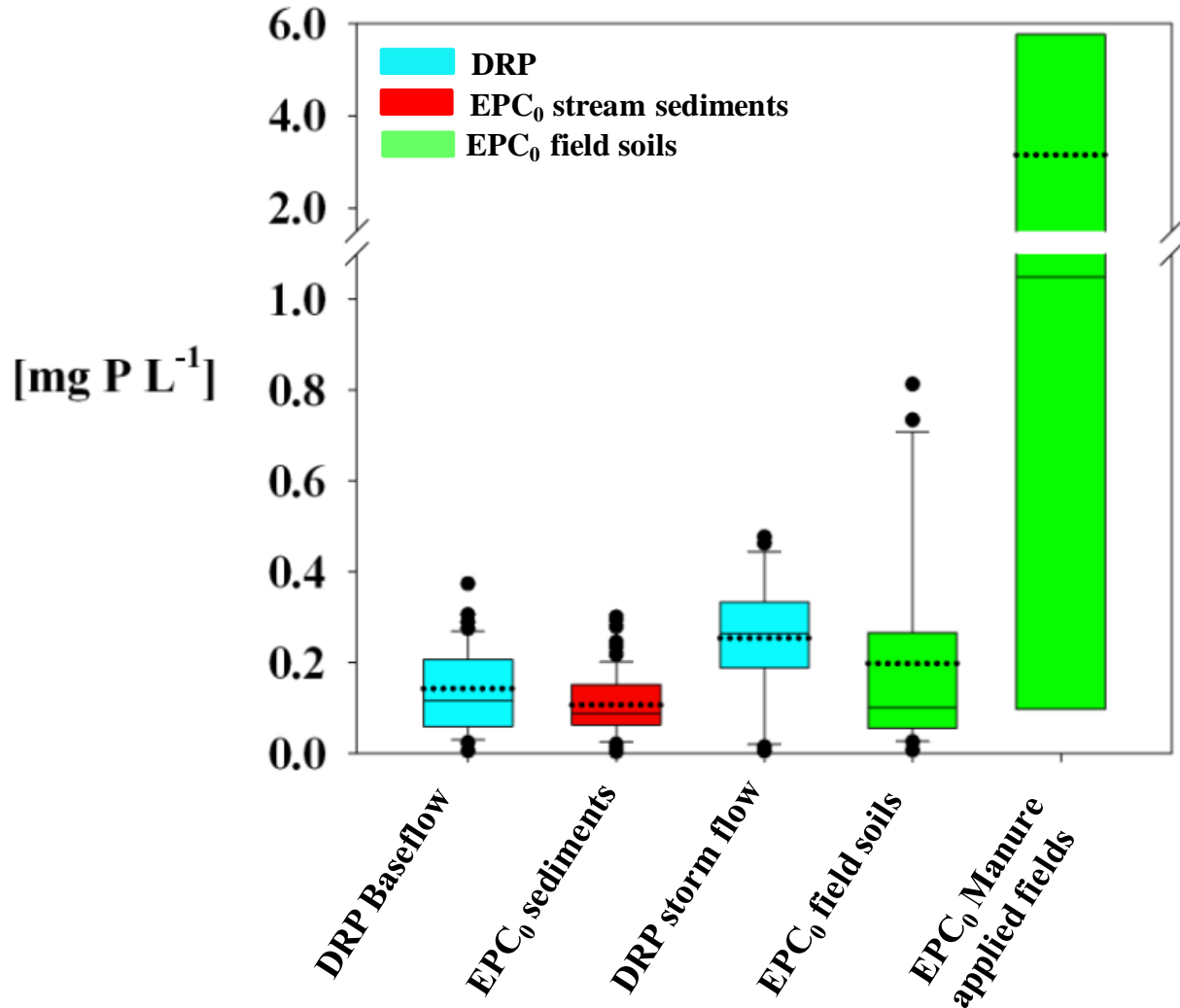


Figure 2.15 Equilibrium P concentration at zero net P sorption (EPC_0) of stream sediments and field soils and its comparison with dissolved reactive P (DRP) in stream waters under baseflow and storm flow conditions in Upper West Emma Creek watershed. Each box depicts the smallest observation, lower quartile, mean (dotted line), median (solid line), upper quartile, largest observation, and data outliers of each data set.

Conclusions

Phosphorus chemistry of the various in-stream sediment types remained constant through the main channel. However, the EPC_0 of bank, DepS and DepSub was consistently higher at location 3. This may be attributed to the direct access of animal into the stream system is having an impact on these sediments; however, the nature of our experimental design does not allow us

to conclusively state that the animal access caused the increase in the EPC_0 . Of the stream sediments, bank sediments had higher silt and clay content; and therefore, they had high adsorption capacities. Conversely, sediments from RB, PB, DepS, and DepSub features were mostly sandy; and therefore, they had low adsorption capacities. Additionally, bank sediments had the highest mean values for P_{lab} , P_w and P_{ox} and the lowest DPS value. Therefore, bank sediments have the highest potential to release P into the stream system mainly through erosion and they represent the largest in-stream P source for this watershed. On the other hand, bed sediments (RB, PB, DepS, and DepSub) had relatively low P_{lab} concentrations, and therefore, do not represent a long term P supply.

A comparison between stream sediments and field soils indicates that field soils had a much larger available P pool than stream sediments, especially the manure amended fields. Additionally, P assimilation capacity of field soils was greater than stream sediments. The lack of P buffering capacity of stream sediments was indicated by low P adsorption capacity, low P_{lab} , and high DPS.

Dissolved P concentrations in stream water were consistently higher during storm flow than during baseflow. Additionally, the mean EPC_0 of stream sediments is slightly less than the mean DRP during baseflow; therefore, the sediments may act as a P sink under current conditions. However, due to the high DPS and low P adsorption capacity, the sediments would not be a substantial P sink. On the other hand, field soils had a large range in EPC_0 , some of which exceed the DRP in the stream water. Thus, it is expected that sediments with EPC_0 higher than DRP will release P to the stream water.

The channel bed is characterized by sandy sediments which have very little remaining P assimilation capacity. Of the stream sediments, bank sediments had the highest potential of

release P into the stream mainly through erosion. It was estimated that bank erosion from third and fourth order streams (7.6 km) accounts for nearly 41% of the total sediment load. Thus, by assuming that all of the P_{lab} was desorbed from the sediment during transport bank sediments have the potential to load around 17 ± 3 kg of DRP to the stream system annually. However, this represented just 0.33% of the total DRP load reported at location 1.

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CHAPTER 3 - Red Rock Creek Watershed: Impact of Animal Agriculture

Introduction

Animal agriculture has often been identified as a major impairment of stream water quality and responsible for eutrophication processes in downstream water bodies (Hoorman et al., 2008). Generally, in watersheds with high-input agriculture and livestock operations, manure or litter is applied in fields in order to supply crop nutrient needs. Nutrient accumulation in soils receiving annual manure or litter applications may lead to increased levels of P in surface runoff which finally will result in increased stream P concentrations. In-stream sediments are responsible for regulating water column P concentrations (McDaniel et al., 2009). Consequently, an increase in the DRP concentration in the stream water will, therefore, increase the P saturation status in the surface of the sediments. It is expected that sediments which have been exposed to higher in-stream P concentrations will have higher EPC_0 ; therefore, higher potential to release P to the stream system. Thus, in order to better understand how animal agriculture might influence the P storage and release from stream sediments relative to upland P sources and P loading in Kansas streams a second watershed with increased intensity of animal agriculture was selected. This was studied through the same 4 interrelated objectives proposed in Chapter 2 as restated below:

1. To quantify P in stream sediments originating from different stream features and its potential for release and transport in stream water.
2. To estimate stream bank erosion.

3. To quantify P in field soils under different management practices and its potential for release and transport in surface runoff.
4. To compare P sorption and release characteristics of stream sediments and field soils to P concentrations in stream water.

Materials and Methods

Study Site Description

Red Rock Creek (RRC) is a sub-watershed of the Cheney Lake Watershed. It is located on the North Fork of the Ninnescah River in south central Kansas (Figure 3.1). The primary use of the watershed land area (136 km²) is cropland (63%), of which wheat (35%), corn (18%), soybeans (17%), sorghum (21%) and alfalfa (8%) are major crops. Grassland comprises 16%, woodland 4% and CRP 11%. Urban and water ways compromise 6% of the total land mass. Based on an estimation given by the Cheney Lake Watershed, Inc around 6.2% of the fields received manure in 2009, however, this is just an estimate that is subject to change from one year to other. Livestock production is concentrated in fourteen dairies with a total of 1748 animals, and nine beef operations with a total of 549 animals (Figure 3.1). Primary soil map units within the watershed are Nalim loam (Fine-loamy, Mixed, Superactive, Mesic Udic Argiustolls), Farnum (Fine-Foamy, Fixed, Superactive, Mesic Pachic Argiustolls), Funmar Loams (Fine-Loamy, Mixed, Superactive, Mesic Pachic Argiustolls), and Saltcreek-Funmar-Farnum Complex (Saltcreek: Fine-Loamy, Mixed, Superactive, Mesic Udic Argiustolls). Stream bed sediments (i.e., riffle bed and pool bed) are mostly sandy with a total sand composition between 80 to 98% and total silt between 2.1 - 14%.

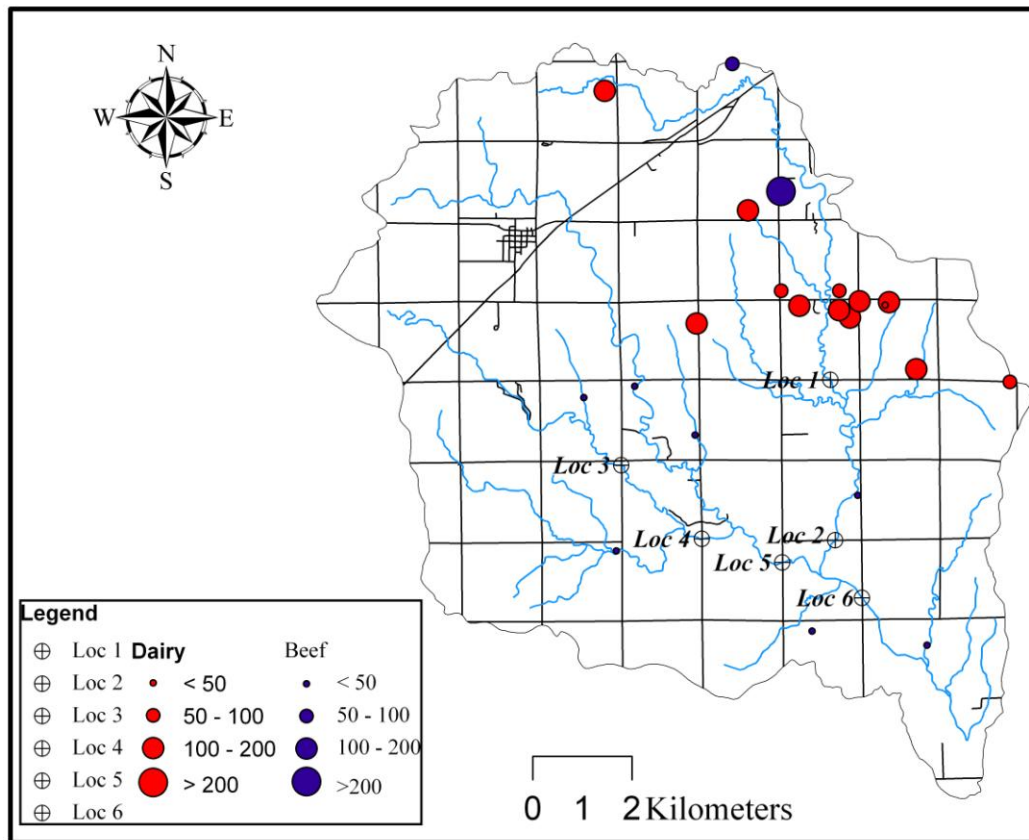


Figure 3.1 Stream-reach locations in Red Rock Creek watershed. Livestock production is represented by red (dairy) and purple (beef) points. Point size indicates number of animals per operation. Loc refers to stream-reach location.

Six stream reaches with different drainage area were selected along the two main branches at RRC (Figure 3.1 and Figure 3.2).

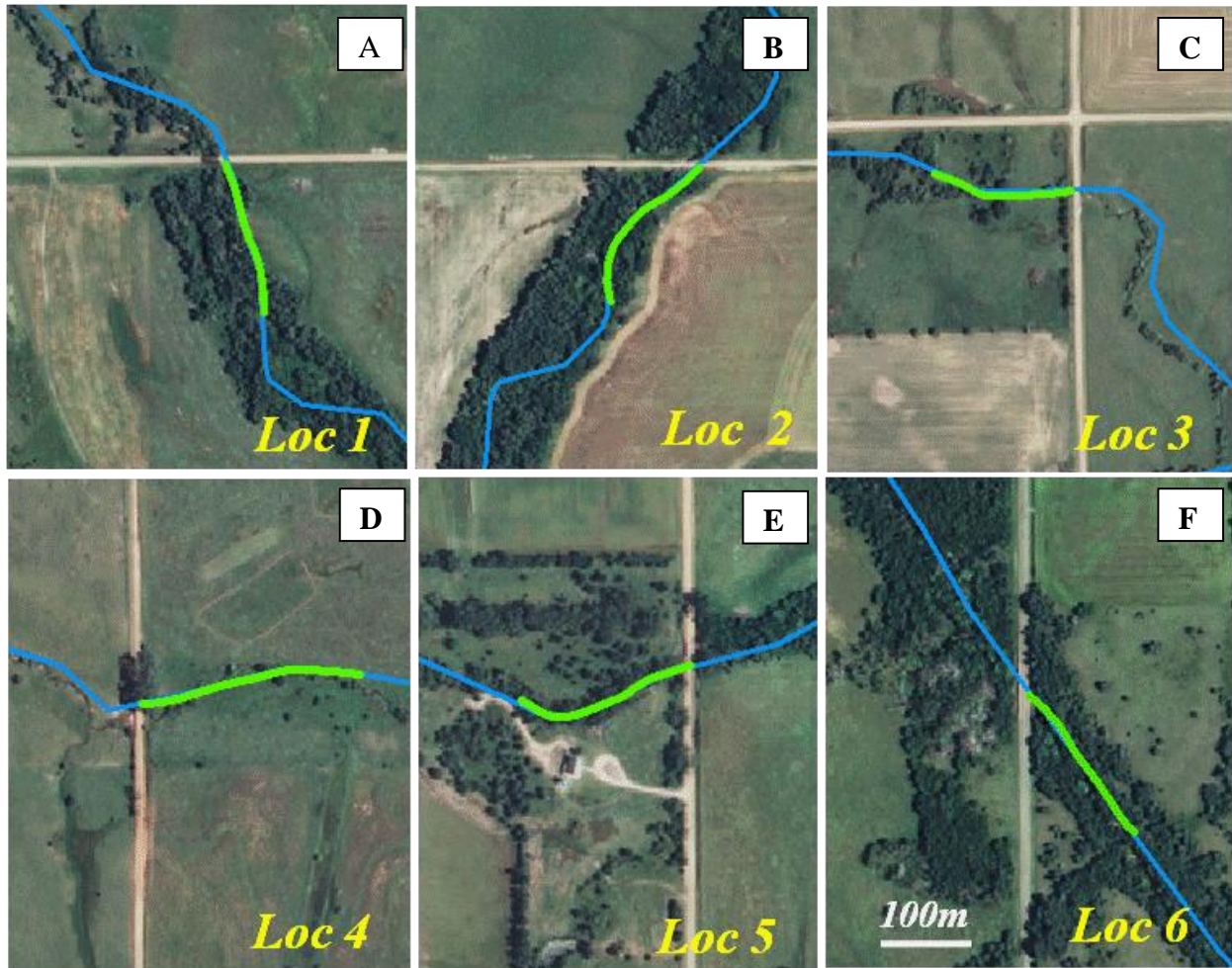


Figure 3.2 Aerial photograph of each of the six study stream-reaches at Red Rock Creek Watershed. (A) Location 1 (loc 1), (B) location 2 (loc 2), (C) location 3 (loc 3), (D) location 4 (loc 4), (E) location 5 (loc 5), and (F) location 6 (loc 6).

Locations 1, 2, 4, 5 and 6 did not have animal activity around the stream reach. Cattle were observed at location 3 during summer 2008. However, during summer 2009 the animals were relocated into another field due to the absence of water flow in this section of the stream channel. Animal activity was not observed at location 1; however, evidence (e.g., cattle prints and feces) of animals impacting directly the stream water was found. Location 1, 2, 5 and 6 were surrounded by forest vegetation (Table 3.1).

Table 3.1 Characteristics of each stream-reach location at Red Rock Creek Watershed.

Stream location	Drainage Area km²	Livestock activity	Riparian vegetation
Location 1	22	Cattle presence	Forest
Location 2	52	NP	Forest
Location 3	17	Cattle presence	Grass land
Location 4	19	NP	Grass land
Location 5	62	NP	Forest
Location 6	121	NP	Forest

*NP refers to no presence.

Field Methods

Sediment and Soil Sampling

Sediment and soil sampling was performed in the same way that was done for the Upper West Emma Creek watershed (Chapter II, sediment and soil sampling). However, the sediment sampling at RRC was performed during June through July of 2008 and June through July of 2009. Similarly, 8 fields were selected from wheat, pasture, row crop, and manure applied production systems. Soil samples from row crop fields (corn and sorghum) were collected during November of 2008 while sampling for pasture lands, manure applied and wheat fields was performed during June through July of 2009 (Figure 3.3).

Water Sampling

Methods of water sampling in RRC were similar to those used for the UWEC watershed. Three portable samplers (ISCO model 6700) were installed at locations 1, 5, and 6 to collect storm and flow samples from January 2008 through August 2009. Flow was calculated by using the Manning's equation, and storm sampling was performed by using the equation 2.1 (See Chapter 2, water sampling).

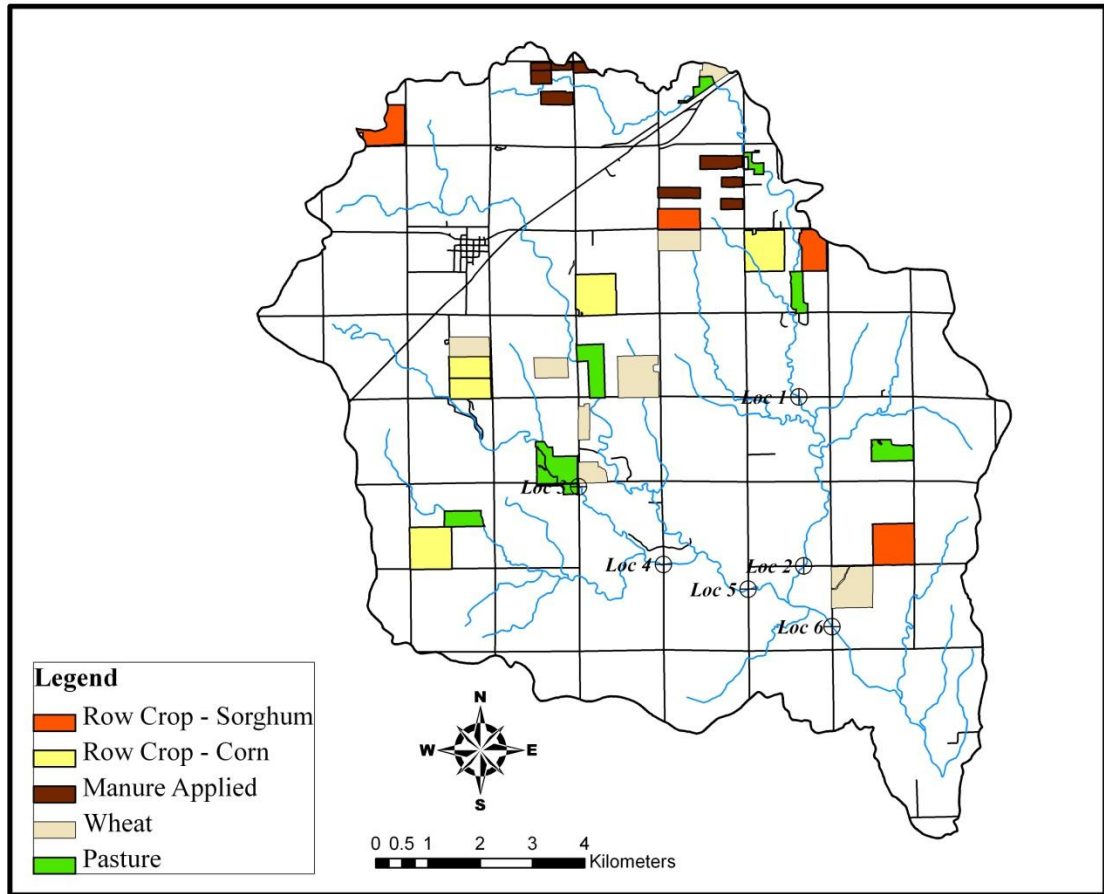


Figure 3.3 Soil sampling locations for wheat, row crops, manure applied and pasture fields in the Red Rock Creek Watershed.

Stream Channel Characterization

Cross sectional surveys were performed during May of 2008 and June of 2009 at the locations where ISCO samplers were installed (i.e., Location 1, 5 and 6). Similarly to the UWEC watershed, bank erosion rates were estimated with bank pin measurements by selecting representative bank features at locations where ISCO samplers were installed (location 1, 5, and 6) (See Chapter 2, stream channel characterization). Pins were installed during May of 2008 and exposure was measured in June of 2009.

Laboratory Methods

Sediment, Soil and Stream Water Analysis

Sediment and soil samples were analyzed for gravimetric moisture, EPC_0 , maximum P adsorption capacity (P_{max}), P binding energy (k_L), anion exchange extractable P (P_{lab}), P desorption rate (P_{rel}), oxalate extractable Al (Al_{ox}), Fe (Fe_{ox}), and P (P_{ox}), total carbon (Tcarbon), total nitrogen (Tnitro), total clay (Tclay), total silt (Tsilt), and total sand (Tsand). The degree of P saturation (DPS) was calculated based on the oxalate extractable ions. Water samples were analyzed for molybdate reactive dissolved P (DRP) using standard methods. Further details of the laboratory methods can be found in Chapter 2 - Laboratory methods.

Data Analysis Comparison

Differences among stream reaches and sediment types were evaluated using analysis of variance as computed with SAS Proc Mixed (SAS Institute Inc., 2004). Year was considered as a random variable because year did not have significant effect on any of the P related parameters of the stream sediments. Similar to the UWEC watershed, field data were analyzed independently by using the Proc Mixed protocol. Finally, to compare stream sediments versus field soils, all data was analyzed with a single model in Proc Mixed protocol. Correlation coefficients, means and standard errors were also determined with SAS v9.1. Additionally, a test of slice effects was performed to test the location effect for each feature, and the feature effect at each location. Finally, water quality data (i.e., baseflow, storm flow and grab samples) was compared with the EPC_0 of soil and sediments by applying the unequal variances protocol for independent samples (Steel et al., 1980). The calculation was performed in Microsoft excel v. 2007.

Results and Discussion

Stream Location Effect on Sediments Phosphorous Chemistry

The analysis of variance (ANOVA) showed that stream location had a significant influence ($p < 0.001$) on the P adsorption/desorption parameters (i.e., EPC_0 , P_{lab} , P_{rel} and P_{max}) of the stream sediments (Table 3.2).

Table 3.2 Significance of main effects and interactions from type III tests of fixed effects in the analysis of variance (ANOVA) for chemical and physical characteristics of stream sediment samples taken from pool bed, riffle bed, depositional surface, depositional subsurface, and bank features (Feature effect) at six reach segments (location effect) in Red Rock Creek. Asterisks indicate the level of significance from F-tests, where *, **, and * indicate $p < 0.05$, 0.01 and 0.001 respectively and ns = not significant.**

Analytical parameter †	Units	Effect		
		Stream Location	Channel feature	Feature by Location
EPC_0	$mg L^{-1}$	***	***	ns
P_{lab}	$mg kg^{-1}$	***	***	*
P_{rel}	$mg kg^{-1} h^{-1}$	***	*	ns
P_{max}	$mg kg^{-1}$	***	***	ns
k_L	$L mg^{-1}$	ns	***	ns
Fe_{ox}	$mg kg^{-1}$	***	***	ns
P_{ox}	$mg kg^{-1}$	***	***	ns
Al_{ox}	$mg kg^{-1}$	***	***	ns
DPS	%	***	ns	ns
P_w	$mg kg^{-1}$	*	ns	ns
Tsand	%	***	**	ns
Tsilt	%	***	*	ns
Tclay	%	***	**	ns
Tnitro	%	***	*	ns
Tcarbon	%	***	*	ns

† EPC_0 refers to the Equilibrium P concentration at zero net P adsorption, P_{lab} refers to Labile P, P_{rel} refers to Rate of initial P release, P_{max} represent P maximum adsorption capacity and k_L represent the P binding energy from the Langmuir equation, Fe_{ox} , Al_{ox} and P_{ox} refers to oxalate extractable ions, DPS refers to degree of P saturation, P_w refers to water extractable P, and T_{sand}, T_{silt}, T_{clay}, T_{nitro}, and T_{carbon} refers to total sand, silt, clay, nitrogen and carbon, respectively.

Similarly, oxalate extractable ions ($p < 0.001$) and particle size distribution ($p < 0.001$) of the stream sediments was different between the stream locations. This suggests that sediment chemical as well as physical composition is changing at each location and that; therefore, it is having an influence on the P behavior of the stream sediments. This may be partially explained by the wide variety of soil types across the watershed that influences in-stream sediment. Additionally, upstream land use as well as animal activity may have also impacted each stream location. Location 3 had the highest mean EPC_0 followed by location 2 (Figure 3.4). During summer 2009 location 3 did not have flowing water and therefore the stream sediments were drier than usual.

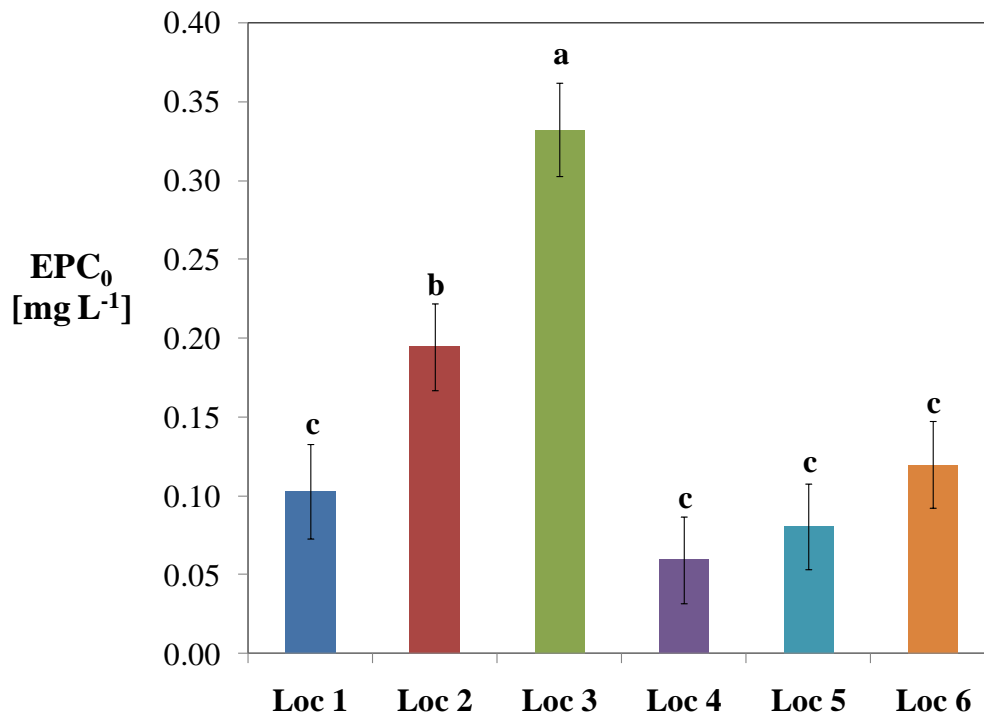


Figure 3.4 Equilibrium P concentration at zero net P sorption (EPC_0) of the stream sediments at each stream location. Different letters above bars denote significant differences between features as a function of the stream location (Loc) using $p < 0.05$. Vertical bars represent the standard deviation of all sediment samples collected at the same location

Previous studies have shown that desiccation of sediments can lead to a decrease in P binding (Baldwin et al., 2000). Additionally, it has been documented that sediments which have been exposed to repeated wetting/drying cycles show a reduction in P affinity compared to sediments that are rarely dried out (Watts et al., 2002). Consequently, this may explain why location 3 had a higher EPC_0 value when compared with the other stream locations.

The same trend was observed for the P_{lab} and P_{rel} results which agree well with the aforementioned hypothesis (Figure 3.5). Since stream sediments at location 3 have experienced a drying cycle due to the lack of flowing water, the affinity of the P attached to the surface of the sediments may have decreased. Consequently, P_{lab} and P_{rel} were significantly higher at location 3 (Figure 3.5).

In addition to the dryer conditions due to landscape position or stream order found at location 3, other factors such as animal activity close to the water surface may be also influencing the P available pool at this stream location. For example, McDaniel et al. (2009) found more bioavailable P such as orthophosphate in sediments from dairy-farmed than sheep-farmed streams, especially when the stream sediments were dry. Additionally, Haggard et al. (2007) found that land use had a significant effect on sediment P parameters, and therefore, water chemistry.

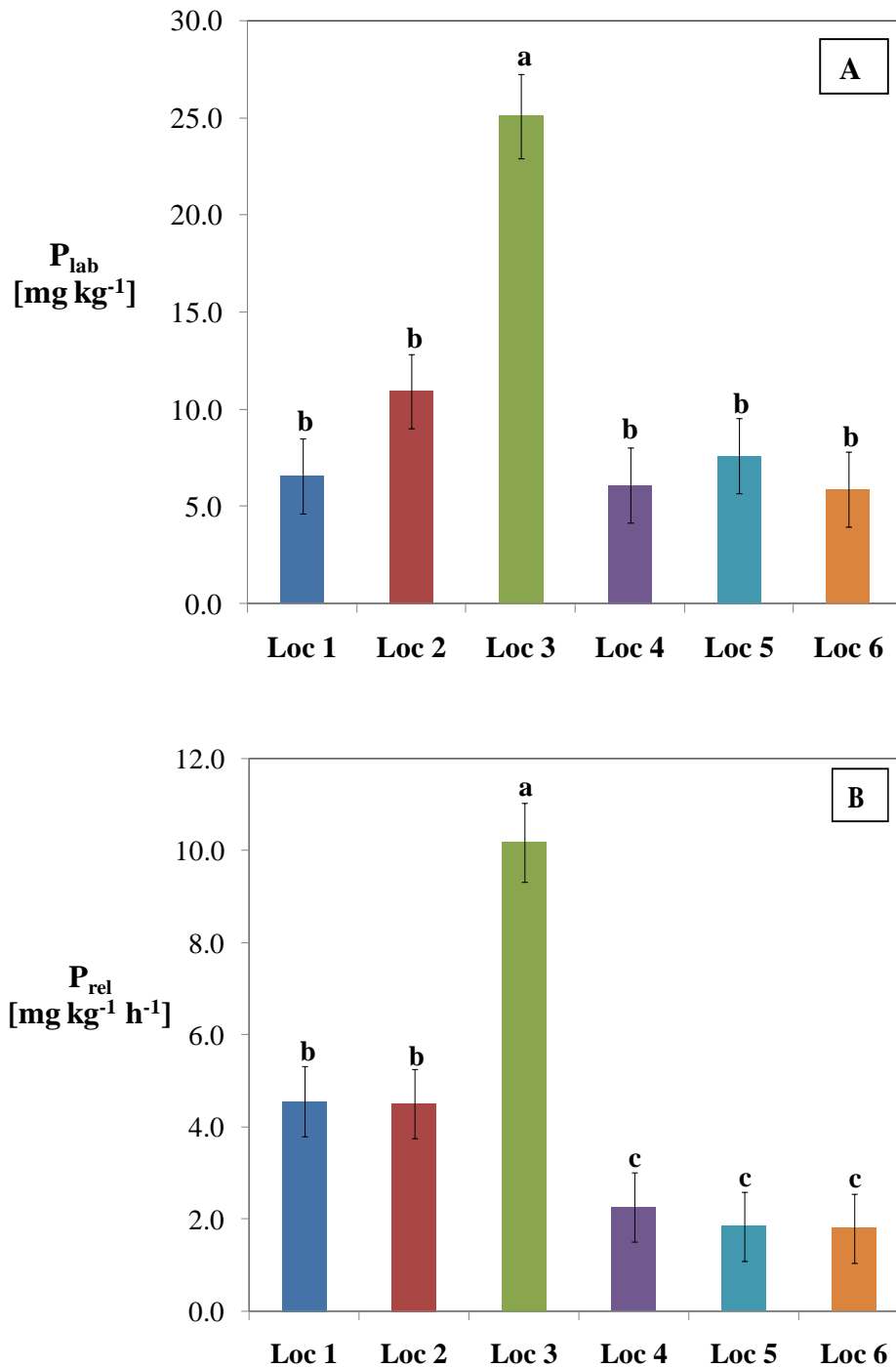


Figure 3.5 (A) Mean Labile P (P_{lab}) and (B) mean P release rate (P_{rel}) values of stream sediments at each stream location. Different letters above bars denote significant differences between location using $p < 0.05$. Vertical bars represent the standard deviation of all sediment samples collected at the same location (Loc).

Results indicate that location 5 had the highest P_{\max} of all stream locations; however, they are over 50% saturated (Figure 3.6). Additionally, location 1 had the lowest DPS, a relatively low P_{lab} , and low DPS which indicates a high P assimilation capacity of this stream section.

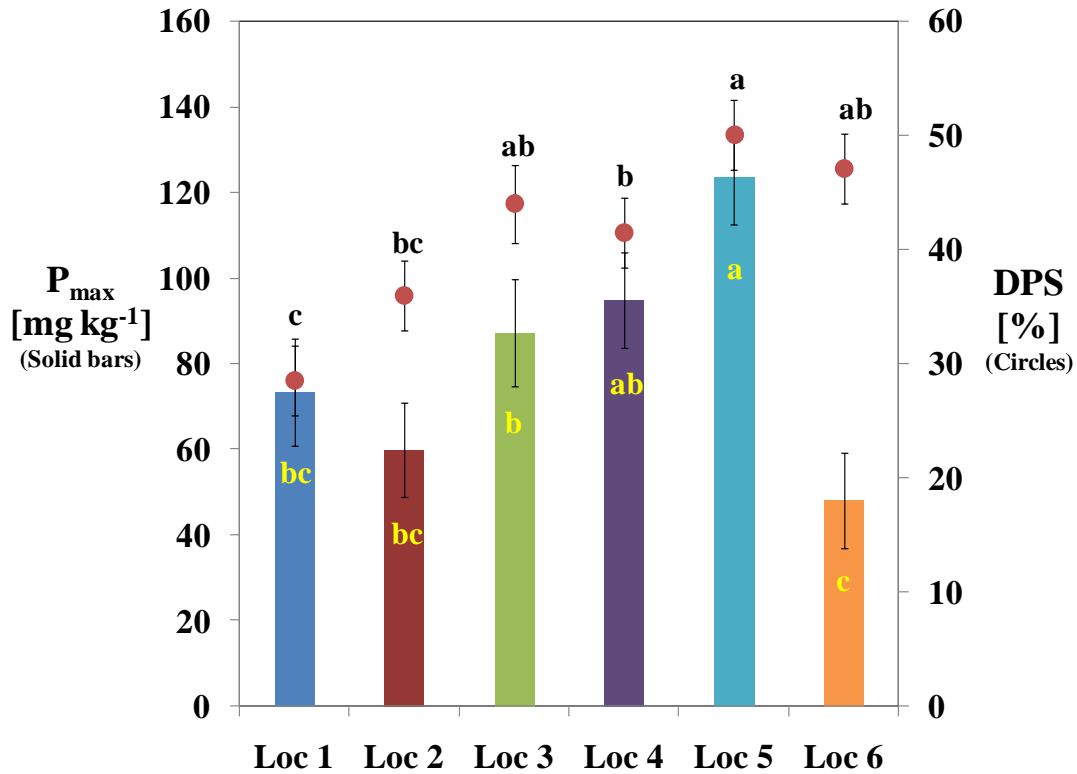


Figure 3.6 Phosphorus buffering capacity of the stream sediments at each stream location. Vertical bars represent the standard deviation of P_{\max} and DPS of all sediment samples collected at each location. Different letters denote significant differences between locations using $p < 0.05$. Vertical bars represent the standard deviation of all sediment samples collected at the same location.

Oxalate extractable elements and particle size characterization were also significantly different at each stream location (Table 3.3).

Table 3.3 Means of oxalate extractable Fe, Al, and P and particle size distribution as a function of the stream location. Different letters denote significant differences between stream locations using $p < 0.05$.

Analytical parameter†	Units	Stream Location					
		Loc 1	Loc 2	Loc 3	Loc 4	Loc 5	Loc 6
Fe _{ox}	mg kg ⁻¹	208 bc	199 c	367 a	231 bc	275 b	162 c
P _{ox}	mg kg ⁻¹	37.3 b	40.6 b	77.2 a	64.5 a	75.4 a	33.5 b
Al _{ox}	mg kg ⁻¹	92.5 cd	108.7 bcd	132.5 abc	180.1 a	151.4 ab	67.6 d
Tsand	%	85.5 a	85.8 a	82.5 a	75.3 b	81.2 ab	90.8 a
Tsilt	%	10.5 b	10.1 b	12.3 ab	16.6 a	12.6 ab	6.5 b
Tclay	%	4.0 bc	4.1 bc	5.2 abc	8.2 a	6.3 ab	2.8 c
Tnitro	%	0.04 b	0.04 b	0.06 a	0.03 b	0.04 b	0.03 b
Tcarbon	%	0.25 b	0.27 b	0.63 a	0.31 b	0.38 ab	0.18 b

† Fe_{ox}, Al_{ox} and P_{ox} refers to oxalate extractable ions, Tsand, Tsilt, Tclay, Tnitro, and Tcarbon refers to total sand, silt, clay, nitrogen and carbon, respectively. Loc refers to stream-reach location.

Finally, a comparison between the mean EPC₀ values and the DRP concentrations in the stream water at the moment of the sediment collection may indicate which stream locations are releasing P into the stream system. Dissolved reactive P in the stream water is much lower than the EPC₀ of the stream sediments at location 3 ($p < 0.05$), location 4 ($p < 0.05$), and location 5 ($p < 0.05$) (Figure 3.7). Therefore, these locations may have the highest potential to be loading P to the stream system.

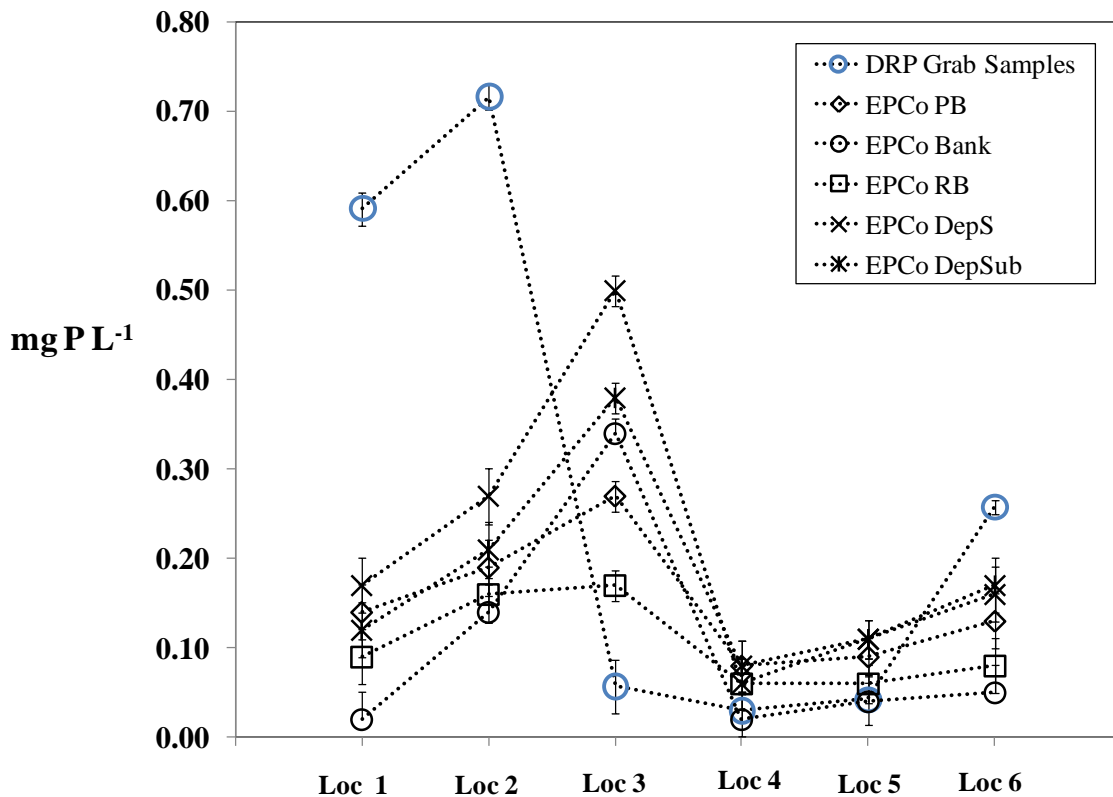


Figure 3.7 Equilibrium P concentration at zero net P sorption (EPC_0) of stream sediments and dissolved reactive P (DRP) concentrations in grab samples at each stream-reach location. Vertical bars represent the standard deviation of all sediment samples collected at the same location.

Stream Sediment Characterization as a Function of Stream Feature

Stream feature significantly affected all the measured variables with the exception of DPS and P_w (Table 3.2). Table 3.4 shows mean values for the physico-chemical parameters of sediments from each stream feature. The EPC_0 was highest for DepS sediments, which indicates that sediments from DepS features would maintain a higher DRP concentration in the stream water. Anion exchange extractable P (P_{lab}) was found higher for bank sediments and, therefore, bank features represent the largest in-stream P source for this watershed. Adsorption capacity

(P_{\max}) of the bank sediments was twice as much as P_{\max} from PB, RB, DepS and DepSub sediments.

Table 3.4 Chemical and physical parameters of stream sediments taken from bank, pool bed (PB), riffle bed (RB), depositional surface (DepS), and depositional subsurface (DepSub) features in Red Rock Creek watershed using $p < 0.05$.

Analytical parameter †	Units	Stream Features				
		Bank	PB	RB	DepS	DepSub
EPC_0	$mg L^{-1}$	0.101 cd	0.149 bc	0.102 c	0.212 a	0.178 ab
P_{lab}	$mg kg^{-1}$	15.0 a	11.6 ab	10.6 ab	7.9 b	6.9 b
P_{rel}	$mg kg^{-1} h^{-1}$	5.55 a	3.36 b	2.87 b	5.57 a	3.64 b
P_{\max}	$mg kg^{-1}$	149.5 a	75.9 b	70.9 b	56.9 b	52.9 b
k_L	$L mg^{-1}$	0.26 a	0.18 bc	0.20 b	0.13 c	0.15 bc
Fe_{ox}	$mg kg^{-1}$	449 a	213 bc	258 b	139 c	142 c
P_{ox}	$mg kg^{-1}$	109.9 a	48.7 b	49.8 b	32.3 b	33.1 b
Al_{ox}	$mg kg^{-1}$	302.3 a	98.5 b	87.9 b	65.3 b	56.8 b
DPS	%	36.6 a	45.5 a	38.9 a	40.7 a	44.4 a
P_w	$mg kg^{-1}$	1.53 a	1.31 a	1.08 a	1.50 a	1.15 a
Tsand	%	54.3 b	89.5 a	89.5 a	92.0 a	92.2 a
Tsilt	%	31.5 a	7.5 b	7.0 b	5.7 b	5.5 b
Tclay	%	14.2 a	3.0 b	3.6 b	2.2 b	2.3 b
Tnitro	%	0.08 a	0.03 b	0.03 b	0.03 b	0.02 b
Tcarbon	%	0.86 a	0.25 b	0.30 b	0.15 b	0.12 b

† EPC_0 refers to the Equilibrium P concentration at zero net P adsorption, P_{lab} refers to Labile P, P_{rel} refers to Rate of initial P release, P_{\max} represent P maximum adsorption capacity and k_L represent the P binding energy from the Langmuir equation, Fe_{ox} , Al_{ox} and P_{ox} refers to oxalate extractable ions, DPS refers to degree of P saturation, P_w refers to water extractable P, and Tsand, Tsilt, Tclay, Tnitro, and Tcarbon refers to total sand, silt, clay, nitrogen and carbon, respectively.

Degree of P saturation (DPS) was similar between stream sediments with a range of 36 % to 45%. Consequently, bed sediments (i.e., RB and PB) and depositional sediments (i.e., DepS and DepSub) had lower P buffering capacities indicated by lower P_{\max} and high DPS. A significant relationship ($r^2 = 0.694$ and $P < 0.001$) was found when correlating P_{\max} with Tclay of all stream sediments (Figure 3.8).

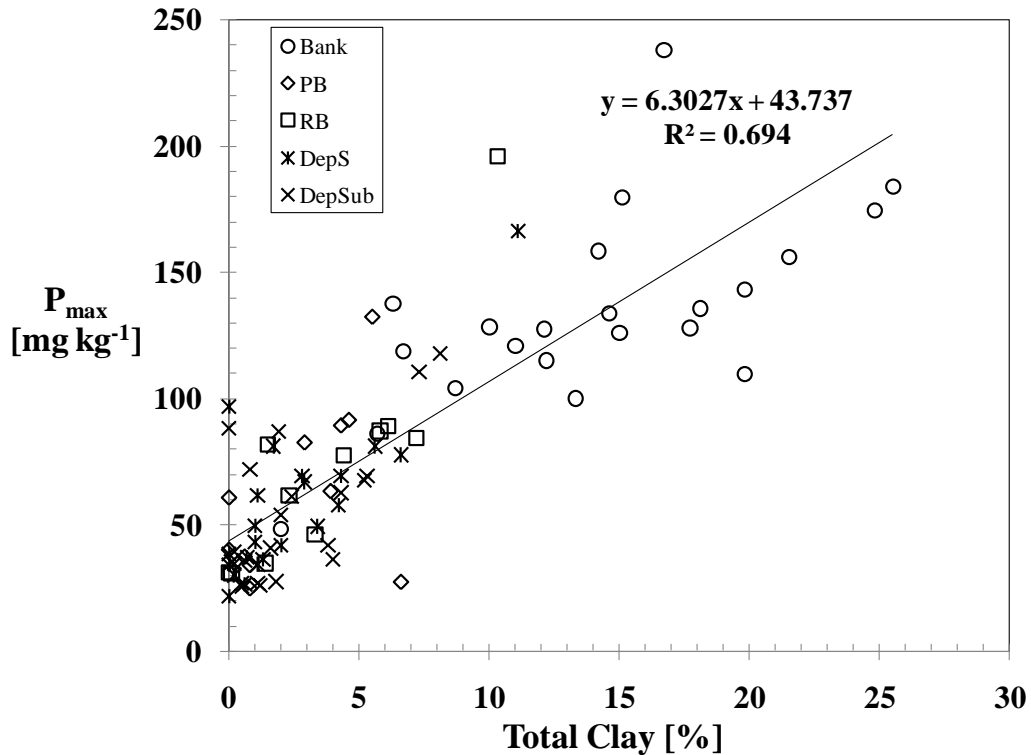


Figure 3.8 Relationship between Adsorption capacity (P_{\max}) and clay content of stream sediments sampled at bank, pool beds (PB), riffle beds (RB), depositional feature surface (DepS) and depositional features subsurface (DepSub).

Amorphous and poorly crystalline forms of oxalate extractable Al and Fe were well correlated with P_{\max} . A highly significant ($r^2=0.657$ and $P<0.001$) linear relationship was found between P_{\max} and Fe_{ox} between P_{\max} and Al_{ox} ($r^2=0.67$ and $P<0.001$) (Figure 3.9) indicating that clay, Fe_{ox} , and Al_{ox} content are good predictors of the P uptake and assimilation capacity of the stream sediments at the RRC watershed.

Cross Sectional Changes and Erosion Potential along the Main Channel

Cross-sectional profile changed at location 1 and location 6 (Figure 3.10). The 2009 cross section of the location 5 is not available due to lost rebar monuments. The pool bed from location 1 has scoured and the pool from loc 6 moved to the right with sediment deposition on the left.

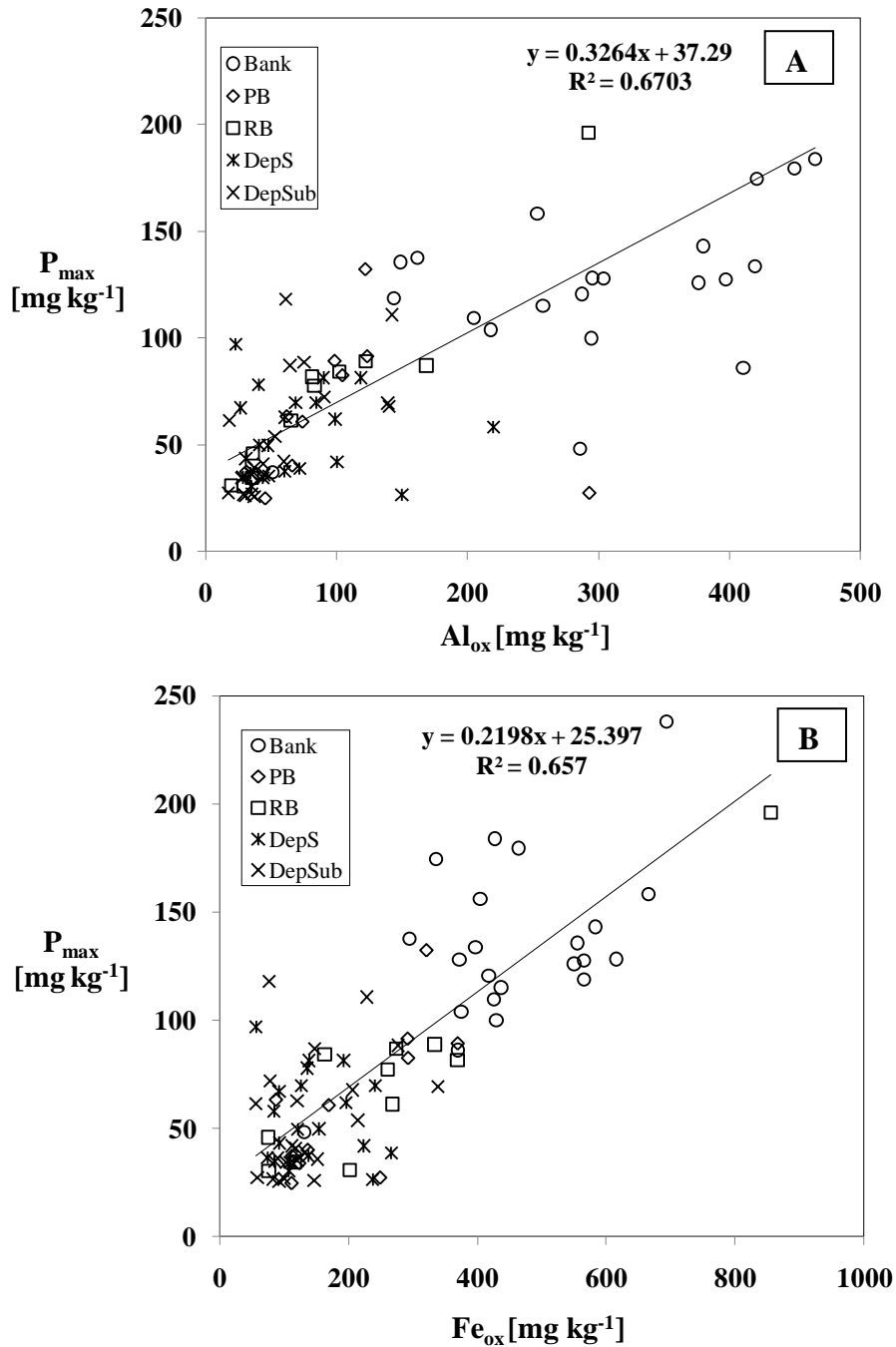


Figure 3.9 (A) Relationship between Maximum Adsorption Capacity (P_{max}) and Al_{ox} and (B) relationship between P_{max} and Fe_{ox} content of stream sediments sampled at bank, pool beds (PB), riffle beds (RB), depositional feature surface (DepS) and depositional features subsurface (DepSub).

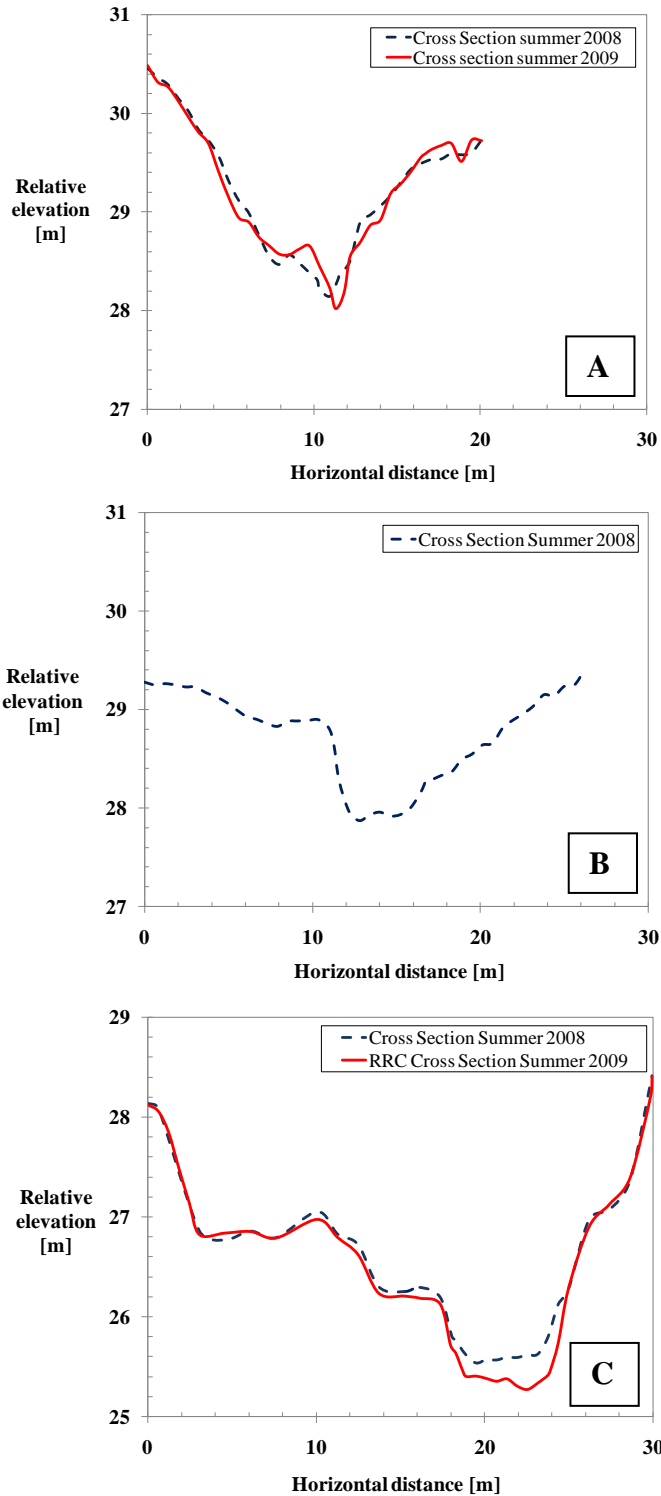


Figure 3.10 Cross sectional profiles for three sampling locations in the Red Rock Creek watershed. (A) Location 1, (B) Location 5, and (C) location 6. Note: Elevation measurements are relative to an arbitrarily selected benchmark at each location for which elevation was assumed to be 30.48 m.

Average bank pin exposure from 2008 to 2009 was between 0.007 and 0.038 m (Table 3.5). This resulted in erosion losses between 0.9 to 7.7 Mg from the three stream reaches, with an average erosion rate of 0.024 Mg m⁻¹.

Table 3.5 Bank pins exposure data at location 1, location 5, and location 6.

	Pin Exposure		
	Location 1	Location 5	Location 6
	m		
Bank Pin at 0.61 m	0.012	0.006	0.002
Bank pin at 1.22 m	0.065	0.009	0.011
Average	0.038	0.008	0.007

Table 3.6 Bank erosion estimation at location 1, location 5, and location 6.

Location	Pin exposure [m]	Bank height [m]	Stream-reach length [m]	Bank erosion [m ³ / stream reach]	Sediment mass [Mg/ stream reach]
Location 1	0.038	1.09	155	6.4	7.7
Location 5	0.008	0.90	100	0.7	0.9
Location 6	0.007	0.70	159	0.8	0.9
Total			414		9.5

A total sediment load of 8062 Mg yr⁻¹ and a total of 6.9 Mg/yr of DRP were exported from the watershed at location 6 from June 2008 through May 2009 (Barnes et al., 2009 - Unpublished data). Therefore, by just taking into account 2nd, 3rd, and 4rd order streams (37.6 km) and assuming a constant erosion rate of 0.024 Mg m⁻¹ along them, bank erosion contributes about 900 Mg of sediments to the stream system from June 2008 through May 2009. Therefore, during the monitoring period around 11% of the suspended sediment load in RRC comes from stream bank erosion of 2nd, 3rd, and 4rd order streams. Additionally, based on the average P_{lab} (15 ± 1 mg P Kg⁻¹) (Table 3.6), bank erosion may have contributed with around 14 ± 1 kg of dissolved P to the stream system from May 2008 to June 2009 which represents 0.2% of the total DRP annual load.

Upland Soil P Chemistry and Characterization

Soils from manure amended fields had higher EPC_0 (2.18 mg P L^{-1}) than the other field soils (Table 3.7). Manure amended fields also contained the highest P_{lab} (113 mg P kg^{-1} soil) followed by wheat no till fields. Management practice (till vs no till) did not have a significant effect in P availability in wheat fields ($p > 0.05$ for wheat till Vs wheat no till). Similarly, manure applied fields had the highest P_{max} ; however, they are over 50% saturated ($DPS=53\%$). Of the field soils, manure applied fields had the largest available P pool in the RRC watershed. Finally, particle size composition was similar ($p > 0.05$) between soils from different cropping systems indicating that changes in P related parameters are associated to management practices better than soil physical composition itself.

Table 3.7 Phosphorous related parameters of upland soils from different cropping systems in Red Rock Creek watershed. Different letters denote significant differences between different cropping systems ($p < 0.05$). Pair wise comparisons were performed for those variables where cropping system resulted in a significant difference.

Cropping system	Analytical parameters [†]									
	EPC ₀	P _{lab}	P _{rel}	P _{max}	k _l	Fe _{ox}	P _{ox}	Al _{ox}	DPS	P _w
	mg L ⁻¹	mg kg ⁻¹	mg kg ⁻¹ h ⁻¹	mg kg ⁻¹	L mg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	%	mg kg ⁻¹ -
Manure amended	2.74 a	113.1 a	87.6 a	234.5	0.05 bc	768	279 a	552	53.0 a	16.5 a
Pasture	0.59 b	32.6 b	32.1 b	110.5	0.12 bc	484	135 b	422	35.2 b	5.7 b
Wheat no till	0.34 b	49.4 b	24.8 b	174.7	0.15 bc	514	154 b	575	33.3 b	5.1 b
Wheat till	0.68 b	38.8 b	29.3 b	163.6	0.20 ab	507	174 b	580	39.6 b	5.6 b
Row crops	0.24 b	41.8 b	17.3 b	104.2	0.26 ab	564	144 b	448	34.6 b	4.8 b
p-value F^{††}	0.006	<0.0001	<0.0001	0.093	<0.0001	0.075	0.0004	0.088	0.008	0.0002

[†] EPC₀ refers to the Equilibrium P concentration at zero net P adsorption, P_{lab} refers to Labile P, P_{rel} refers to Rate of initial P release, P_{max} represent P maximum adsorption capacity and k_l represent the P binding energy from the Langmuir equation, Fe_{ox}, Al_{ox} and P_{ox} refers to oxalate extractable ions, DPS refers to degree of P saturation, P_w refers to water extractable P, and T_{sand}, T_{silt}, T_{clay}, T_{nitro}, and T_{carbon} refers to total sand, silt, clay, nitrogen and carbon, respectively.

^{††} p-values for the test cropping system effect from the ANOVA for each analytical parameter

Comparisons between Stream Sediments and Upland Soils

The EPC_0 was similar between stream sediments, with an average of about 0.14 mg L^{-1} . Although some field soils had a much greater EPC_0 , there was high variability and the means were not different from the stream sediments with the exception of manure amended soils that had the highest EPC_0 of all fields and stream features (Figure 3.11).

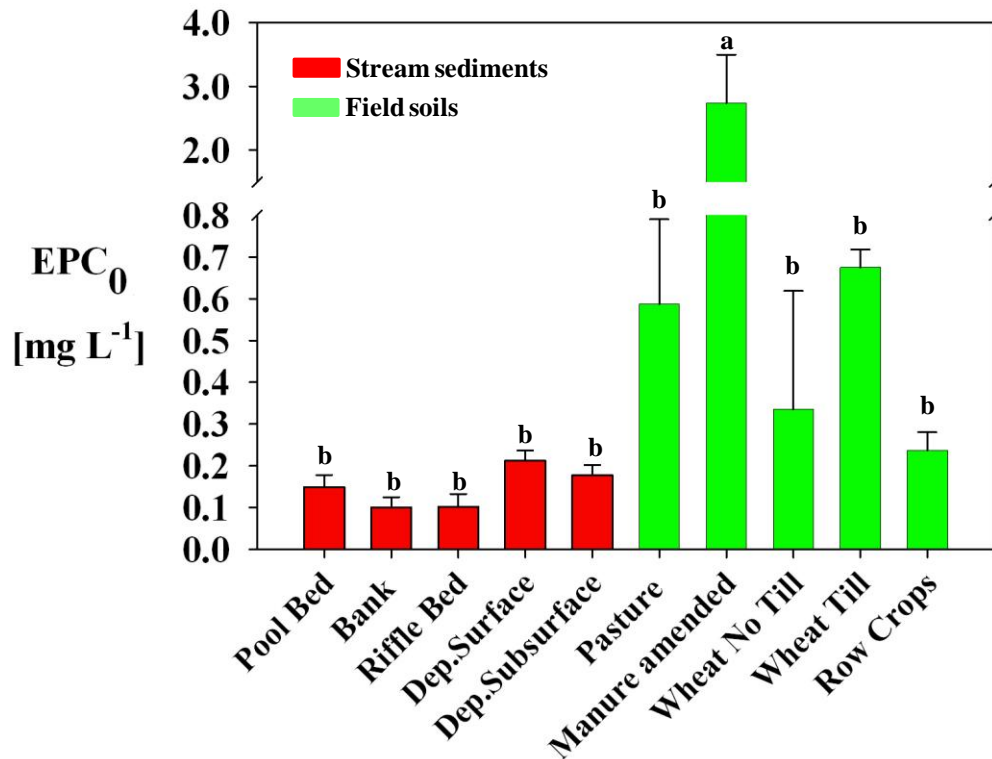


Figure 3.11 A comparison of the equilibrium P concentration at zero net sorption (EPC_0) of stream sediments and Field soils in the Red Rock Creek (RRC) watershed. Different letters above bars denote significant differences between in-stream sediments and field soils using $p < 0.05$. Vertical bars represent the standard deviation of all sediment and soil samples collected.

Of stream sediments and field soils, manure applied fields had the highest P_{lab} , and therefore, they represent the largest available P pool in RRC. The average P_{lab} of the stream sediments is one third of the average P_{lab} of the crop soils and just one tenth of the manure amended soils. Thus, stream sediments do not represent a large long-term P supply (Figure 3.12).

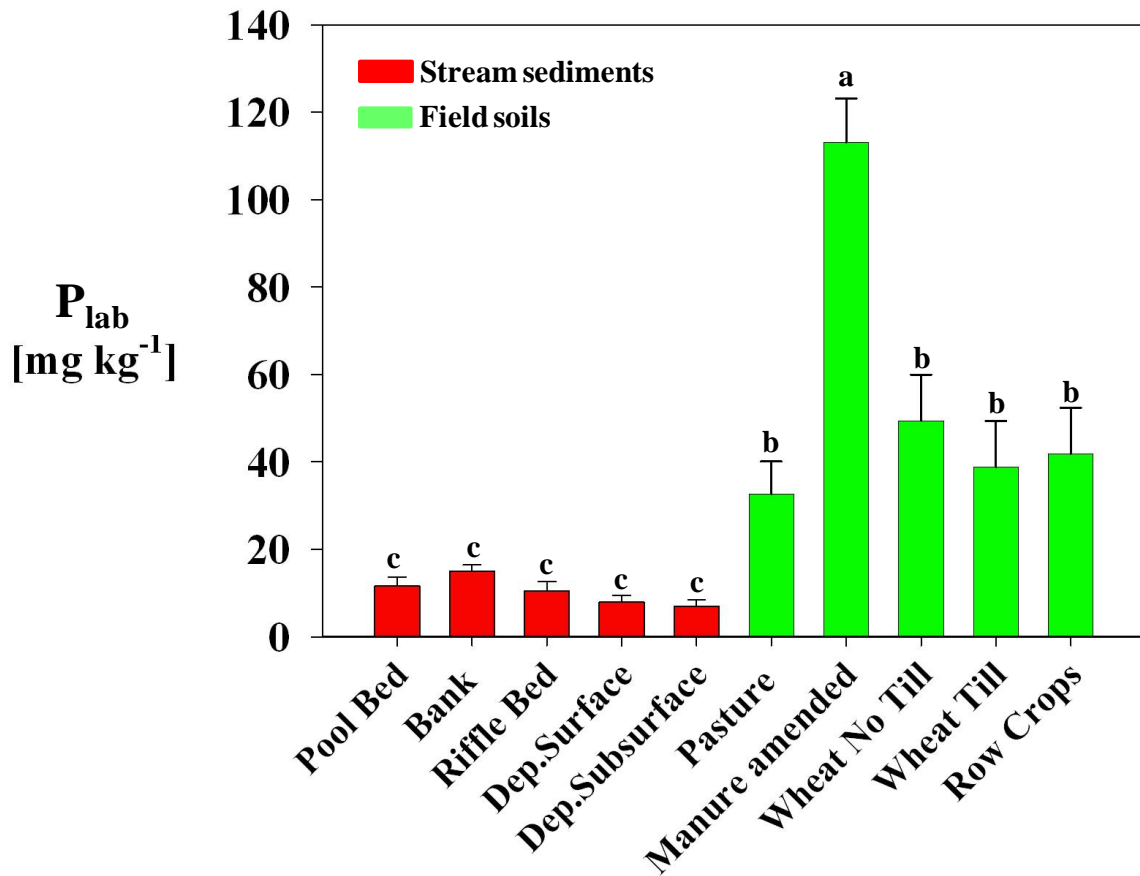


Figure 3.12 A comparison of labile P (P_{lab}) of stream sediments and field soils in the Red Rock Creek (RRC) watershed. Different letters above bars denote significant differences between in-stream sediments and field soils using $p < 0.05$. Vertical bars represent the standard deviation of sediment and soil samples collected at each category.

Overall stream sediments had low P buffering capacities, indicated by lower P adsorption capacities, low P_{lab} , and high degree of P saturation (DPS) (Figure 3.13). Of the stream sediments, bank sediments had the highest adsorption capacity and they may still have adsorption capacity remaining since they are around 37% saturated. The DPS was similar within stream sediments and field soils with the exception of the manure amended fields which had the highest DPS (DPS=53%).

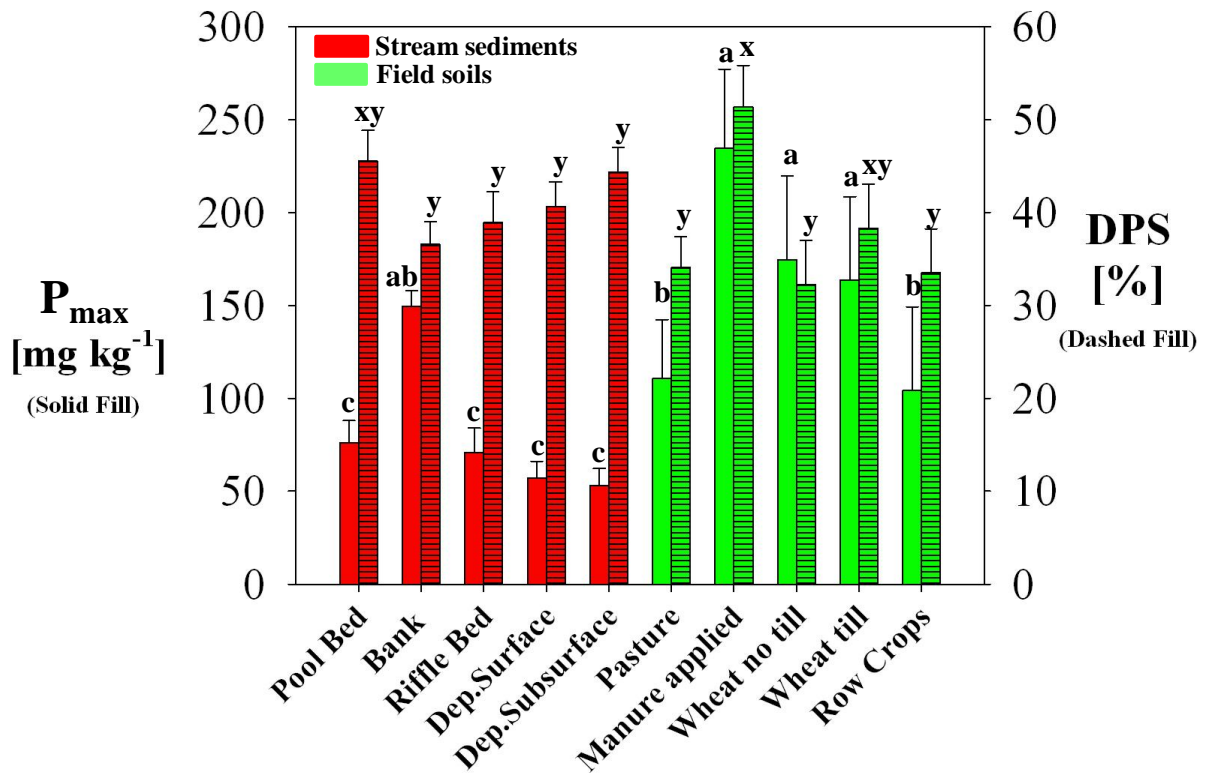


Figure 3.13 Maximum adsorption capacity (P_{max}) and degree of P saturation (DPS) of stream sediments and field soils in the RRC watershed. Different letters above bars denote significant differences between in-stream sediments and field soils using $p < 0.05$. Vertical bars represent the standard deviation of all samples collected at each category.

Comparisons between EPC_0 Values from Soils and Sediments and P Concentration in the Stream Water

During storm flow, DRP was much higher ($p < 0.001$) than during baseflow (Figure 3.14). Additionally, the EPC_0 of stream sediments tends to be higher ($p < 0.001$) than the DRP concentrations during baseflow. Thus, stream sediments in the RRC watershed may be considered a source of P during baseflow conditions.

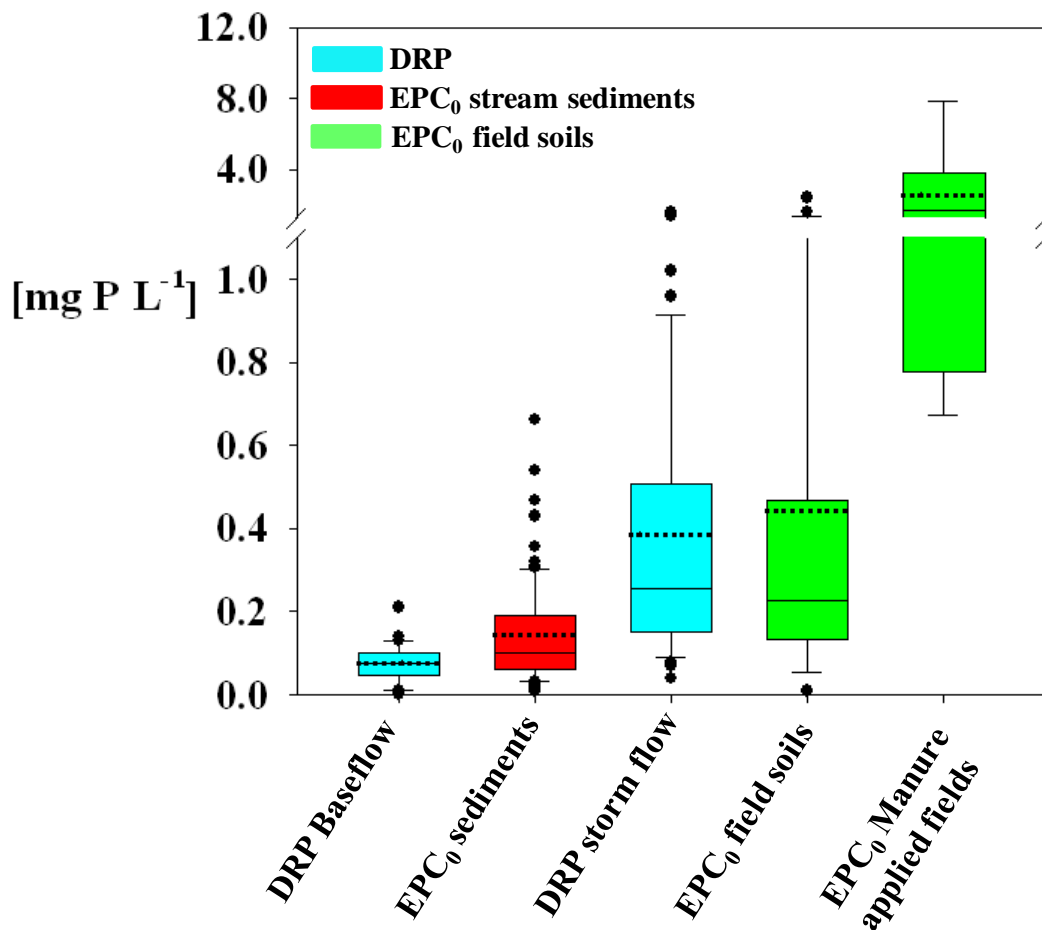


Figure 3.14 Equilibrium P concentration at zero net P sorption (EPC_0) of stream sediments and field soils and its comparison with dissolved reactive P (DRP) in stream waters under baseflow and storm flow conditions in the Red Rock Creek (RRC) watershed. Each box depicts the smallest observation, lower quartile, mean (dotted line) median (solid line), upper quartile, largest observation, and data outliers of each data set.

Field soils presented a larger range in EPC_0 than stream sediments; therefore, those field soils in which EPC_0 exceeded the DRP concentrations during storm flow are expected to release P into the stream system. Manure applied fields had extremely high EPC_0 values; therefore, they have the highest potential of P release to the stream system during storm flow events. It should be noted that, similar to Upper West Emma Creek watershed, there were some conventionally fertilized fields with EPC_0 in excess of the storm flow DRP, suggesting that these fields can also represent an important P source in the watershed.

Conclusions

Phosphorus adsorption as well as desorption parameters (i.e., EPC_0 , P_{lab} , P_{rel} and P_{max}) were affected by stream location in the RRC watershed. This may be partially explained by the huge variety of soils found in this watershed that finally influence in-stream sediment composition as well. Additionally, the intensity of the animal agriculture as well as the lack of flowing water in low order streams (location 3) may have increased P availability which was indicated by high P_{lab} , high P_{rel} and high DPS. Of the stream locations, location 3 was identified as a source of P since the EPC_0 of the stream sediments were much higher than the DRP concentrations found during baseflow conditions.

Phosphorus chemical behavior also changed as a function of the stream feature. Of the stream sediments, bank sediments had the highest P_{lab} and P_{rel} . Consequently, bank features represent the larger in-stream P source for this watershed. Sediments from PB, RB, DepS and DepSub had low P assimilation capacity which was indicated by low P_{max} and high DPS. Total clay, Al_{ox} and Fe_{ox} were good predictors of the adsorption capacity of the stream sediments in this watershed.

The cross sectional study showed that location 1 and location 6 suffered cross sectional changes in one year period (2008-2009). Changes were reflected by the scour of the pool beds, sediment deposition, and lateral channel movement. It was estimated that bank erosion from second, third, and fourth order streams (37.6 km) contributed with 902 Mg of sediments to the stream system which represent the 11% of the total sediment load in this watershed. Furthermore, based on the average labile P, bank erosion may have contributed around 14 ± 1 kg of dissolved P to the stream system which represents 0.2% of the DRP total annual load.

Stream sediments had lower P assimilation capacity relative to field soils suggesting that in-stream sediments will not adsorb any more P, therefore, they will not be able to buffer P

increases in the stream system. Additionally, field soils had a large range in EPC_0 , some of which exceed the DRP in the stream water. Thus, it is expected that field soils with EPC_0 higher than DRP will release P to the stream system. Finally, the comparison between stream sediments and field soils showed that field soils had higher P concentrations therefore they would tend to maintain higher DRP concentration in water relative to stream sediment.

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CHAPTER 4 - A Comparison between UWEC and RRC Watersheds

Similarities and differences were observed between both watersheds. For example, bank features had the highest labile P, and therefore, they represented the largest in-stream P source at both watersheds. However, bank features at UWEC had a P_{lab} two times greater than the bank features at RRC ($p < 0.05$). It was also found that at both watersheds stream sediments, with the exception of bank sediments, had overall low P assimilation capacities, indicated by lower P_{max} , and high degree of P saturation (DPS). A lack of P assimilation capacity indicates that sediments will not be able to adsorb any more P, therefore, they will not buffer P increases in the stream system. Consequently, RB, PB, DepS, and DepSub sediments did not represent a substantial source of P.

A comparison of P related parameters between both watersheds indicated that sediments from PB ($p > 0.05$), RB ($p > 0.05$) and DepSub ($p > 0.05$) had similar P_{lab} and DPS at both watersheds. However, adsorption capacities of the stream sediments, excluding the bank sediments, were much higher ($p < 0.0001$) at the RRC watershed. This was supported by the fact that T_{clay} ($p < 0.05$) and T_{silt} content ($p < 0.05$) were found higher in the bed and depositional sediments in RRC. The higher P adsorption nature of the RRC sediments may result in a higher P retention capacity of the RRC watershed when compared with UWEC watershed. However, with the data collected in this study is not possible to conclude about the P retention capacity of these two systems.

Similar to the UWEC, manure applied fields at RRC had the highest P_{lab} of all field soils. Additionally, P_{lab} mean values of the manure amended fields did not significantly ($p > 0.05$) change from one watershed to the other. When compared to UWEC, manure amended fields in

RRC represented a much larger available P pool. This may be explained by the fact that manure applied fields account for the 6% of the total area in RRC watershed (8.1 km²) as opposed to only 1% (1.2km²) in UWEC watershed. The other cropping systems reported similar P_{lab} (p<0.05) for both watershed.

It was estimated that bank erosion in UWEC contributed with 630 Mg of sediments to the stream system which represented a 41% of the total sediment load. On the other hand, bank erosion contributed with 900 Mg of sediments to the stream system in RRC which represented 11% of the total sediment load. Moreover, total sediment load was five times greater in RRC than UWEC. This is an indication of that RRC have more upland sediment inputs than UWEC. Additionally, it is concluded that soils represented the largest P available pool at both watersheds due to high upland sediment inputs and their high labile P concentrations. Finally, it was found that RRC had similar DRP concentrations during baseflow to those at UWEC. DRP concentrations during storm flow in RRC, however, were found much higher (p<0.001) than those at UWEC. Finally, since P_{lab} was found similar between field soils from both watersheds, high DRP concentrations in the water surface in RRC may be attributed to the high P inputs involved in a watershed with higher animal agriculture.

CHAPTER 5 - Conclusions and Recommendations

The P adsorption and desorption study performed on the stream sediments showed that in-stream sediments in 2nd and 3rd order streams draining agricultural watersheds such as those found in pool beds, riffle beds and depositional features do not represent a major source of P in Kansas streams. Because of the nature of the bank sediments they have higher P_{lab} . Thus, upon erosion events they are the largest in-stream P source. A comparison between in-stream sediments and field soils showed that upland soils have a much larger P available pool which can be potentially be released by soil erosion and runoff during a storm flow event. Of the field soils, manure amended systems had the highest P_{lab} , and therefore, they represent a long term P supply. Conventionally fertilized fields also represent an important P source mainly because they account for larger areas between the watersheds. Bank erosion played an important role in the total sediment load in UWEC watershed. Therefore, efforts to minimized P inputs through bank erosion should be done. Among possible strategies that may be considered for in-stream bank stabilization are: willow posts to let the creation of natural riparian zones, stone toes, pools and riffles, and stream barbs. On the other hand, RRC had high sediments loads where bank erosion just represented 11% the total sediment load, and therefore, in order to minimize P inputs into the stream system especial attention should be placed in upland fields whereas minimizing P inputs into the fields or implementing management practices such as no till, reduced or minimized tillage, contour farming, and crop rotations.