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Subsurface Transport of Phosphorus to Streams: A Potential Source of Phosphorus not Alleviated by Best Management Practices (BMPs)

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SUMMARY TABLE OF STUDENT SUPPORT

Student Status	Number	Disciplines
Undergraduate	2	Geology, Biosystems and Agricultural Engineering
M.S.	1	Biosystems and Agricultural Engineering
Ph.D.		
Post Doc		
Total	3	

ABSTRACT

For phosphorus (P) transport from upland area to surface water systems, the primary transport mechanism is typically considered to be surface runoff with subsurface transport assumed negligible. However, certain local conditions can lead to an environment where subsurface transport may be significant. The objective of this research was to determine the potential of subsurface transport of P along streams characterized by cherty or gravel subsoils, especially the impact of preferential flow paths on P transport. At a field site along the Barren Fork Creek in northeastern Oklahoma, a trench was installed with the bottom of the trench at the topsoil/alluvial gravel interface. Fifteen piezometers were installed at various locations surrounding the trench in order to monitor flow and transport. In three experiments, water was pumped into the trench from the Barren Fork Creek to maintain a constant head. At the same time, a conservative tracer (Rhodamine WT) and/or potassium phosphate solution were injected into the trench at concentrations at 3 and 100 mg/L for Rhodamine WT and at 100 mg/L for P. Laboratory flow-cell experiments were also conducted on soil material less than 2 mm in size to determine the effect that flow velocity had on P sorption. Rhodamine WT and P were detected in some piezometers at equivalent concentrations as measured in the trench, suggesting the presence of preferential flow pathways and heterogeneous interaction between streams and subsurface transport pathways, even in non-structured, coarse gravel soils. Phosphorus transport was retarded in non-preferential flow paths but not in preferential flow pathways. Breakthrough times were approximately equivalent for Rhodamine WT and P suggesting no colloidal-facilitated P transport. Results from laboratory flow-cell experiments suggested that higher velocity resulted in less P sorption for the alluvial subsoil. Therefore, with differences in flow rates between preferential and non-preferential flow pathways in the field, variable sorption was hypothesized to have occurred. The potential for nutrient subsurface transport shown by this alluvial system has implications regarding management of similar riparian floodplain systems.

SUBSURFACE TRANSPORT OF PHOSPHORUS TO STREAMS: A POTENTIAL SOURCE OF PHOSPHORUS NOT ALLEVIATED BY BEST MANAGEMENT PRACTICES (BMPS)

I. PROBLEM AND RESEARCH OBJECTIVES

The adverse impact of increased nutrient loadings on surface water quality has drawn considerable attention in recent years. Polluted drinking water, excessive algal growth, taste and odor issues, and fish kills are only a few of the negative effects that can result from an overload of nutrients. While nitrogen is a concern, phosphorous (P) is generally considered the most limiting nutrient. Daniel et al. (1998) found that concentrations of P critical for terrestrial plant growth were an order of magnitude larger than concentrations at which lake eutrophication may occur. Excessive soil P concentrations can increase potential P transport to surface waters or leaching into the groundwater and have negative implications.

1.1 Subsurface Nutrient Transport Studies

Subsurface P transport is a less studied and understood transport mechanism compared to transport by overland flow, although numerous studies have reported P in groundwater and subsurface P transport (Turner and Haygarth, 2000; Kleinman et al., 2004; Nelson et al., 2005; Andersen and Kronvang, 2006; Hively et al., 2006). For example, from research on four grassland soils, Turner and Haygarth (2000) documented that subsurface P transfer, primarily in the dissolved form, can occur at concentrations that could cause eutrophication. Kleinman et al. (2004) noted that the P leaching is a significant, but temporally and spatially variable transport pathway. Nelson et al. (2005) indicated that P leaching and subsurface transport should be considered when assessing long-term risk of P loss from waste-amended soils. Andersen and Krovang (2006) modified a P Index to incorporate potential P transport pathways of tile drains and leaching in Denmark. Hively et al. (2006) considered transport of total dissolved P (TDP) for both baseflow and surface runoff. Other researchers are beginning to emphasize colloidal P transport in the subsurface, as P attaches to small size particles capable of being transported through the soil pore spaces (de Jonge et al., 2004; Heathwaite et al., 2005; Ilg et al., 2005).

The potential for subsurface nutrient transport in association with vegetated buffer strips (VBS) along the riparian areas of surface water systems has recently been emphasized. The VBS can be either grass or forested, and act as a zone in which runoff is captured and/or sediment trapped, inhibiting sediment-bound nutrient transport to the stream. However, some studies have shown these VBS systems promote subsurface nutrient loading to streams (Osborne and Kovacic, 1993; Vanek, 1993; Cooper et al., 1995; Polyakov et al., 2005). Polyakov et al. (2005) examined current research regarding riparian buffer systems and their ability to retain nutrients. Their findings suggested that conditions, such as the spatial variability in soil hydraulic conductivity, the presence of preferential flow pathways, and limited storage capacity in the riparian zone's soil, could subvert the buffer system's ability and allow for increased nutrient transport. Osborne and Kovacic (1993) showed VBS could actually act like a nutrient source, releasing dissolved and total P into the groundwater. Another study conducted in Sweden showed that the soil

in riparian zones had almost no P retention capacity due to a natural calcium leaching process which started over 3000 years ago (Vanek, 1993). Also, a study by Cooper et al. (1995) showed a high P availability for groundwater transport due to saturation of the riparian zone.

There have been several studies conducted in which observation wells were used to monitor the flow of nutrients in groundwater in riparian zones (Vanek, 1993; Carlyle and Hill, 2001; McCarty and Angier, 2001). Vanek (1993) noted groundwater P concentrations taken from 12 wells in a lake riparian zone ranged from 0.4 to 11.0 mg/L with an average of 2.6 mg/L. Carlyle and Hill (2001) monitored the behavior of P in the subsurface in a river riparian zone and suggested that riparian areas can become saturated with P. They noticed higher soluble reactive phosphorus (SRP) concentrations (0.10 to 0.95 mg/L) in areas characterized by having soils with higher hydraulic conductivities buried under the top soils. They suggested that riparian areas might actually be contributing to the release of P because they increase the redox potential. McCarty and Angier (2001) studied preferential flow pathways in riparian floodplains. Their findings showed increased biological activity in these pathways and could lead to reduced conditions, which, in turn, decrease the ability to remove nutrients.

It should be noted that surface runoff usually consists of high flows over a short period of time, whereas subsurface flow is characterized by lower flow rates over long periods of time. The point is that even though surface runoff has shown higher concentrations in many field studies (i.e., Owens and Shipitalo, 2006), low-concentration subsurface flow occurring over a long period of time could still be making a viable contribution to the total nutrient load of a surface water body. The findings mentioned above show that there is a potential for subsurface nutrient transport. Therefore, there is a need for more research devoted to monitoring and understanding subsurface P transport.

1.2 Hydraulic Conditions Promoting Subsurface Phosphorus Transport

As noted earlier, local or regional conditions can lead to conditions where subsurface transport is significant (Andersen and Kronvang, 2006). Areas such as riparian floodplains commonly consist of alluvial deposits with gravelly soils possessing hydraulic properties conducive to the subsurface transport of P. Gravel or cherty soils are common throughout the Ozark region of Oklahoma, Arkansas, and Missouri. In eastern Oklahoma, cherty soils adjacent to rivers consist of gravelly silt loam to gravelly loam substrate below a thin layer of organic matter. Sauer and Logsdon (2002) studied the hydraulic properties of some of these cherty soils (Clarksville and Nixa series) and concluded that relatively subtle morphological factors can have a disproportionate impact on water flow in the soils, suggesting the need for further research regarding their hydraulic properties. These soils possess infiltration rates as high as 1.22 to 3.67 m/d according to USDA Soil Surveys. Therefore, the potential for subsurface transport is significant.

1.3 Objectives

More research pertaining to the role of subsurface P transport is needed, especially in riparian floodplains. Current best management practices aimed at reducing P load through surface runoff may be ineffective if subsurface flow is a significant transport mechanism and therefore could impact long-term planning of available water supplies. This research attempts to quantify the potential for subsurface alluvial transport of P in a

riparian floodplain, especially the impact of preferential flow paths on P transport. If subsurface P transport is important on these landscapes, questions need to be answered regarding what impact, if any, current best management practices are having on this transport mechanism.

II. METHODOLOGY

In order to study the potential for subsurface transport in a riparian floodplain (Figure 1), a trench-piezometer system was installed in a riparian area (latitude: 35.90^{o}, longitude: -94.84^{o}) approximately 20 m adjacent to the Barren Fork Creek near Tahlequah, OK (Figure 2). The trench system was designed to induce a constant water head and a tracer/P injection source on the subsurface alluvial gravel with subsequent monitoring of flow, tracer, and P transport in the piezometer field. The dimensions of the trench were approximately 0.5 m wide by 2.5 m long by 1.2 m deep. The bottom of the trench was located approximately 25 to 50 cm below the interface between the topsoil and gravel layers, thereby short-circuiting flow and tracer/P directly into the gravel. A bracing system consisted of a frame constructed with 5 cm by 13 cm studs and covered with 2 cm plywood. Fifteen piezometers were installed at various locations around the trench with the majority of the piezometers located between the trench and the river (Figure 2). The piezometers were approximately 6 m (20 ft) long and were constructed of Schedule 40 PVC. Each consisted of at least a 3 m screened section at the base. The piezometers were installed using a Geoprobe® (Kejr, Inc.) drilling machine. Fuchs (2008) discussed additional details on piezometer installation.

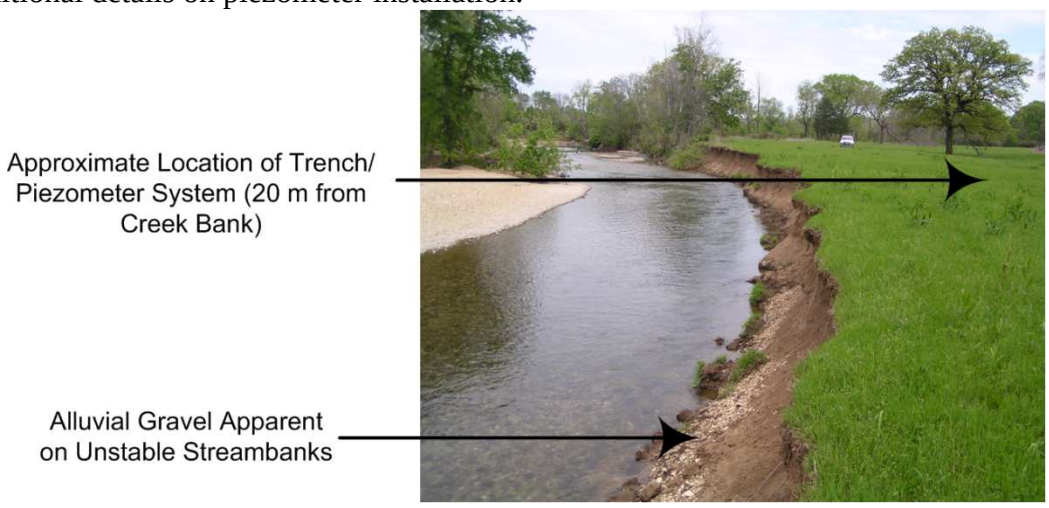
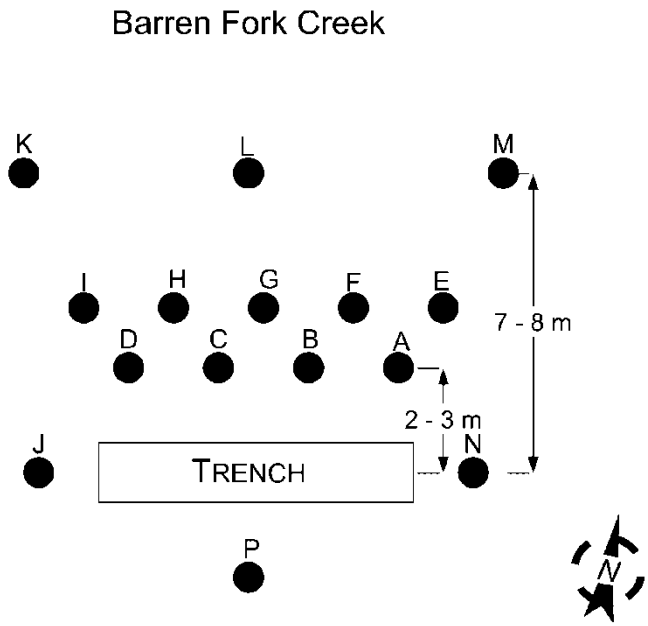


Figure 1. Field site located approximately 25 km east of Tahlequah, Oklahoma adjacent to the Barren Fork Creek.

(a)



(b)

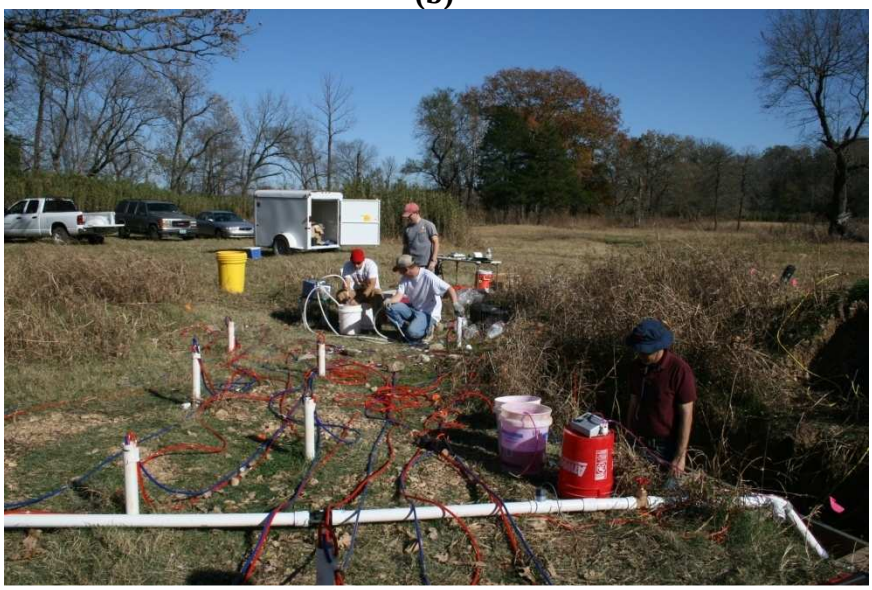


Figure 2. (a) Location of the trench and piezometers and (b) illustration of piezometers relative to the location of the trench. Photograph was taken from piezometer D looking northeast towards piezometers A and E.

2.1 Soil Sampling

Samples from the surface of the alluvial gravel were taken when installing the trench since the unconsolidated gravel was unstable. Although these samples were disturbed, they still provided a reasonable representation of the subsoil. The samples taken from the gravel layer were first sieved to determine the particle size distribution for the

gravel subsoil. After oven drying the sample, the coarse gravel was first separated out using a stack of five sieves ranging from 25.4 mm to 4.75 mm (No. 4). Next, the smaller particles were sieved using a sieve stack as follows: 4.75 mm (No. 4), 2.0 mm (No. 10), 0.85 mm (No. 20), 0.6 mm (No. 30), 0.425 mm (No. 40), 0.25 mm (No. 60), 0.15 mm (No. 100), and 0 mm (pan).

The particle size distribution was analyzed to determine the D_{10}, D_{30}, D_{50}, and D_{60} (i.e., diameter of soil particles in which 10, 30, 50, and 60%, respectively, of the sample is finer). Once the particle size was known, the diameters were used with an empirical equation proposed by Alyamani and Sen (1993) to estimate the hydraulic conductivity of the soil:

$$K = 1300\left[I_0 + 0.025\left(D_{50} - D_{10}\right)\right]^2 \tag{1}$$

where K is the hydraulic conductivity in m/d, D_{50} and D_{10} are in mm, and I_0 is the intercept of the line formed by D_{50} and D_{10} with the grain size axis. This estimate for hydraulic conductivity was compared to another estimate obtained using a falling head test (Landon et al., 2001; Fox et al., 2004). The falling head test was performed by filling the trench with water until steady state conditions were reached, shutting off water to the trench, and recording water levels over time as the trench drained. Data obtained from the falling head experiment were then used with the Darcy equation to estimate the vertical hydraulic conductivity:

$$K_v = \frac{L}{t_1 - t_0} \ln \frac{H_0}{H_1} \tag{2}$$

where K_v is the vertical hydraulic conductivity of the soil in m/d, L is the sediment interval being tested in m (i.e., 0.25 to 0.50 m for the trench system), and H_0 and H_1 are the displacement in m of the water at time t_0 and t_1 respectively (Landon et al., 2001; Fox et al., 2004).

After sieving the soil sample, particles with a diameter less than 2.0 mm were further analyzed for P sorption. Adsorption isotherms were estimated by adding different levels of P (0, 1, 5, 10, 25, 50, 100, 200, 400, and 800 mg P/L) to 2.0 g soil samples. The samples were shaken for 24 hours using a reciprocating shaker and then centrifuged for 10 minutes at 10,000 rpm. The P in solution was then quantified using ICP-AES analysis. Data were fit to linear (equation 3) and Langmuir (equation 4) isotherms to provide information in regard to the ability of the fine sediment fraction of the alluvial soils to adsorb P from solution:

$$q_e = K_d C_e \tag{3}$$

$$q_e = Q^O \frac{bC_e}{1 + bC_e} \tag{4}$$

where q_e is the mass of P sorbed per unit mass of soil, C_e is the equilibrium, dissolved phase concentration, K_d is the distribution coefficient, and Q^0 and b are parameters of the Langmuir isotherm (i.e. Q^0 is the mass of P sorbed per unit mass of soil at complete surface coverage and b is the binding energy).

An ammonium oxalate extraction was also performed on the fine material to determine the degree of P saturation, which is the ratio of P to the total amount of iron and aluminum (McKeague and Day, 1966; Iyengar et al., 1981; Pote et al., 1996). This procedure dissolved the non-crystalline forms of aluminum and iron in the material,

considered to be the main sink for P among acidic soils. Therefore, selective dissolution of these amorphous minerals liberates any P associated with them into solution.

2.2 Tracer and Phosphorus Injection Experiments

Two Rhodamine WT tracer and one P (potassium phosphate, KH_2PO_4) injection experiments were performed to monitor subsurface solute transport from the trench (Table 1). Prior to the injection, each piezometer and the Barren Fork Creek was sampled and analyzed for background P levels. Also, a water level indicator was used to determine the depth to the water table in each piezometer prior to injection. Experiments were performed near base flow conditions in the Barren Fork Creek with ground water tables approximately 3.5 m below ground surface. Next, water was pumped from the Barren Fork Creek into the trench at approximately 0.0044 m^3/s (i.e., 4.4 L/s) in order to induce water movement. The steady-state water level in the trench was held as constant as possible at approximately 40 to 60 cm above the bottom of the trench. Water levels in the piezometers surrounding the trench were monitored over time. Pumping continued until the system reached pseudo-steady state conditions, which was verified when the water levels in the piezometers remained constant.

Rhodamine WT or P (KH_2PO_4) was injected into the trench at a constant rate using a variable rate chemical pump (Table 1). Once the injection began, samples were taken from the piezometers for the duration of the experiment in order to monitor the movement of the Rhodamine WT tracer and P. To sample the piezometers, a peristaltic pump was used. In order to obtain water samples at two different depths for experiment 2 and 3, two hoses were run to each of the piezometers. One hose was lowered to a depth 10 cm below the water table, while another was lowered to a depth 1.10 m below the water table.

Table 1. Summary of Rhodamine WT and phosphorus (KH2PO4) injection experiments. Water was injected at a rate of approximately 0.0044 m^3/s.

Experiment No.	1	2[a]	3[a]
Injection Compound	Rhodamine WT	Rhodamine WT	KH_2PO_4
Concentration (mg/L)	100	3	100
Compound Injection Duration (min)	60	90	90
Duration of Water Injection (min)	120	200	200
Average Water Level in Trench (cm)	44	60	60

[a] Experiments 2 and 3 were performed simultaneously.

The samples were placed into small bottles and then put into a refrigerated cooler and transported back to the laboratory where they were analyzed for Rhodamine WT, P and other cations such as calcium and aluminum. Each sample was analyzed for Rhodamine WT content using a Turner model 111 fluorometer and an Aquaflor handheld fluorometer. Samples were then analyzed for P content using two different methods. The Murphy-Riley (1962) method was used to measure the dissolved inorganic P present in the

samples, and an inductively coupled plasma atomic emission spectroscopy (ICP-AES) machine was used to measure the total dissolved P.

2.3 Laboratory Column Experiments

The fine material (i.e., less than 2.0 mm) obtained from the sieve analysis was also used in laboratory flow-cell experiments (DeSutter et al., 2006) to investigate the P sorption characteristics with respect to the flow velocity. The use of a uniform layer of fine material removed physical non-equilibrium effects due to spatial uniformity in dispersivity. Approximately 5.0 g of the fine material was placed in each of six flow-through cells (Figure 3). This corresponded to a soil depth of approximately 2.3 mm. A Whatman 42 filter was placed at the bottom of each cell to prevent the fine material from passing through the bottom. Each cell had a nozzle at the bottom with a hose running from the nozzle to a peristaltic pump. The pump pulled water with a predetermined P concentration through the cells and fine material at a known flow rate (mL/min) (Figure 3). Two different speeds on the peristaltic pump were used to evaluate the effect that flow velocity had on P sorption. The flow rates used averaged 0.4 mL/min for three low flow experiments and 14 mL/min for three high flow experiments. These flow rates corresponded to average flow velocities of 1.3 and 46 m/d, respectively.

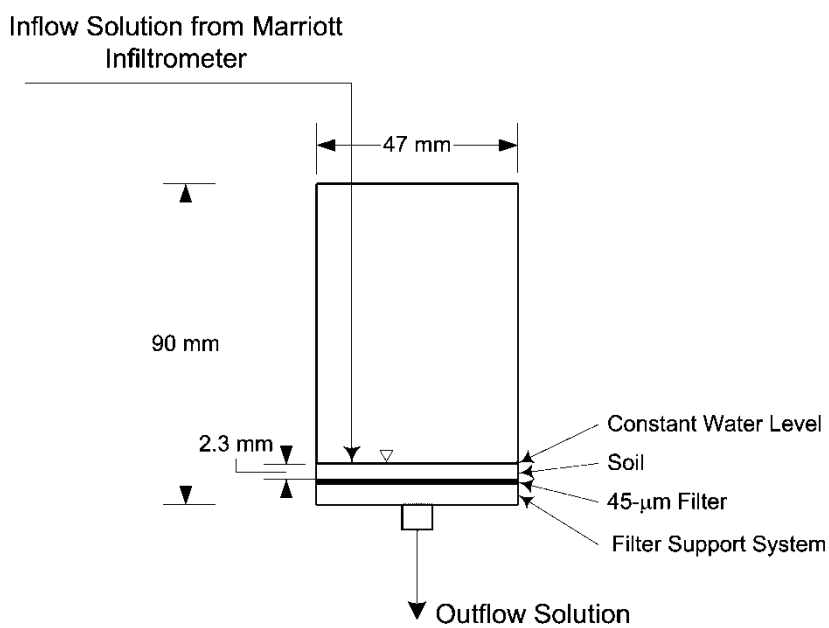


Figure 3. Laboratory flow-through experimental setup. The experimental setup follows that of DeSutter et al. (2006).

First, 20 mL of deionized water was pulled through the soil to determine the background P that was removed from the soil. Next, a KH_2PO_4 solution was injected into each cell at 1.0 mg/L and kept at a constant head using a Mariott bottle system (Figure 3). The low flow experiment was run for approximately 8 hours, while the high flow

experiment was run for 1 hour. This was done to achieve approximately equal P loads to each system. Samples were taken periodically throughout each experiment. The samples were analyzed in the laboratory for P and Ca using both the Murphy-Riley (1962) method and ICP-AES analysis.

The solution dissolved P concentrations obtained from the ICP-AES analysis were then used to evaluate the effect flow velocity on P sorption. Two scientific perspectives were used to analyze these data. The first method was based on contaminant transport theory and compared the outflow dissolved P concentrations from both low flow and high flow velocities over time. The dissolved P concentrations determined by ICP-AES analysis were plotted versus a dimensionless injection time, t^*, where $t^* = tQ/V_{ps}$, where Q is the inflow rate and V_{ps} is the pore volume. From the curve produced from outflow dissolved P concentration versus t^*, a breakthrough time, t_b^*, was estimated for each of the flow velocity experiments. This was assumed to be the time at which 50% of the inflow concentration was detected in the outflow solution.

A sorbing contaminant moves through porous media at a retarded flow velocity, as suggested by the following advection-dispersion-retardation equations:

$$R\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D_L^{(h)}\frac{\partial^2 c}{\partial x^2}$$
$$\frac{\partial c}{\partial t} = -v_s\frac{\partial c}{\partial x} + \alpha_L v_s\frac{\partial^2 c}{\partial x^2} \tag{5}$$

where x is the direction along the length of the column, c is the concentration, v is the pore water velocity, $D_L^{(h)}$ is the hydrodynamic dispersion coefficient, α_L is the dispersivity, and v_s is the sorbed contaminant velocity. The sorbed contaminant velocity is simply the groundwater velocity divided by the retardation factor, R:

$$R = 1 + \left(\frac{K_d \rho_b}{\varepsilon}\right) \tag{6}$$

where ρ_b is the soil bulk density and ε is porosity. Solutions to equation 5 were given by Ogata and Banks (1961) and Hunt (1978):

$$C(x,t) = \frac{C_0}{2} erfc\left(\frac{x - v_s t}{2\sqrt{\alpha_L v_s t}}\right) \tag{7}$$

These data from the flow-through experiments were then used with this equation to inversely estimate v_s and α_L by minimizing the sum of squared errors between predicted and observed outflow concentrations (i.e., x = 0.23 cm). With this estimated v_s, the average flow velocity measured during the experiment (v) was used to estimate R and then K_d. The K_d values estimated from low-flow and high-flow velocity experiments were compared.

Based on the one-dimensional advection-dispersion equations, a ratio relating the breakthrough times and flow velocities was derived assuming the length of the columns were equivalent between flow velocity experiments:

$$\frac{v_h}{v_l} = \frac{t_{b_l}}{t_{b_h}} \tag{8}$$

where t_{b_l} and t_{b_h} are the breakthrough times and v_h and v_l are the velocities for the high flow and low flow tests, respectively. If the ratios differed between experiments, then variable P sorption was occurring and the flow velocity had an effect on the sorption characteristics of the fine (i.e., less than 2.0 mm) material.

These flow-cell data were also analyzed based on the concentrations of dissolved P in the outflow compared to the total amount of P added to the system. If an equal mass of P was added to each system, the measured dissolved P concentrations in the outflows would be approximately equal if flow velocity did not have an effect on sorption. The mass of P added per kg of soil (mg P/kg soil) was found by multiplying Q (mL/min) by the inflow P concentration (mg/L) and by the elapsed time of the experiment (min). These data were plotted against the dissolved P concentrations (mg/L) detected in the outflow solutions for both flow velocities. If velocity had an effect on sorption, the curve for the low velocity data set would be lower than the curve for the high velocity data set.

III. PRINCIPLE FINDINGS AND SIGNIFICANCE

3.1 Soil Properties

From the particle size analysis of the gravel subsoil, it was found that roughly 81% of the material by mass was larger than 2.0 mm (Figure 4). This was significant because 2.0 mm is generally the upper limit used when attempting to characterize the sorption properties of a material. In other words, 81% of the gravel subsoil would likely be considered to have negligible sorption capabilities. According to the Wentworth (1922) scale, this gravel subsoil is classified as coarse gravel. The uniformity coefficient, defined as the ratio of D_{60} (i.e., 19 mm) to D_{10} (i.e., 0.9 mm), equaled 22 and suggested a fairly well-graded soil.

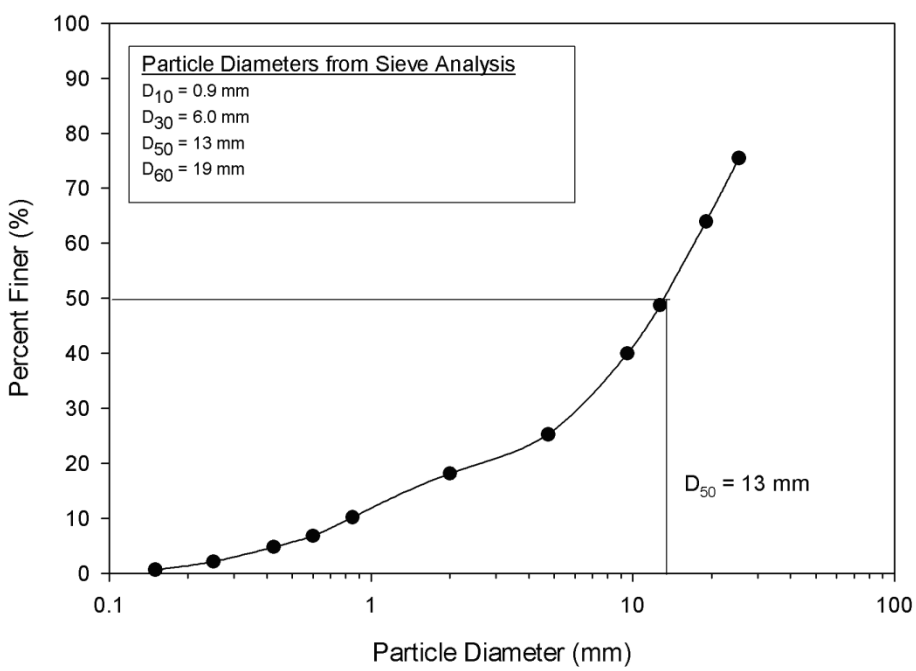


Figure 4. Particle size distribution for gravel subsoil in the riparian floodplain. D_{10}, D_{30}, D_{50}, and D_{60} are the diameter of soil particles in which 10, 30, 50, and 60%, respectively, of the sample is finer.

The particle size distribution was also used to estimate the hydraulic conductivity, K, of the gravel subsoil. Using a D_{50} of 13 mm, a D_{10} of 0.9 mm and I_0 equal to 0.4 mm, the K was estimated to be 640 m/d. Estimates for K_v obtained from the falling head test ranged from 140 to 230 m/d. It should be noted that most of the equations used to calculate K and K_v previously focused on soils with much smaller grain sizes (Landon et al., 2001). As indicated in the particle size distribution, the alluvial system tested here had a large percentage of gravels greater than 10 mm in diameter. Although the estimates for K and K_v obtained from the particle size distribution and falling head test may be elevated representations, they still demonstrate how conductive the gravel subsoil was and could be used as an indicator of the potential for rapid water and nutrient transport in the alluvial system.

The fraction of alluvial deposit less than 2.0 mm (i.e. about 19%) was found to possess considerable sorption capability based on linear (K_d = 4.5 L/kg based on C_e less than 10 mg/L) and Langmuir (Q^0 = 125 mg/kg and b = 0.048 L/kg) isotherms (Figure 5). When compared to other Oklahoma surface soils analyzed for P sorption properties, the Q^0 determined for our sample (125 mg/kg) was slightly lower than the range in Q^0 (191 to 772 mg/kg) of other surface soils analyzed in eastern Oklahoma (Fuhrman, 1998). A weighted linear K_d calculated based on the fraction of material above and below 2 mm resulted in a K_d of 0.9 L/kg. This weighted K_d suggested a P sorption R of 18 to 24 based on estimates of ρ_b for the gravel material of 1.5 to 1.8 g/cm^3 and ε of 0.35 to 0.40.

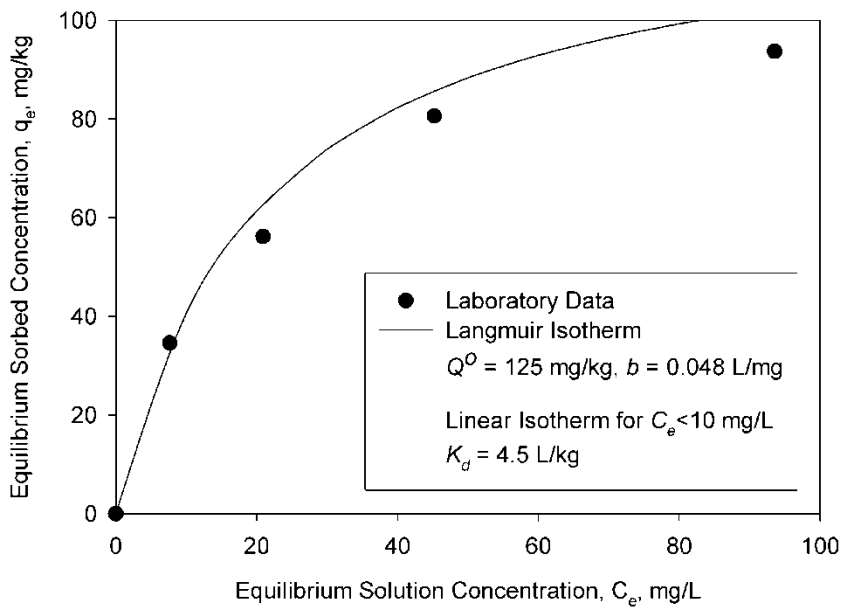


Figure 5. Laboratory data fit to Langmuir isotherm, where Q^o is the mass of phosphorus sorbed per unit soil mass at complete surface coverage and b is the binding energy, for fine soil material (i.e., less than 2.0 mm). The distribution coefficient, K_d, for the

Results from the ammonium oxalate extractions showed a degree of P saturation of 4.2% when not including the α factor of 0.5 (Beauchemin and Simard, 1999). This α factor has been used to adjust the total amount of iron and aluminum that could be available in different soil types. The value was derived from a given set of soils and

laboratory conditions. Thus, it may not be appropriate to use it for all cases. When incorporating the α factor of 0.5, the degree of P saturation for the fine soil was found to be 8.4%. Both P saturation values could be considered lower than agricultural topsoils with a history of P applications beyond crop needs. This suggested that the fine soil material would be capable of sorbing a considerable amount of P. However, this only pertains to the fine material in the gravel subsoil, which is only about 19% of the entire size fraction.

3.2 Tracer and Phosphorus Injection Experiments

In the first experiment, Rhodamine WT was injected at 100 mg/L (Table 1). Samples analyzed from this experiment showed detectable concentrations in all of the piezometers. Concentrations detected in piezometers located 2 to 3 m from the trench (i.e. piezometers A, B, and C) peaked at 36 μg/L with peak concentrations occurring approximately 30 min after injection. Detected levels in piezometers located 7 to 8 m from the trench (i.e., piezometers K, L, and M) were generally less than 30 μg/L with peak concentrations occurring approximately 50 min after initiation of injection (Figure 6a).

Also, Rhodamine WT concentrations detected in piezometers D, I, and J for the first experiment were much higher than those detected in all other piezometers (Figure 6b). Sample concentrations from these piezometers all exceeded 300 μg/L, which was the upper detection limit on the field fluorometer. After dilution in the laboratory, the concentrations in these wells were found to be close to the injected concentration of 100 mg/L. Piezometers D, I, and J were hypothesized to be located in a preferential flow pathway which was more conductive than other subsurface material (Figure 6b).

In the second experiment, Rhodamine WT was injected at approximately 3.0 mg/L with the intent of staying within the range of detection for the field fluorometer (Figure 7). Sample analysis showed a pattern similar to the first injection, with detection levels in piezometers D, I, and J approximately equivalent to the injected concentration of 3.0 mg/L (Figure 7). However, there was no Rhodamine WT detected in any of the other piezometers. This was hypothesized to be due to the fact that the injected concentration of 3.0 mg/L (compared to 100 mg/L in the first experiment) was diluted near the detection limit by the time it reached the outer piezometers.

The results from the second Rhodamine WT injection supported the hypothesis that a highly conductive preferential flow pathway existed in the coarse gravel subsoil. The Rhodamine WT concentrations detected in the preferential flow pathway, i.e. Figures 7 (d), (e), and (f), were roughly two orders of magnitude larger than the concentrations detected in the non-preferential flow piezometers, i.e. Figures 7 (b) and (c). This demonstrated the potential for rapid subsurface transport in this alluvial system.

Another trend visible from the Rhodamine WT injections was that samples taken from 10 cm below the water table showed significantly higher concentrations than samples taken 110 cm below the water table for the piezometers considered to be in the preferential flow pathway (Figure 7). These data supported the possibility of layering (i.e., vertical anisotropy) in the subsoil. These findings also support those of previous researchers, such as Poole et al. (2002), that such preferential flow pathways may be located at specific elevations within the alluvial floodplain. However, unlike the study by Poole et al. (2002), the preferential flow pathway in this research did not correspond to topographic elements on the surface.

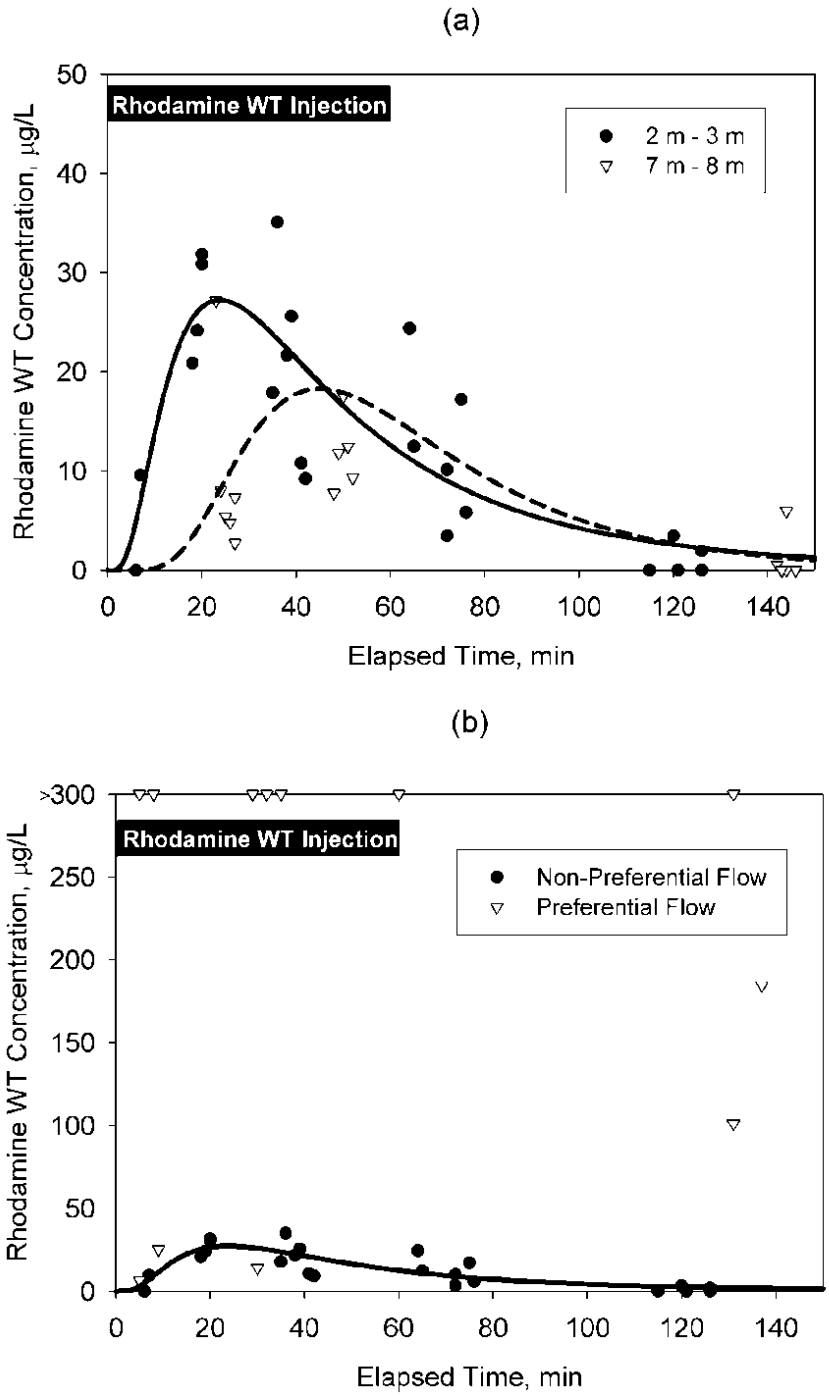


Figure 6. (a) Rhodamine WT concentrations for non-preferential flow piezometers located 2-3 m and 7-8 m from trench during experiment 1. (b) Rhodamine WT concentrations in preferential and non-preferential flow piezometers during experiment 1. Note: Concentrations greater than 300 ppb were above detection limit of field fluorometer.

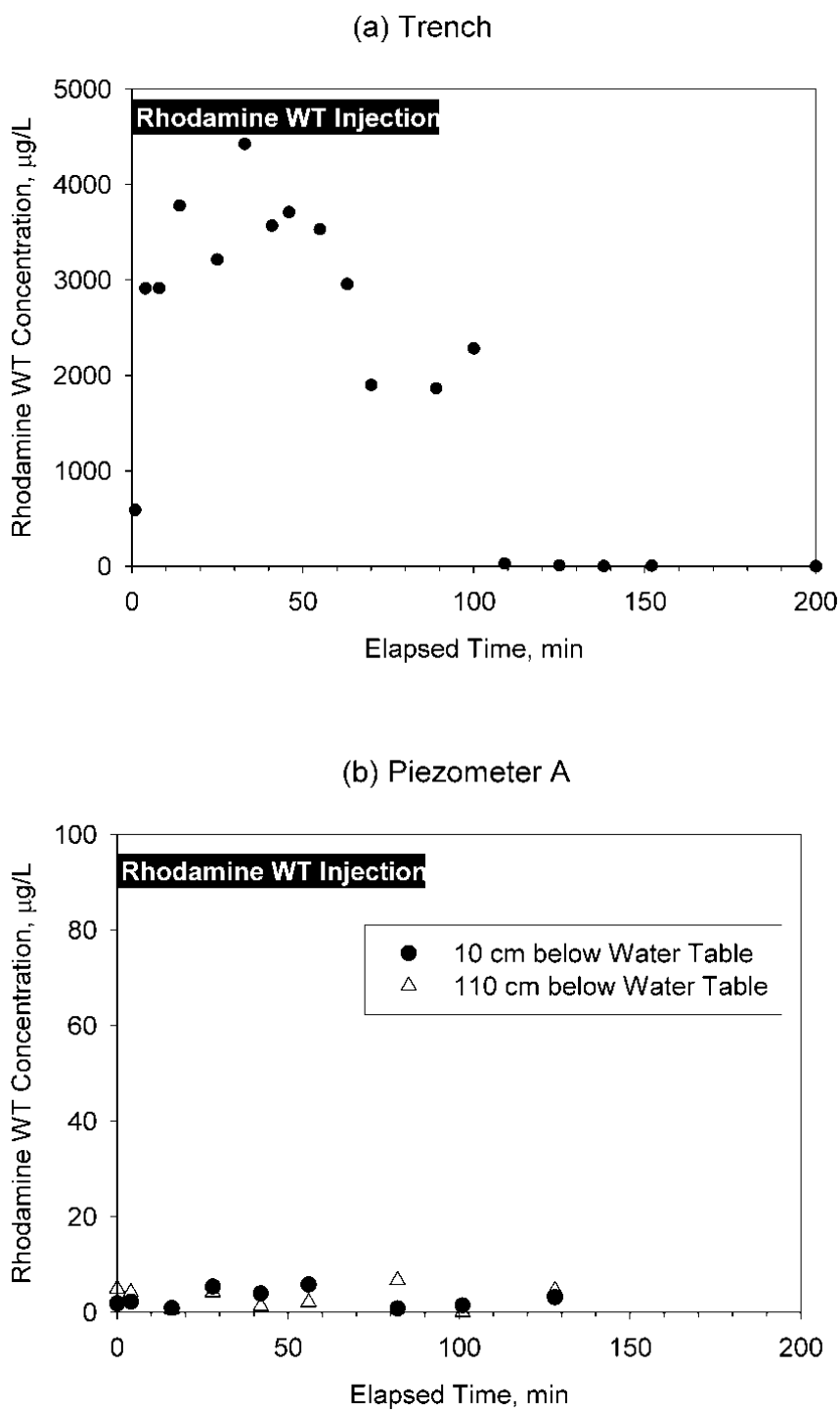
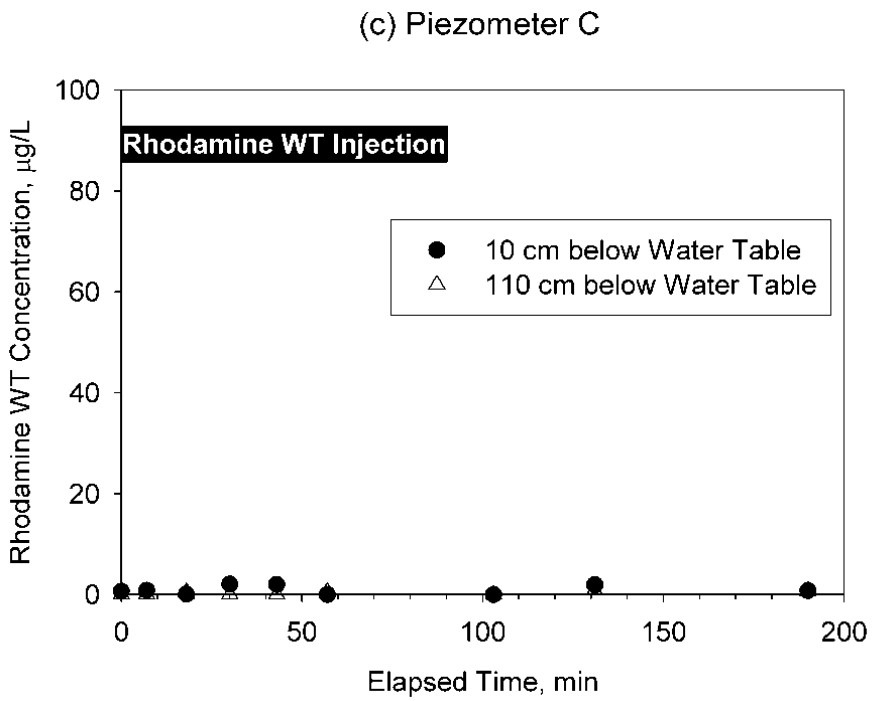


Figure 7. Rhodamine WT concentrations in trench (a) compared to non-preferential flow piezometers (b) and (c) and preferential flow piezometers (d), (e), and (f) during experiment 2.



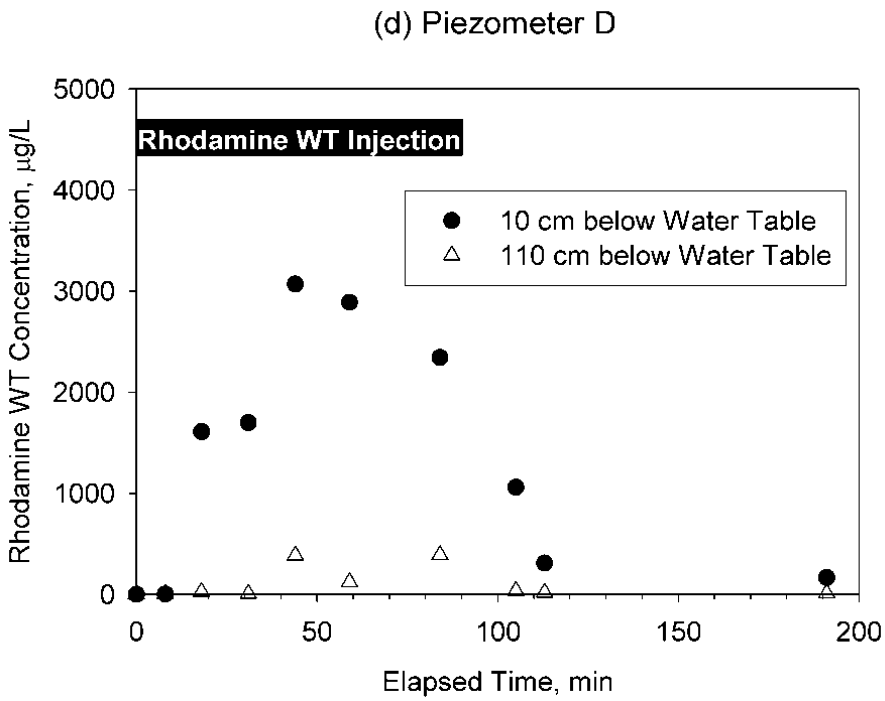
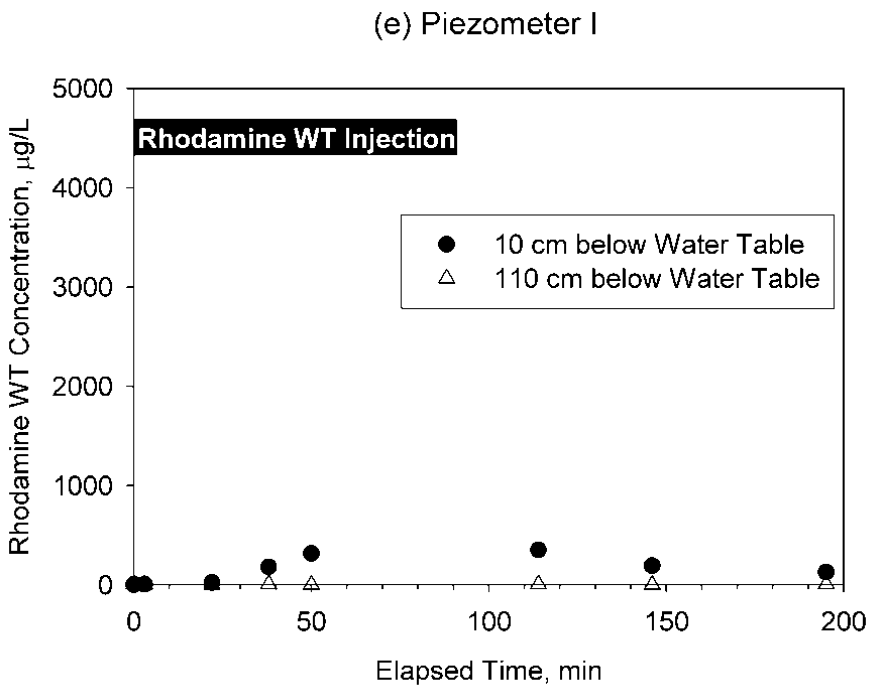


Figure 7 (Continued). Rhodamine WT concentrations in trench (a) compared to non-preferential flow piezometers (b) and (c) and preferential flow piezometers (d), (e), and (f) during experiment 2.



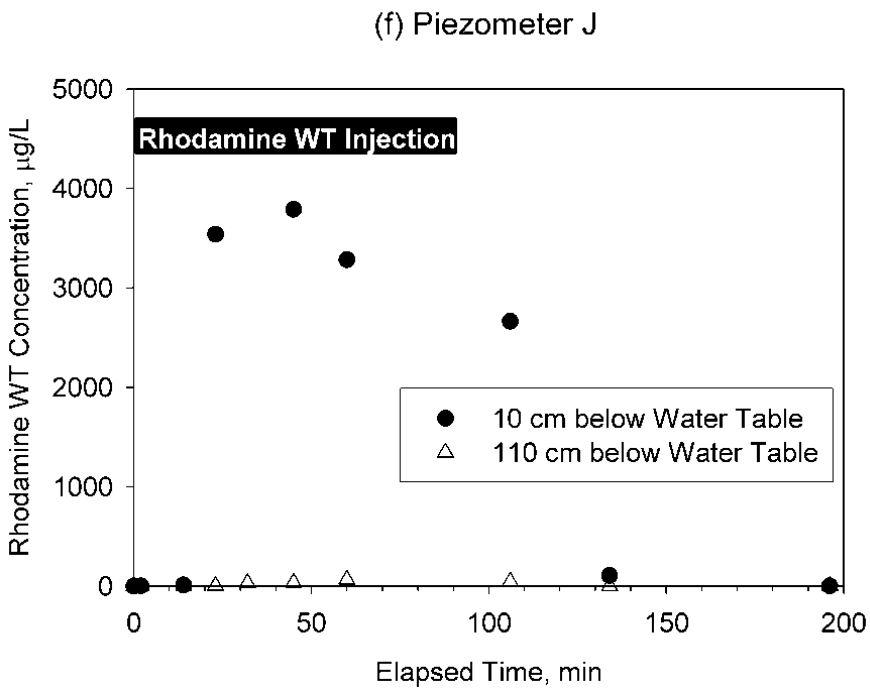


Figure 7 (Continued). Rhodamine WT concentrations in trench (a) compared to non-preferential flow piezometers (b) and (c) and preferential flow piezometers (d), (e), and (f) during experiment 2.

Prior to the injection experiments, the water levels detected in each piezometer showed minor differences (i.e., less than 1 cm). Therefore, a minimal hydraulic gradient existed which was directed towards the preferential flow pathway. However, during injection, water level readings from two of the piezometers (i.e., D and J) in the preferential flow pathway suggested that water was flowing down the side of the piezometer. This qualitative evidence again supports the hypothesis of vertical anisotropy with a confining layer or bottom of the preferential flow pathway located between 1.7 m (i.e., the elevation of the bottom of the trench at the topsoil/gravel interface) and 3.5 m (i.e., the original water table elevation).

Background dissolved P samples prior to the last injection were grouped according to the observed piezometer flow response from the Rhodamine WT experiments: (1) preferential flow piezometers versus (2) non-preferential flow piezometers. A statistically significant difference (α = 0.05, p-value = 0.013) was noted between the background dissolved P concentration in preferential versus non-preferential flow piezometers (Figure 8). Concentrations of dissolved P in the Barren Fork Creek were approximately 1.8 times higher than those observed in the piezometers. The difference between piezometer groupings suggested potential for the preferential flow piezometers to be more directly connected to the stream channel and non-point source loads in the stream.

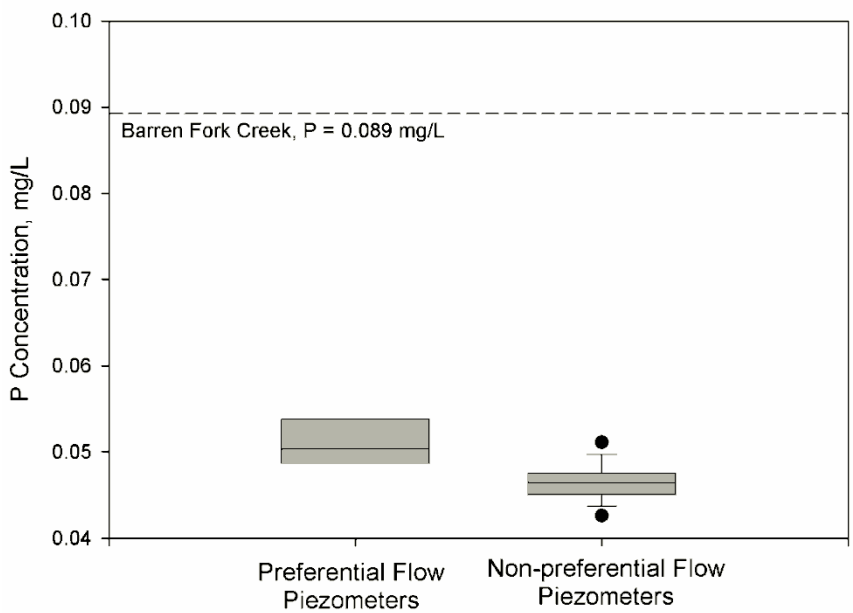


Figure 8. Box plots of background phosphorus (P) concentration in preferential flow versus non-preferential flow piezometers prior to P injection experiment (i.e., experiment 3). 25th and 75th percentiles = boundary of the box; median = line within the box; 10th and 90th percentiles = whiskers above and below the box.

In the third experiment, P was injected into the trench at a concentration of 100 mg/L, as shown in Figure 9. Similar to the Rhodamine WT injections, dissolved P concentrations in preferential flow piezometers again mimicked concentrations injected into the trench: Figures 9 (d), (e), and (f). Also, the breakthrough time of dissolved P in preferential flow piezometers was approximately equivalent to the breakthrough time of

Rhodamine WT. Dissolved P and Rhodamine WT were detected at 50% of the injected concentration approximately 20 to 30 min after injection.

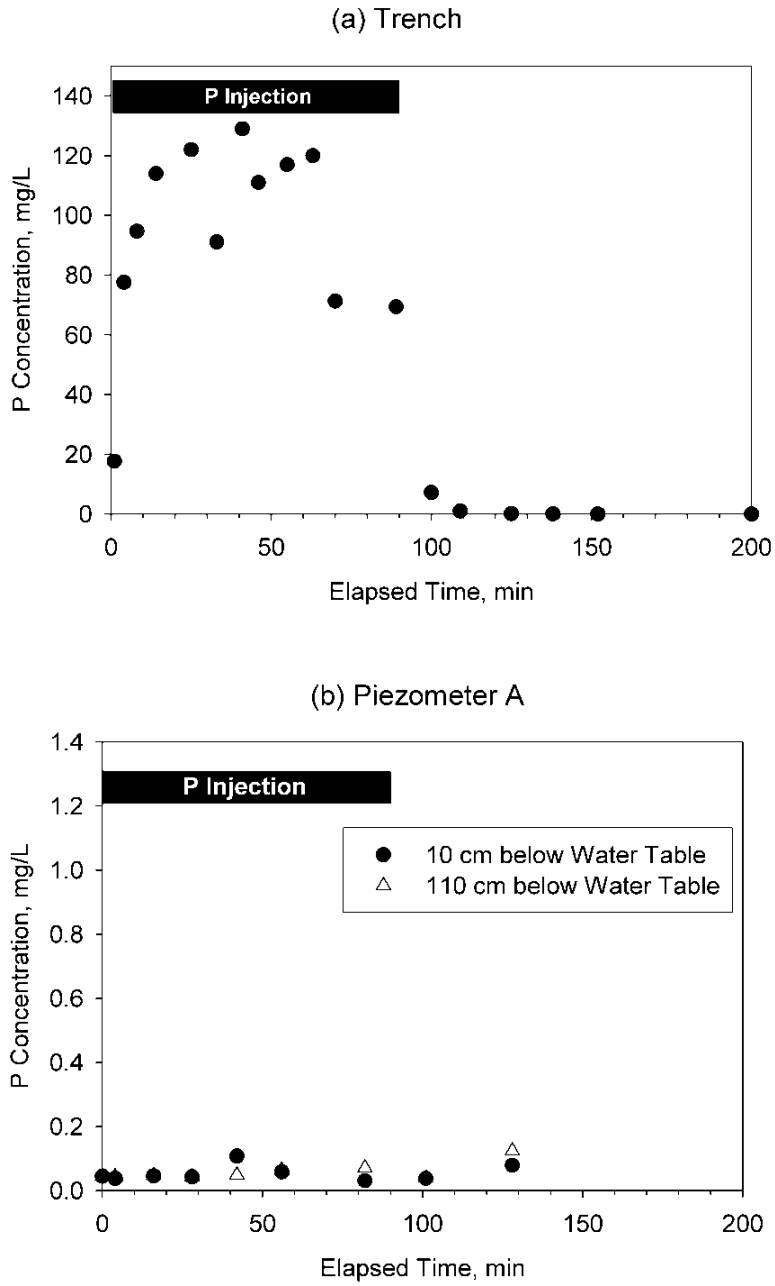
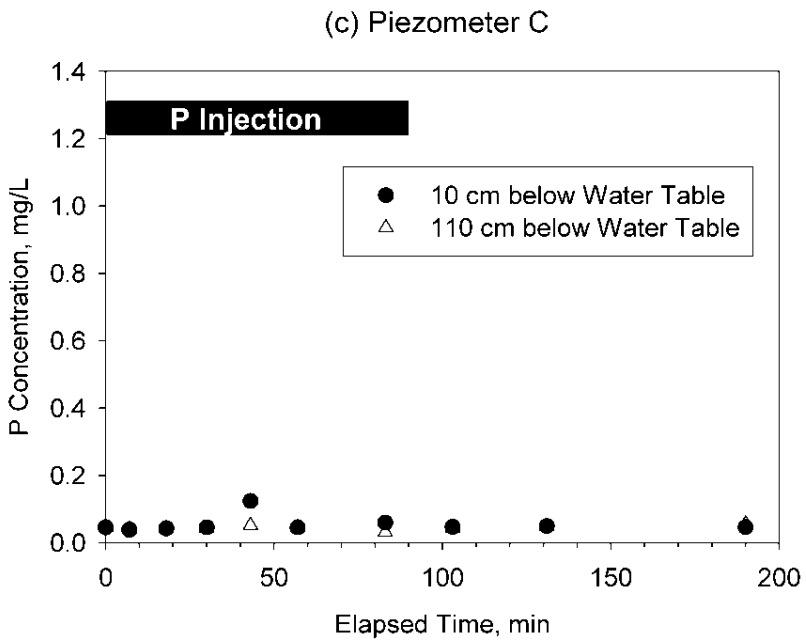


Figure 9. Phosphorus concentrations in trench (a) compared to non-preferential flow piezometers (b) and (c) and preferential flow piezometers (d), (e), and (f) during experiment 3.



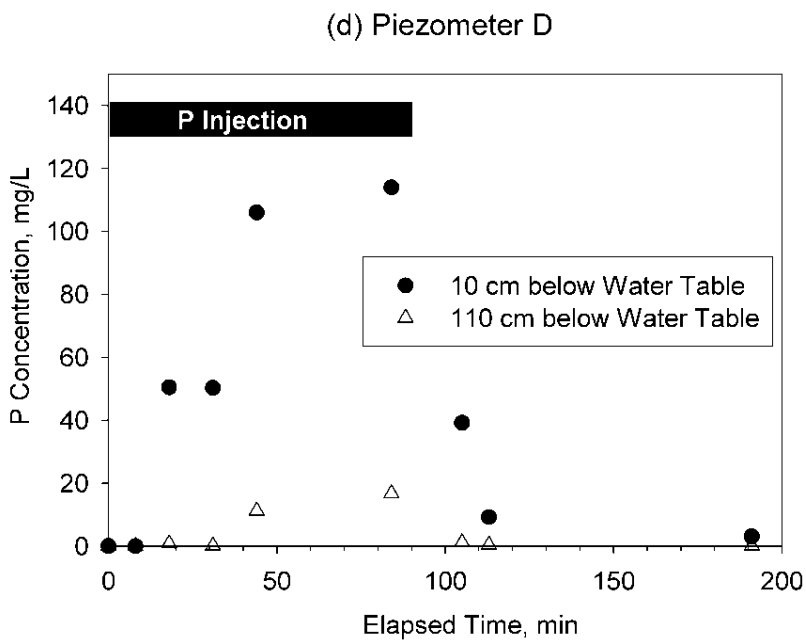
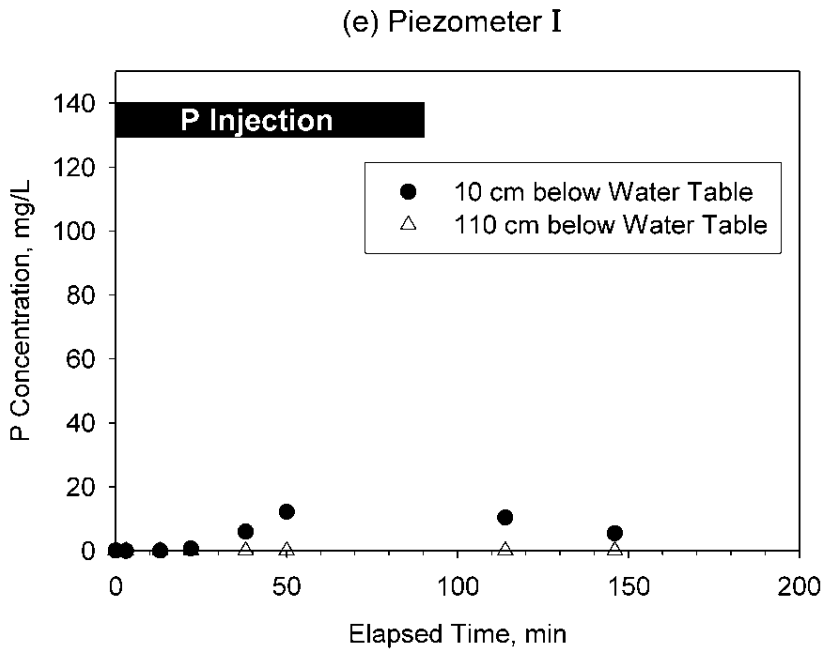


Figure 9 (Continued). Phosphorus concentrations in trench (a) compared to non-preferential flow piezometers (b) and (c) and preferential flow piezometers (d), (e), and (f) during experiment 3.



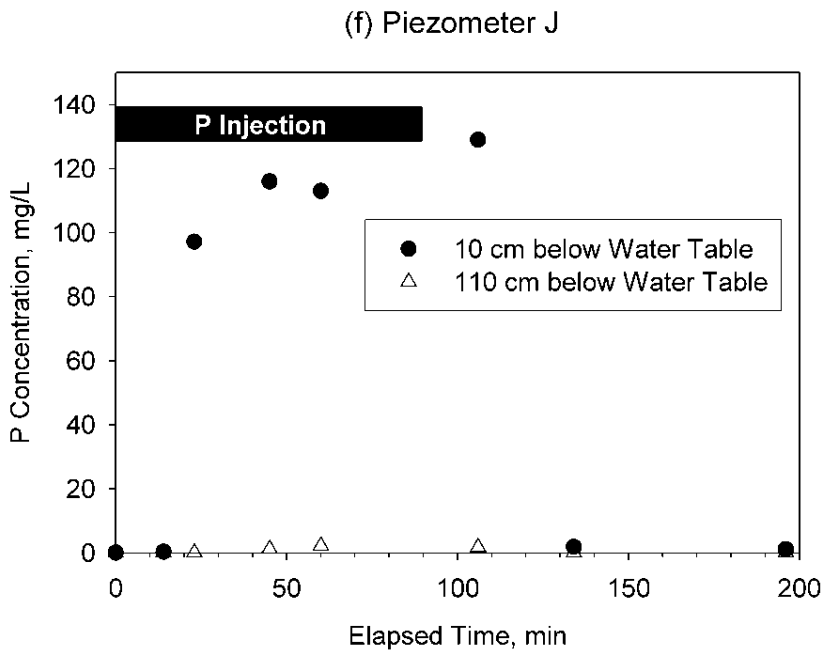


Figure 9 (Continued). Phosphorus concentrations in trench (a) compared to non-preferential flow piezometers (b) and (c) and preferential flow piezometers (d), (e), and (f) during experiment 3.

Such results suggested no enhanced transport of P with colloids. In fact, no visible colloids were observed on a 0.45-μm filter during sampling. Negligible colloids were also supported by the approximately equivalent P concentrations between the Murphy-Riley (1962) and ICP-AES methods. Had colloids been present in this system, the transport velocity of the colloids may have been equivalent to the average groundwater flow velocity in the preferential flow paths due to the fact that the colloid size would be much smaller than the soil pore size in this coarse gravel (McCarthy and Zachara, 1989; Ramaswami et al., 2005).

The long tailings shown in both the Rhodamine WT and P preferential flow piezometer data suggested that the alluvial system experienced non-equilibrium conditions. Direct comparison of Rhodamine WT and dissolved P in specific preferential flow wells indicated that P and Rhodamine WT possessed equivalent periods of detection. Both dissolved P and Rhodamine WT reached background levels at approximately 120 min in piezometers D and J, as shown in Figures 7(d), 7(f), 9(d), and 9(f), and approximately 200 min in piezometer I, as shown in Figures 7(e) and 9(e). These results signaled the presence of heterogeneities in aquifer dispersivity, a result that is not unexpected in such geomorphologically active alluvial stream systems, and/or chemical kinetics.

In non-preferential flow piezometers, dissolved P was not detected above background concentrations (i.e., 40 μg/L) even in piezometers 2 to 3 m from the trench. Rhodamine WT was detected in non-preferential flow piezometers 2 to 3 m from the trench at concentrations near 40 μg/L. This result suggested that sorption retarded the movement of P to these non-preferential flow piezometers, and that no significant sorption was observed for piezometers D and J. Two hypotheses were proposed for the lack of sorption that was suggested in piezometers considered to be in the preferential flow pathway: (1) the presence of fewer particles with significant P sorption capability and/or (2) lack of contact time between aqueous and solid phases due to the higher flow velocities. To evaluate the first hypothesis, undisturbed soil cores would be needed from the preferential flow path. However, this was difficult to obtain in the coarse gravel substrate. Therefore, this hypothesis was not evaluated. The second hypothesis was evaluated using flow-cell experiments in the laboratory.

3.3 Laboratory Flow Experiments

Both the contaminant transport and load perspectives suggested that flow velocity had an effect on the sorption capabilities of the system. Figure 10a shows the dissolved P concentrations for both velocities plotted versus dimensionless time. Concentrations detected in the outflow solution for the high velocity experiment are approximately 90% of the inflow dissolved P concentration after less than 1 min. Therefore, the breakthrough time, t_b, for the experiment is less than 1 min. The exact time at which 50% of the sample was detected is not known because the first sample (i.e., at 0.5 min) corresponded to 60% of the inflow concentration. The exponential fit to these data (Figure 10a) was used to estimate a t_b^* of 2.7, which corresponded to a t_b of 0.4 min. For the low flow experiment, the outflow concentration gradually increased with time and reached approximately 75% of the inflow concentration after 8 hours of injection. The t_b determined for the low flow experiment was approximately 155 min, which corresponded to a t_b^* of 25.4 (Figure 10a).

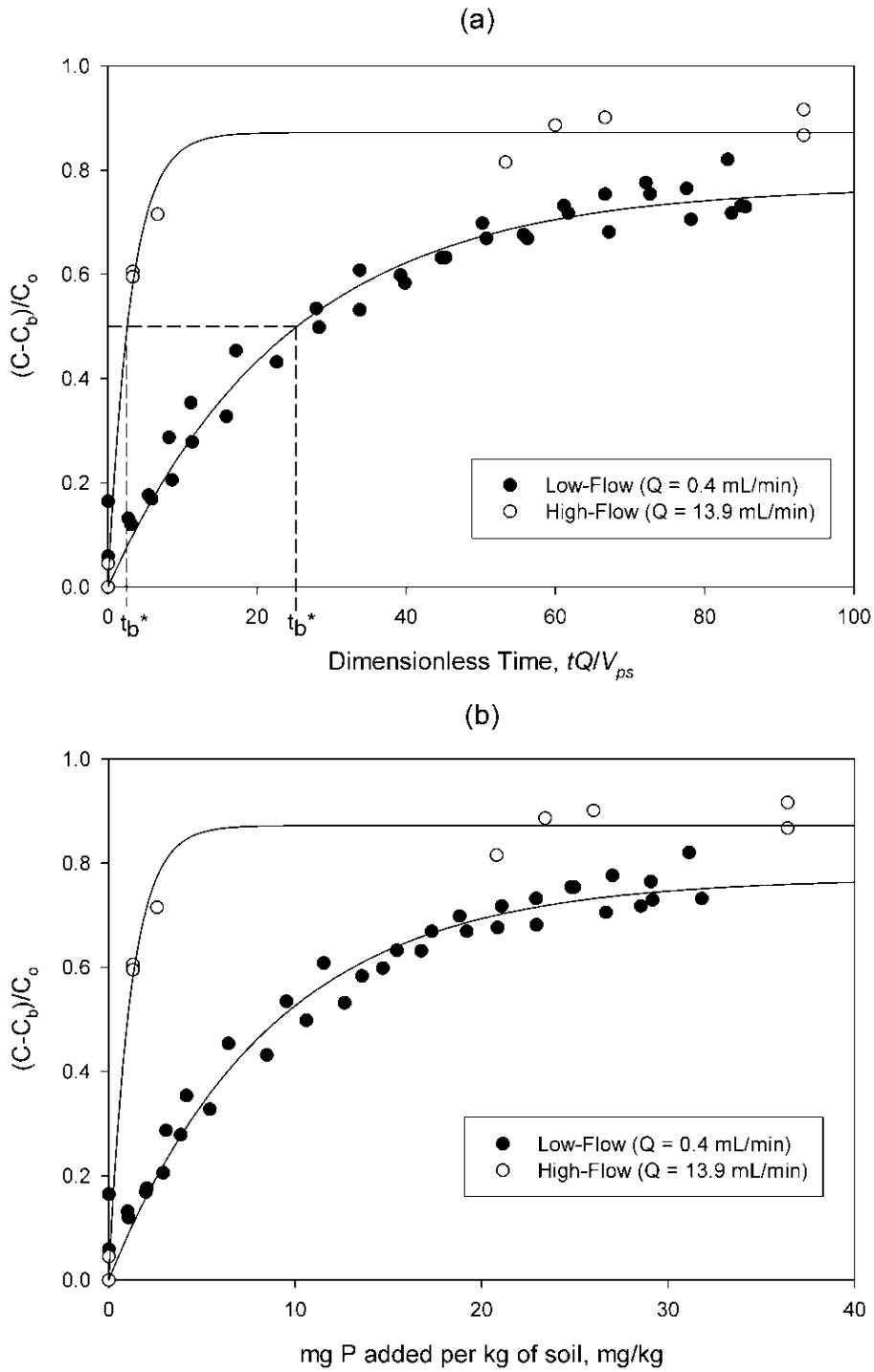


Figure 10. Phosphorus (P) concentrations detected in outflow (C) versus (a) dimensionless time and (b) mg P added per kg of soil, where Q is the flow rate, V_{ps} is the pore space volume, C_b is the background P concentration released from the soil, C_o is the inflow P concentration, and t_b^* is the dimensionless breakthrough time.

These data suggested that increased P sorption was occurring in the low flow experiment. Specifically, the velocity ratio between the high flow and low flow experiments was approximately 36 when using average flow velocities of v_h = 46 and v_l = 1.3 m/d, respectively. Compared to the ratio of the breakthrough times of approximately 390, additional P sorption was occurring during the low-flow experiment. This could likely be due to the small reaction time between the P and soil surfaces during the high-flow experiment. In previous laboratory studies, differences were observed in water soluble P extraction at two different shake times (i.e., 1 hr and 16 hr) indicating that kinetics played a significant role in desorption/adsorption. Even though there was no visible preferential flow pathways (i.e., edge flow) in the laboratory flow-cell experiments, such pathways may have existed. If pathways existed, they were consistent among three replicates at the high flow velocity.

These flow-cell data were also analyzed by comparing the total mass of P added to the dissolved P concentrations detected in the outflow, as shown in Figure 10b. Variables such as inflow P concentration, mass of P added and mass of soil sample were held constant. The only parameter changed between the two experiments was flow velocity. From Figure 10b, it is noticeable that the outflow P concentrations detected for the low flow experiment were consistently less than the concentrations obtained during the high flow experiment at the same mg of P added per kg of soil. Similar to the contaminant transport analysis, these data also suggest that more P sorption was occurring during low flow velocity experiments and that flow velocity had an effect on sorption.

This fine (i.e., less than 2.0 mm) material consists of secondary minerals with larger surface areas, such as kaolinite and non-crystalline Al and Fe oxyhydroxides, and is characterized by valence-unsatisfied edge hydroxyl groups. Due to the valency, these edge hydroxyl groups are highly active and account for the majority of P sorption in the material. Although isotherm data on the fine material showed that material had lower sorption properties than other surface soils in Oklahoma, it did suggest that the material was capable of sorbing P. Therefore, the finding that P was sorbing in the low flow experiment is reasonable.

The flow-cell experiments suggested that neither variation in fine particle distribution nor P sorption kinetics could be eliminated as factors hypothesized to contribute to the field-observed increased sorption in non-preferential pathways compared to preferential flow pathways. Most likely, a combination of both the presence of fewer fine particles (i.e. soil particles less than 2.0 mm in diameter which possess greater P sorption capability) and the lack of contact time between aqueous and solid phases due to the higher flow velocities in the preferential flow path contributed to the variability in P sorption observations. Estimates for K_d obtained from the Ogata and Banks (1961) and Hunt (1978) equations were 11 L/kg and 0.9 L/kg for the low flow and high flow experiments, respectively. It should be noted that direct comparisons of K_d between the batch and flow-cell experiments is difficult. The batch sorption and flow-cell experiments are different tests with non-similar soil to solution ratios. Furthermore, reaction products were being removed during the flow-cell experiments, but not during the batch experiment. Removal of reaction products allowed the reaction to continue to proceed more easily.

The differences in the K_d values suggested that nonequilibrium processes were occurring in the system. These processes can be divided into physical and chemical nonequilibrium. Physical non-equilibrium is the result of dissolved P moving into the

micropores between the soil particles. Because there was not a large amount of fine clay in the material, the effect of microporosity is likely negligible. Therefore, the differences in the K_d are likely due to a chemical kinetics, meaning that the amount of sorption observed varies due to the time associated with the reaction between dissolved P and the soil surfaces. If one was attempting to derive parameters for a predictive model as opposed to simply demonstrating the presence and influence of chemical kinetics, a non-equilibrium model, such as those discussed by Pang and Close (1999) and McGechan and Lewis (2000), would be more appropriate for analyzing the column data than the equilibrium model used in this research.

4.4 Research Implications

This research demonstrated that preferential flow pathways can occur even in non-structured, coarse gravel substrates and demonstrated that the heterogeneity in the riparian floodplain subsoil can promote significant subsurface nutrient transport. This research directly confirmed previous research findings by Carlyle and Hill (2001) and McCarty and Angier (2001). Preferential flow pathways may create direct hydraulic connections between nonpoint source loads in the stream and the alluvial gravel subsoil. These direct connections could lead to a transient storage mechanism, where nutrient loads concurrent with large storm events could potentially migrate from the stream into the adjacent floodplain, contaminating the alluvial storage zone. Second, a direct connection may exist between upland sources of P and the streams such that a significant nonpoint source load may not be currently considered in analyzing for the impact of P application and management on such landscapes. Future research should be aimed at quantifying the preferential flow path length, where this research only identified relatively short flow paths (i.e., 2 to 3 m), and likelihood of connectivity with the stream. Tools which may prove effective at quantifying such characteristics include geophysical techniques such as electrical resistivity imaging (Sima et al., 2008).

This research has wide reaching implications for how riparian floodplains are managed. Millions of dollars are spent each year to mitigate surface runoff and sediment and nutrient loads. Although these management plans can be effective, this research has shown that subsurface P transport could also be a contributing factor in certain conditions. Because the nutrient load studied here was input directly into the subsurface, the overall subsurface load contribution could not be quantified. The next step is determining if similar conditions like this are common and if a direct connection exists between nutrient sources on the surface and the conductive subsurface material.

IV. CONCLUSIONS AND FUTURE WORK

This research demonstrated that subsurface movement of P can be an important transport mechanism, especially in areas such as riparian floodplains with hydraulic conditions conducive to the rapid transport of P. The movement of water and contaminants in riparian floodplains, even those classified as non-structured, coarse gravel, is not homogeneous and can be impacted by the presence of preferential flow pathways. In the presence of preferential flow paths, P could be transported through alluvial groundwater without any reduction in its concentration. In contrast, in the absence of preferential flow paths, P transport was hindered.

Minimal sorption of P to subsoil material in the preferential flow pathways occurred because of two hypothesized factors: (1) the presence of fewer fine particles (i.e. soil particles less than 2.0 mm in diameter) and (2) lack of contact time between aqueous and solid phases due to the higher flow velocities. Laboratory flow experiments suggested that higher velocity of flow through the subsoil resulted in less P sorption. These findings suggested that high concentrations of dissolved P (i.e., concentrations mimicking the injected concentration) detected in the piezometers located in the preferential flow pathway were a result of the greater flow velocity. The velocity, in turn, likely led to a smaller reaction time between the dissolved P and soil surfaces, prohibiting measurable sorption. The lack of dissolved P above background concentrations in piezometers outside of the preferential flow pathway may have been a result of the P solution moving much slower through the subsoil and therefore sorbing to the fine material.

Because of the quantity of data generated during the field tracer studies, future research is underway to better understand the water quality changes in the alluvial ground water during the injection experiments. Future work is also aimed at investigating the preferential flow pathways in more detail. Electrical resistivity mapping will be used at the field site to attempt to identify and map the preferential flow pathways.

V. Acknowledgements

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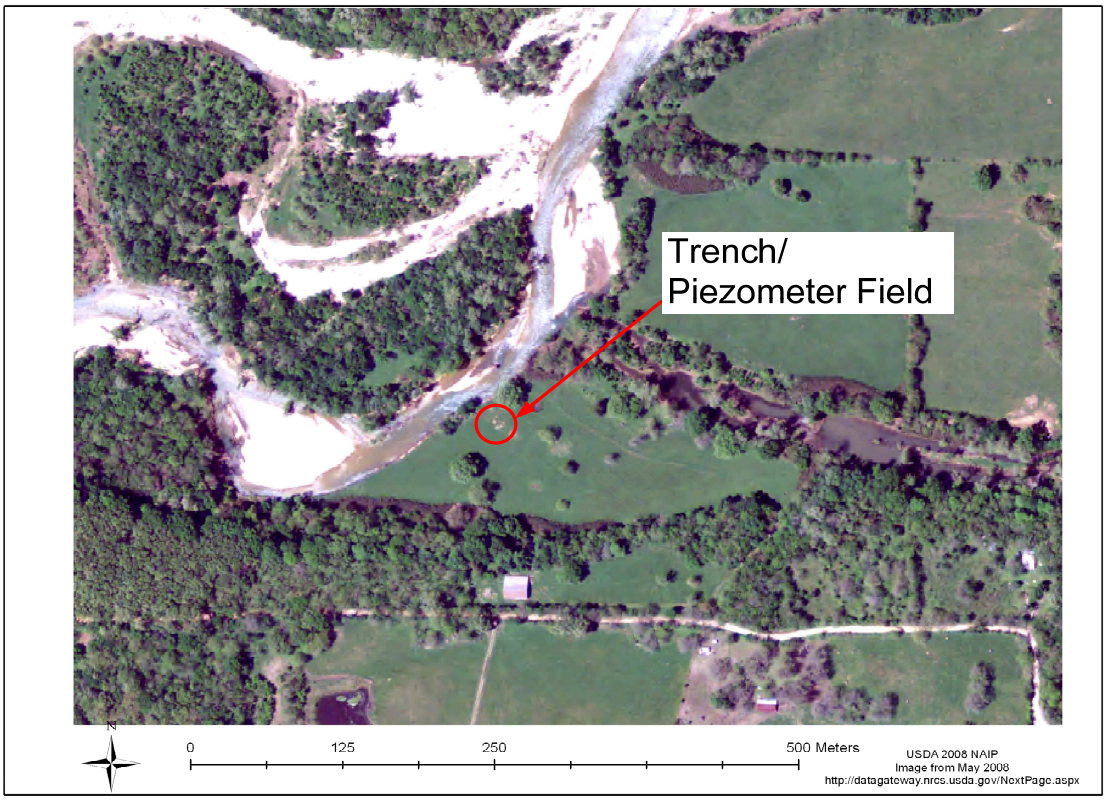
APPENDIX. AERIAL PHOTO OF FIELD SITE ALONG BARREN FORK CREEK