SEDIMENT-PHOSPHORUS CHEMISTRY

IN OZARK PLATEAU STREAMS

IN NORTHEAST OKLAHOMA

By

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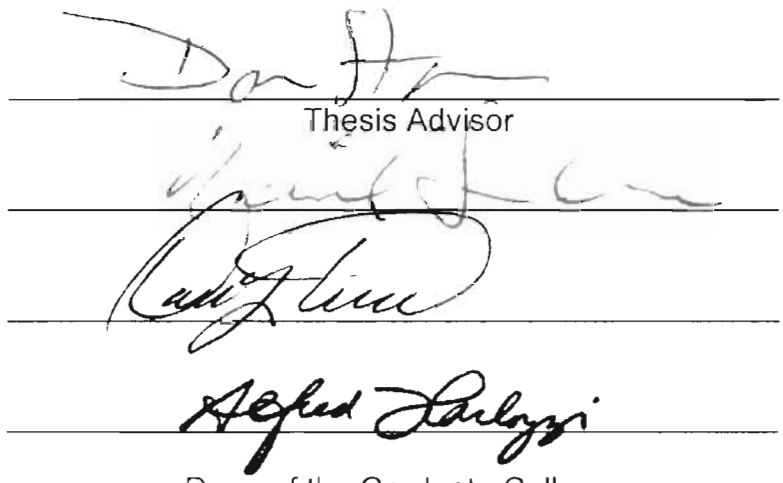

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

CHAPTER I

INTRODUCTION

Nitrogen (N) and phosphorus (P) are vital nutrients in aquatic ecosystems, but excessive nutrient loading may cause algae blooms and accelerated eutrophication that often leads to a decline in water quality and biodiversity. Most point source (PS) pollution has been abated through the promulgation of the Clean Water Act and its amendments (Anderson, 1999; Harrison *et al.*, 1999). However, some recent investigations have shown that PS pollution has a profound impact on nutrient dynamics, especially in lotic ecosystems (Haggard *et al.*, 2000). Nonetheless, increases in anthropogenic activities, such as agricultural and urban development, and the diffuse nature of its associated nonpoint source (NPS) pollution from surface runoff and/or ground water contamination has become a major water quality concern (Sams *et al.*, 1999).

Nitrogen and/or P are often the limiting nutrient regulating primary production, specifically algal growth, in aquatic ecosystems (East *et al.*, 1998; Leppakoski *et al.*, 1999; Toetz *et al.*, 1999). To understand nutrient dynamics in aquatic ecosystems, researchers have studied nutrient transport and transformation in both lentic (lakes) (Sonzogni *et al.*, 1982; Dorioz *et al.*, 1997) and lotic (rivers and streams) ecosystems (Meyer, 1979; Hill, 1982; Klotz, 1985; Haggard *et al.*, 1999). Some interesting concepts regarding nutrient dynamics in

water bodies include *Nutrient Spiraling, Self-Purification, Flood Plain Theory* and the *River Continuum Concept*. The role of benthic sediments in nutrient, especially P, dynamics in streams has been studied extensively in the past (Meyer, 1979; Bache and Williams, 1971; Klotz, 1985; Klotz, 1988) and quite recently (Haggard *et al.*, 1999; House *et al.*, 1995; Triska *et al.*, 1994). Benthic sediments have been suggested to control water column P (Klotz, 1988; Meyer, 1979) and may provide a temporary or a long-term buffer to increasing P loads in streams (Haggard *et al.*, 1999). Different hydrologic and physico-chemical characteristics of a stream and its watershed, such as land use practices (Klotz, 1985; Taylor and Kunishi, 1971), stream water velocity (Meyer, 1979), sediment particle size distribution (Klotz, 1985; Meyer, 1979), and sediment density (Sonzogni *et al.,* 1982), can influence P and NH_4-N sorption by benthic sediments.

Several investigators have used different methods and techniques to assess the importance of sediment-nutrient interactions in aquatic ecosystems: P sorption index (PSI), equilibrium P concentration (EPCo), Benthic sediment bioavailable P (NaOH-Extractable P, SBAP), Exchangeable P ($MgCl_2$-Exctractable P, ExP), Exchangeable NH_4-N (KCl-Extractable NH_4-N, ExN), organic matter content, and sediment particle size distribution. Additionally, the distribution of nutrients between the water column and benthic sediments is used to compare potential bioavailable sources. Whereas water column nutrients are traditionally measured to assess biotic demand, the sediment-bound fraction maybe more available to select biotic organisms.

Lakes Eucha and Spavinaw are located on the Ozark Plateau of northeastern Oklahoma and northwestern Arkansas. Since 1990 these impoundments have been the major source (56%) of the City of Tulsa's drinking water supply. However, recently numerous complaints have been registered regarding the smell and taste of the finished drinking water coming from this reservoir system. The average P concentration in Eucha Lake tripled between 1975 and 1995, and the average NO_3-N concentration doubled during the same time period (Oklahoma Conservation Commission, 1997). Lake Eucha was classified as eutrophic with P being the limiting nutrient (Oklahoma Conservation Commission, 1997).

For my research project, I sampled benthic sediments from four Lake Eucha tributaries with varying levels of PS and NPS impact and assessed seasonal and spatial variability in sediment P dynamics. Dry Creek, Cloud Creek, and Cherokee Creek are NPS affected streams with pasture and forest being the major land fractions. The major agricultural land uses in these basins are poultry farming, swine operations, dairy and beef cattle, and the application of animal wastes to pastures. Columbia Hollow is a Waste Water Treatment Plant (WWTP) impacted stream that provides a classic example of a highly eutrophic stream.

CHAPTER II

OBJECTIVES

1. **Characterize water chemistry in four tributaries of Lake Eucha.**

H_0: Nutrient concentrations among Dry Creek, Cloud Creek, Cherokee Creek and Columbia Hollow are not different. H_A: Nutrient concentrations among Dry Creek, Cloud Creek, Cherokee Creek and Columbia Hollow are different due to varying level of PS/NPS impact.

2. Evaluate, **characterize, and determine the amount of easily exchangeable P and NH_4-N in sediments and the partitioning of these nutrients between the water column and benthic sediments.**
3. **Evaluate water column EPCo and its relationship to the benthic sediment P concentrations.**

H_0: Water column P is in equilibrium with the sediment P in four selected streams. H_A: Water column P is not in equilibrium with the sediment P in four selected streams and benthic sediments act as a sink or source for the water column P.

4. **Compare sediment nutrient attributes between four streams.**
   a) **NPS vs. PS impacted streams.**

H_0: Sediment buffering capacities of NPS (Dry Creek, Cloud Creek and Cherokee Creek) and PS (Columbia Hollow) impacted streams do not differ.

H_A: Sediment buffering capacities between NPS (Dry Creek, Cloud Creek and Cherokee Creek) and PS (Columbia Hollow) impacted streams are different.

b) Potentially low vs. high NPS impacted streams.

H_0: Sediment buffering capacities of NPS (Dry, Cloud and Cherokee Creeks) impacted streams are not different. H_A: Sediment buffering capacities between NPS impacted streams are different.

5. Compare biotic vs. abiotic sinks of P.

H_0: PSI for autoclaved ('dead') sediments are not different from PSI values for 'live' sediments for each particular stream. H_A: PSI for autoclaved ('dead') sediments are lower than PSI for 'live' sediments for each particular stream.

6. Characterize benthic sediment particle size distribution and organic matter content. Evaluate the relationship of the sediment particle size distribution with sediment buffering capacity.

H_0: There is no significant correlation between particle size distribution, organic matter content and benthic sediment buffering capacity within a stream. H_A: There is a significant positive correlation between PSI and percent fine material and organic matter content.

7. Evaluate effects of seasonal variability within a stream.

H_0: There is no seasonal variability for each particular stream. H_A: There is a significant difference between winter and summer PSI, EPCo, organic matter content, and particle size distributions.

8. Investigate trends among various parameters and significant correlations.

CHAPTER III

LITERATURE REVIEW

Point and Nonpoint Sources of Pollution

PS pollution has been a major concern in the past, but in the 1970's water quality management focused on cleaning up PS contributors. This approach has yielded some improvements nationwide but there are still some problem sites (Bolton and Greenway, 1999). The US EPA has had significant success in reducing PS pollution by enforcing the 1972 Clean Water Act and its revisions over the last 28 years (Anderson, 1999; Harrison *et al.*, 1999). However, a recent investigation has shown that considerable (km-scale) distances are required to assimilate PS inputs of nutrients (Haggard *et al.*, 2000).

Recently NPS pollution has become the focus of water quality and watershed management. One third of all US rivers and streams were not meeting designated beneficial uses, and in 1996 NPS pollution was the leading cause of the impairment (EPA, 1996). Primary contributors of NPS pollution are agricultural and urban runoff (Sams *et al.*, 1999) and N, sediment, and P are the main pollutants of concern. Sediment loading has the greatest adverse impact across the US and in the near future the focus may shift to NPS pollution of pesticides and hormones from agricultural streams. Excessive nutrient loading

can lead to problems with drinking water, declines in commercial and recreational fisheries, increases in water temperature, elevation of pH levels, and consequent economic losses (USGS, 1999).

Major Stream Nutrients: N and P

Nutrients are necessary for the survival of all living organisms. The most important nutrients in aquatic ecosystems are typically P and N (East *et al.*, 1998; Leppakoski *et al.*, 1999). Excessive nutrient loadings in rivers and streams cause high autotrophic and heterotrophic production and may lead to accelerated eutrophication, especially in downstream reservoirs. Thus, streams with soluble reactive P (SRP) concentrations equal to or greater than 20 μg/L are usually not able to support large macrophyte communities due to extensive algal growth and lack of oxygen in the sediments (Barko *et al.*, 1991). The higher the autotrophs' number, the greater the community respiration and production rate, which often causes anoxia conditions and loss of aquatic organisms (Itkonen *et al.*, 1999; Lurry and Dunn, 1997; Tikkanen *et al.*, 1997). Anoxic conditions stimulate the release of many elements bound to benthic sediments, a phenomenon that reinforces algal growth and eutrophication, which in turn leads to a decline in water quality and biodiversity.

In many studies, trends in surface water nutrient loading are showing an increase in N flux and a decrease in P flux as a result of increased application of N-based fertilizers, increased improvements in Waste Water Treatment Plants, and decreased use of P-based detergents (Lurry and Dunn, 1997). In the Mississippi River basin excessive N loading is the major cause of hypoxia in the

Gulf of Mexico. However, in many aquatic ecosystems, excessive P is the primary cause of eutrophication, especially in Oklahoma (Morace and Snyder, 1997; Embrey and Inkpen, 1998; Sonzogni *et al.*, 1982; Oklahoma Conservation Commission, 1997).

Forms of P and N

There are three functional types of P in aquatic ecosystems, total dissolved P (TDP) consisting of dissolved inorganic (orthophosphate) (DIP) and dissolved organic P (DOP), particulate organic P and particulate inorganic P. These forms are involved in ecosystem assimilation and transformation. Dissolved inorganic P (DIP) is also associated with P sorption by the sediment. Exchangeable P is viewed as an intermittent form between DIP in the water column and inactive P in the sediment (Furumai *et al.*, 1989). Algae use alkaline phosphatase to convert DOP to DIP. Soluble Reactive P (SRP) is one frequently measured P form (House *et al.*, 1995), and is often called Murphy and Riley reactive P or dissolved reactive P. SRP represents the amount of reactive DIP and the fraction of reactive DOP passing through 0.45 μm GF filter. It is determined by the ascorbic acid method (Murphy and Riley, 1962) against freshly made P standards.

There are six basic forms of N: gaseous (N_2), ammonia (NH_3), ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and organic N; the last five forms are found in streams (Richey *et al.*, 1985). NH_4^+ is important in terms of its impact on streams because it is found in animal wastes and many ammonium fertilizers that are being extensively used in the agriculture (Richey *et al.*, 1985). Also, compared

to NO_3^- only a small fraction of NH_4^+ is found in streams, thus processes governing NH_4^+ transformation are important.

P Transportation in Streams

Both lentic (lakes) (Sonzogni *et al.*, 1982; Dorioz *et al.*, 1997) and lotic (rivers and streams) (Meyer, 1979; Hill, 1982; Klotz, 1985; Haggard *et al.*, 1999) ecosystems have been studied recently to understand the impact of PS and NPS pollution on P dynamics. A myriad of abiotic and biotic processes impact nutrient transport and transformation in aquatic systems. Among them are land use practices, atmospheric input, stream geology and vegetation availability as well as water velocity, discharge and chemical composition of the streambed sediment (Meyer *et al.*, 1988).

The nutrient spiraling concept is used to describe P utilization and transportation in lotic environments. DIP in the water column is eventually incorporated into living tissues of aquatic organisms. It can then be passed through several links of the aquatic food chain before is it released through an excretion or decomposition and made bioavailable as DIP. Since the cycle involves flowing water in streams, nutrients can travel a substantial distance downstream during the completion of one nutrient cycle. This process is often referred to as *nutrient spiraling* (Newbold *et al.*, 1981). The length of the spiral depends on the stream characteristics.

Self-purification is a natural process present in aquatic ecosystems which demonstrates the resilience of flowing water ecosystems. This process involves longitudinal depletion of the nutrient in the water column from the nutrient source.

Self-purification is most apparent in PS impacted streams (Hill, 1982), but the phenomenon has also been observed in undisturbed ecosystems with relatively low P concentrations (Meyer, 1979). Generally, stream water column SRP decreases downstream from an input of P as a result of biogeochemical processes (Tate *et al.*, 1995; Klotz, 1988; Richardson and Qian, 1999; House *et al.*, 1995). For example, Hill (1982), observed that SRP concentration declined from 300-700 μg/L to 10-50 μg/L within a 7-8 km reach in a PS impacted stream. Hill (1982) suggested that benthic sediments can be an important mechanism for P retention in streams.

The River Continuum Concept states that upstream processes impact downstream processes and that in lotic ecosystems materials undergo spiraling rather than cycling (Meyer, 1988). This theory is very important in understanding the effect of an upstream PS or a large storm event on the downstream community's structure and composition. During large storm (surface runoff) events nutrients entering the stream system are not significantly retained because the transport of nutrients with flowing water dominates. The River Continuum Concept and the Spiraling Concept suggest that upstream loading has a longitudinal effect; PS pollution may impact water column nutrient concentration for several km downstream (Meyer, 1988).

Flood Pulse Theory states the importance of the flood plain that acts as a sink or source for nutrients. The flood pulse is the major force that controls biota in the floodplain and that contributes to the movement of nutrients in and out of the lotic system (Junk *et al.*, 1985).

Phosphorus and Benthic Sediment

According to Bencala (1984), there are several factors that influence DIP dynamics in a stream: convection, dispersion, transient storage and benthic sediment retention. In stream systems benthic sediments have been suggested to control water column P (Klotz, 1988; Meyer, 1979), and sediment adsorption may provide a short- or a long-term buffer for increasing P loads in a stream (Haggard *et al.*, 1999). Self-purification in aquatic ecosystems is a direct result of sediment sorption and/or P precipitation and bryophyte uptake even in relatively undisturbed waterbodies (Meyer, 1979).

Equilibrium P Concentration (EPCo) is achieved when sediments are neither sorbing nor desorbing P from the water column (Taylor and Kunishi, 1971). EPCo may serve as a good predictor of whether benthic sediments are acting as a source or a sink of water column P. When water column SRP concentration is greater than EPCo, sediments sorb P from the water column and act as a P sink. When stream water SRP concentration is lower than EPCo, there may be a net release of P by benthic sediments and sediments act as a P source (House *et al.*, 1995; Meyer, 1979, Taylor and Kunishi, 1971). Inequilibrium between EPCo and water column P may indicate that some other factors, such as biotic uptake or a recent large storm event, contribute to the regulation of stream water P concentration (Haggard *et al.*, 1999). Taylor and Kunishi (1979) also observed that the difference between stream water SRP and benthic sediments EPCo decreases with distance from a PS in the tributary of Mahantango Creek, PA.

EPCo is pH dependent (the higher the solution pH, the lower the EPC_0), but no significant correlation between EPCo and temperature has been observed (Meyer, 1979; Klotz, 1988). Under equilibrium conditions, EPCo is reached more slowly under base flow than under high flow conditions (Taylor and Kunishi, 1971) as a result of water turbulence that dominates the amount of the water that is in direct contact with benthic sediments. EPCo is also positively correlated with the percent fine material (Haggard *et al.*, 1999; Klotz, 1988). The rate of a chemical reaction increases with an increase in the surface area of the substance to the volume ratio. This concept is applicable to the P sorption by benthic sediments; the greater the fraction of fine material in sediments, the faster the process of P sorption (Klotz, 1985; Meyer, 1979; Hill, 1982; Haggard *et al.*, 1999). Hill (1982) proposed that the factor responsible for different PSI values between two rivers receiving similar P input was the difference in particle size distribution. In his study of two agricultural and two forested streams, Klotz (1985) found that both the PSI level and the fraction of fine material were higher in agricultural streams than in forested streams and there was a significant correlation between the two variables (also see Meyer 1979). Haggard *et al.* (1999) also observed a high correlation between EPCo and percent silt. Phosphorus can bind to aluminum (Al) (Meyer, 1979; McLaughlin *et al.*, 1981) and iron (Fe) oxides (House *et al.*, 1995; Tate, 1995; McLaughlin *et al.*, 1981) to form insoluble precipitates. Phosphorus can also form co-precipitates with magnesium (Mg) (Gonsiorczyk *et al.*, 1998) and calcium (Ca) (House, 1990; House and Denison, 1998).

Under equilibrium conditions, sediments usually retain P during periods of base flow. At high discharge events, P is transported downstream while new sites for P uptake are created in the upstream zone from new sediments coming from the upland area. P retention is greatly influenced by the benthic sediments' chemical composition and particle size distribution (Meyer, 1979; Hill, 1982). Sediments with high sorption capacity make the P spiraling length shorter than sediments with low sorption capacity.

The ability of benthic sediments to sorb increasing amounts of P from the water column is called the sediment P buffering capacity and is measured by the P Sorption Index (PSI). High PSI values for a stream suggest that a large amount of P can be potentially sorbed by benthic sediments (Klotz, 1985). The sediment P buffering capacity is temperature dependent; the higher the temperature, the higher the reaction rate and the PSI values (Meyer, 1979; Bache and Williams, 1971). PSI is positively correlated with exchangeable Al, Fe, organic matter content and the finer fractions of the sediment particle size distribution (Klotz, 1988).

Although sorption-desorption processes by the sediment play a primary role in the P dynamics in aquatic ecosystems, P uptake by benthic algae, bryophytes and macrophytes can also influence this process (Klotz, 1985; Meyer, 1979). The benthic sediments may provide a bioavailable source of P. Sediment provided about 50% of P for the macrophytes' growth in the study of Barko *et al.* (1991) and up to 70% of P in the study conducted by Chambers *et al.* (1989). Benthic sediment bioavailable P (NaOH-Extractable P, SBAP) is usually equal to

or less than 60% of the total P in sediments, but this is highly dependent on the P source, water characteristics, size and composition of runoff and even atmospheric inputs (Sonzogni *et al.*, 1982). Klotz (1985), in his study of two agricultural and two forested streams, found that SBAP was higher in sediments collected from agricultural streams than in sediments collected from forested sites. He attributed it to the difference in particle size distribution as a result of the association of adsorbed P and finer fractions of sediment.

Exchangeable P ($MgCl_2$-Exctractable P, ExP) is loosely sorbed and readily exchangeable and is involved in exchange reactions between water column P and benthic sediments P (Ruttenburg, 1992) or DIP (Furumai *et al.*, 1989). Exchangeable P concentration is greater in eutrophic aquatic systems than in oligotrophic systems, representing 4-8% and 1-3% of the total P in the sediments, respectively, in the study of Gonsiorczyk *et al.* (1998).

Many biogeochemical processes control P dynamics in a stream. In some instances the sediment alone (Klotz, 1988) and in other cases the sediment in combination with macrophytes, algae and the microbial community can act as a buffer to increasing P loading to a stream (Haggard *et al.*, 1999; Chambers *et al.*, 1989).

Different hydrologic and physico-chemical characteristics of a stream and its watershed can influence P sorption by sediments. For example, land use practices influence the composition and amount of nutrients in a stream (Klotz, 1985; Taylor and Kunishi, 1971; Meyer *et al.*, 1988). Stream water velocity increases the contact between P in the water column and sediments (Meyer,

1979). According to Meyer (1979), the lower the water velocity, the greater the water contact with sediments and the greater the P removal rate from the water column. Under high water velocity condition, there is a greater sediment mass movement and a faster P loss from the sediment. EPCo, on the other hand, is reached slower under low flow compared to high flow conditions (Taylor and Kunishi, 1971). Also, the availability of suspended sediments provides a temporary sink of P (House *et al.*, 1995). According to House *et al.* (1995), during large storm events sorption by the suspended sediment can greatly exceed sorption by the stream benthic sediment (9% and 2.6%, respectively). Frequency and intensity of storm events can also regulate the amount of nutrients in the stream (Dorioz *et al.*, 1997; House *et al.*, 1995). The high density of the benthic sediment may provide greater surface area for P sorption (Sonzogni *et al.*, 1982). Sediment organic matter content can regulate DIP concentrations in the water column (House *et al.*, 1995). Thus, significant positive correlation has been observed between the amount of OM in benthic sediments and the sediment P buffering capacities (Meyer, 1979).

Biotic versus Abiotic P Sinks

Both biotic and abiotic processes influence water column P concentration in streams. Abiotic factors include benthic sediment sorption-desorption, and precipitation and dissolution equilibria. The most important biotic factors are microbial, algal and macrophyte uptake and mineralization.

Different studies have attempted to address the concept of sediment biotic vs. abiotic P sinks (Haggard *et al.*, 1999; Klotz, 1985; Klotz, 1988; House *et al.*,

1995; Hill, 1982; Meyer, 1979). These investigations have sometimes referred to biotic as 'live' and abiotic as 'dead' sediment P sorption (Haggard *et al.*, 1999; Klotz, 1985). 'Live' sorption is considered 'total' sorption because both biotic and abiotic factors are responsible for P uptake. The degree to which the sediment's physico-chemical composition dominates its biological characteristics has been investigated by autoclaving the sediment samples and comparing P sorption ability of 'live' versus autoclaved ('dead') sediment. Haggard *et al.* (1999) observed a significant difference between the sorption ability of 'live' and 'dead' sediments; as total sorption increased the importance of 'live' sorption increased. Furthermore, House *et al.* (1995) observed that 'live' sediment sorption dominated 'dead' sediment sorption in his study. However, Klotz (1988) found no significant difference between 'live' PSI and 'dead' sediments' PSI values. In Klotz's (1988) study the major controller of the sediment sorption ability was suggested to be abiotic factors, such as benthic sediment chemical (Fe and Al, organic matter content) and physical characteristics (sediment particle size distribution).

A wealth of studies have shown that sediment sorption is the main controller of P dynamics in streams (Meyer, 1979; Hill, 1982; Taylor and Kunishi, 1971). Thus, P uptake by the microbial and algal community was suggested to be insignificant in Mahantango Creek, PA (Taylor and Kunishi, 1971). An investigation in Bear Brook, an undisturbed stream in the Hubbard Brook Experimental Forest, also revealed that biological factors have a minor effect on P removal from the water column (Meyer, 1979). Meyer (1979) suggested that

microbial uptake is important in the P dynamics in a stream at low P concentration, whereas at high P concentration, P availability out-competes the ability of the biological community to consume and process this nutrient. Hill (1982) found that 44% of P input was retained in Nottawasaga River and 92% in Duffin Creek with the abiotic processes dominating P uptake, but macrophytes and algae were also substantial.

Stream Water Column SRP and Sediment EPCo

A significant positive correlation was observed between stream water SRP and sediment EPCo (Klotz, 1988; Taylor and Kunishi, 1979; Meyer, 1979). For instance, the correlation coefficient between the two variables in the study conducted by Klotz (1988) was equal to 0.979. In his next study (1991) stream water column SRP was correlated with the benthic sediment EPCo over the entire annual cycle. In addition, Meyer (1979) found that P added during the experiments in Bear Brook was removed from the water column by benthic sediments. However, following an artificial injection, P was not released back into the water column, indicating that either the rate of desorption is much slower or biotic sorption was important.

Seasonal Variability

House and Denison (1998) looked at seasonal variability in the P concentration in the water column and in sediments of the River Way in southern England. The greatest P availability was in spring and summer which was explained by low flow events during the spring/summer time and accumulation of small particles that were responsible for high sediment buffering capacity. Klotz

(1991) observed significant fluctuations in EPCo over an annual cycle. At one of the sites, the highest EPCo was obtained in the summertime, which was attributed to organic matter decomposition and P regeneration. At his next site, high EPCo during the summertime was explained by an increase in sediment P buffering capacity as a result of Ca accumulation during base flow events (Klotz, 1991).

Methodology and Limitations

Among factors that influence the measurement of P sorption by sediments are the experimental design and laboratory methodology. For example, the rate of shaking of sediments and solutions might have a significant influence on the outcome of the experiment as was observed by Hill (1982) and Bache and Williams (1971); P sorption by undisturbed sediments and soil was lower than P sorption by agitated sediments and soil. Other important factors might be the time period of equilibration of sediments and solutions (Taylor and Kunishi, 1971), methods used for solutions preparation (McLaughlin *et al.*, 1981) and the solid:solution ratio (Ruttenburg, 1992).

CHAPTER IV

MATERIALS AND METHODS

Study Area

Lakes Eucha and Spavinaw are located in the Ozark Plateau of northeastern Oklahoma and northwestern Arkansas (Figure 1). Since 1990 these impoundments have been the major source (56%) of the City of Tulsa's drinking water supply. However, the average P concentration in the Eucha Lake tripled between 1975 and 1995, and the average NO_3-N concentration doubled during the same time period (Oklahoma Conservation Commission, 1997). Lake Eucha was classified as eutrophic with P being the limiting nutrient in the system (Oklahoma Conservation Commission, 1997).

The primary land use in the reservoir is pasture and forest. The major agricultural activities are cattle and dairy operations, swine and poultry farming, row crop production and land application of animal waste. The primary WWTP in the Lake Eucha basin, located in the City of Decatur, Arkansas, gets its input mainly from the local community and a poultry processing plant. The effluent from the Decatur WWTP is discharged into Decatur Branch, a tributary of Columbia Hollow, one of the four selected streams in my investigation. Columbia Hollow also has significant NPS contributors. The other three streams are Dry

Creek, Cloud Creek, and Cherokee Creek, and are impacted by NPS pollution (Figure 1).

Dry Creek

Dry Creek is a shallow, relatively low NPS impacted 4th order stream that flows directly into Lake Eucha. The drainage area is 51.3 km^2 and the land use is 76% forest and 24% pasture (Table 1). The longitudinal and latitudinal coordinates for Dry Creek and other streams are given in Table 1. The 200 m study reach was mainly composed of riffles and runs. The sampling sites were located in a relatively unshaded portion of the channel with the riparian vegetation on one side of the stream. Aquatic macrophytes were absent from the study reach on the sampling dates and diatoms were present in the study reach all year round. The stream was chosen because it is a low NPS impacted stream.

Cloud Creek

Cloud Creek is directly east of Dry Creek. It is a relatively shallow 3rd order stream and drains an area of 47.2 km^2 consisting of 63% pasture, 36% forest and 1% urban land use. The 200 m study reach was slightly shaded by riparian vegetation.

Cherokee Creek

Cherokee Creek is a shallow 3rd order stream draining 50.2 km^2 area, composed of 66% pasture, 32% forest and 2% urban development. My 200 m study reach had variable canopy cover, varying from complete shading to open.

Both Cloud Creek and Cherokee Creek were selected because they are highly impacted by NPS pollution.

Columbia Hollow

Columbia Hollow is a 3rd order tributary of Spavinaw Creek draining a basin of 17.6 km^2. Four percent of the land is under urban development, 73% is pasture and 23% is forest. The benthic sediment was covered with a thick layer of filamentous periphyton.

Sample Collection and Preparation

Sediment samples were collected from each stream reach during base flow in the summer of 1999, winter of 2000 and summer of 2000. Benthic sediments were collected from the top 10-cm and composited along transects perpendicular to stream flow. Three composite samples were collected in a riffle, in a slow run and in a fast run (9 samples total) at each stream. A V-shaped device made of two 3' x 3' pieces of 1/2" plywood connected with two hinges was placed directly upstream of the sampling point to slow water velocity and to minimize small particle loss. The composite samples were placed in polyethylene bags, and stored on ice and in the dark until return to the laboratory. The benthic sediment samples from each stream were wet sieved through a 4.75-mm stainless steel mesh and stored in the refrigerator until utilized for extraction procedures. The temperature of all sediment samples, water samples and solutions was adjusted to room temperature before performing extractions.

Triplicate water samples were collected from each stream, filtered through a 0.7-μm Whatman® glass-microfibre filter into acid-washed polyethylene bottles

and preserved with H_2SO_4 at pH<2 and stored on ice until water chemistry analysis. Stream water conductivity was recorded on the sampling dates at each sampling site.

Laboratory Methods

Water Chemistry

Filtered surface water samples were analyzed for SRP, NO_3-N, NH_4-N and Cl^- concentration. NO_3-N was analyzed by the cadmium-copper reduction (QuikChem Method 10-107-04-1-A). NH_4-N was determined by the alkaline phenol, sodium hypochlorite and nitroprusside reaction (QuikChem Method 10-107-06-1-B). SRP was determined by the ascorbic acid method (Murphey and Riley, 1962). Chloride was analyzed by the mercuric thiocyanate method (QuikChem Method 10-117-07-1-C).

Phosphorus Sorption Index (PSI)

Sediment P buffering capacity was determined by measuring the P sorption index (PSI) using the method of Klotz (1988) and Bache and Williams (1971). Approximately 20-30 g of wet sieved sediment were placed in a 250 mL Erlenmeyer flask along with 96 mL of 0.03 M $CaCl_2$ solution, which stimulated ambient stream conductivity. Next, the solution was spiked with 4 mL of 50 mg/L KH_2PO_4 to achieve a final P concentration of 2000 µg/L. The flask was sealed with a rubber stopper and vigorously shaken for 10 sec every 10 min for a one hour interval. A 5 mL aliquot was separated from the solid phase using a polystyrene serological pipet and filtered through a 0.7-µm Whatman® glass

microfibre filter and 0.45-μm Cole-Parmer Filter Membrane. All samples in this extraction were diluted with 10 mL using reverse osmosis (RO) water. SRP was determined as previously described. The remaining sediment and solution was transferred into pre-labeled and pre-weighed Al pans and dried at 80° C for 48 h to express P sorption per unit dry weight. Benthic sediment PSI was determined via:

$$PSI = X/\mathrm{LOG}_{10}C$$

where *PSI* is the sorption index, *X* is the P adsorbed from the initial concentration of 2000 mg/L (mg P per g dry sediment) and *C* is the final P concentration in the solution after 1 h (mg/L) (Klotz, 1988; Bache and Williams, 1971).

In order to assess the biotic contribution to the buffering capacity of benthic sediments, I determined PSI on 'live' and 'dead' samples. Pre-weighed and pre-sieved sediment subsamples were first autoclaved for 25 min at 1.02 atm and 121 °C to create 'dead' samples. PSI was then determined. The input of the biotic component was calculated as the difference between 'live' (total) PSI minus 'dead' PSI.

Equilibrium P Concentration (EPCo)

EPCo is the concentration of the dissolved P in the water column when there is neither net sorption nor desorption of P by the stream sediment (Klotz, 1985; Klotz, 1988). EPCo was determined using the method suggested by Taylor and Kunishi (1971) as modified by Haggard *et al.* (1999). Approximately 9-11 g of pre-sieved wet sediments were placed in a 50 mL Erlenmeyer flask. Four P standards were used in the experiment, 0, 50, 100 and 150 μg P/L for Dry, Cloud

and Cherokee Creeks and 0, 2000, 4000 and 8000 μg P/L for Columbia Hollow. The P standards were made in $CaCl_2$ solution equivalent to the stream water ambient conductivity. In the summer of 2000, filtered stream water was also used to determine EPC_0 to assess the effects of using standard $CaCl_2$ solution. Fifty mL of P standard was added to sediment samples in the flasks. The sediment solutions were equilibrated for 60 min by shaking vigorously for 5 s every 15 min. Then, a 15 mL aliquot was taken using serological pipets and filtered through 0.7-μm Whatman® glass microfibre filter and 0.45-μm Cole-Parmer Filter Membrane. EPCo was determined by regressing the μg P sorbed per dry sediment weight (μg/g) vs. initial P concentration in the $CaCl_2$ solution or standard. EPCo was estimated as the x-intercept.

Exchangeable P ($MgCl_2$-Extractable P, ExP)

The method for $MgCl_2$-extractable P determination was described in Ruttenburg (1992) and modified by Haggard *et al.* (1999). Approximately 20-30 g of pre-sieved sediments were placed in a 250 mL flask and mixed with 100 mL of 1 M $MgCl_2$ solution. The samples were shaken for 5 s at 15 min intervals for 1 h. After incubation, a 15 mL aliquot was taken from the sediment solution using a 25 mL polystyrene serological pipet and filtered through 0.7-μm Whatman® glass microfibre filter and 0.45-μm Cole-Parmer Filter Membrane into a pre-labeled test tube for SRP determination. The remaining sediment solution was collected in a pre-weighed Al pan and oven-dried at 80 °C for 48 hours for dry weight determination.

Benthic Sediment Bioavailable P (NaOH-Extractable P, SBAP)

SBAP was determined following the method suggested by Sonzogni *et al.* (1982). Approximately 20-30 g of wet sieved sediments were extracted with 100 mL of 0.1 *N* NaOH solution in a 250 mL flask. The samples were mixed on a shaker for 5 s at 15 min intervals for 1 h. After the incubation, a 15 mL aliquot was taken from the sediment slurry using a 25 mL polystyrene serological pipet and filtered through a 0.7-μm Whatman® glass microfibre filter and a 0.45-μm Cole-Parmer Filter Membrane for SRP determination. The remaining sediment suspension was collected into a pre-weighed Al pan and oven-dried at 80 °C for 48 h for dry weight determination.

KCl-exchangeable NH_4-N, ExN

The method for determination of loosely sorbed or exchangeable NH_4-N was suggested in Bremner (1965) and described in Richey *et al.* (1985). Approximately 20-30 g of sieved sediments were extracted with 100 mL of 2 M KCl solution in 250 mL flasks. The sediment slurries were shaken vigorously for 5 s at 15 min intervals for 1 h. After incubation, 15 mL of the sediment solution was passed through a 0.7-μm Whatman® glass microfibre filter and a 0.45-μm Cole-Parmer Filter Membrane for NH_4-N determination. The alkaline phenol, sodium hypochlorite and nitroprusside reaction (QuikChem Method 10-107-06-1-B) and salicylate-nitroprusside method (QuikChem Method 10-107-06-2-A) were used to determine KCl-exchangeable NH_4-N. The remaining sediment suspension was collected into a pre-labeled Al pan and oven-dried at 80 °C for 48 h for dry weight determination.

Organic matter content (OM)

OM content of the sediment samples was determined using the loss-on-ignition method (Western States Laboratory Proficiency Testing Program, 1997). OM was calculated by weight loss after drying sediment samples at 360 °C in a muffle furnace for 2 h. Percent organic matter content (OM) was calculated from the equation:

$$OM=(W_2-W_3)/(W_3-W_1)*0.9$$

where W_1 is the Al pan weight, W_2 is the sample weight after 2 h drying at 150 °C, and W_3 is the final weight of the sample after 2 h burning at 360 °C and *0.9* is the correction coefficient.

Sediment particle size distribution

Particle size distribution was determined on a sediment subsample using the ASTM standard hydrometer method for fine silt and clay fractions and dry sieving for sand and silt fractions (ASTM, 1985). Samples were dried at 90 °C, then sieved through 2.00 mm, 600-, 300-, 150-, and 75-μm mesh. Size fraction was expressed as percent of total dry weight. USDA standard classification was used (sand - 2-0.05 mm, silt – 0.05-0.002 mm, clay - <0.002 mm).

Statistical Methods

Differences among streams and among seasons for each stream were evaluated using a 2 x 3 factorial arrangement of treatments in a completely randomized block design (CRBD). Regression technique was used to determine correlations between different characteristics of stream water column and benthic

sediment. Analysis of variance (ANOVA) was used to compare 'live' and autoclaved ('dead') PSI values as well as two methods for EPCo determination. In all cases, the significance level was set at $\alpha = 0.05$.

CHAPTER V

RESULTS

The statistical analysis of the data collected from July 1999 to August 2000 showed that the four selected streams differed with regard to their water chemistry composition, conductivity, their benthic sediment sorption ability, SBAP, $MgCl_2$-extractable P, and EPC_0 as well as KCl-extractable NH4-N. Furthermore, some seasonal differences were observed within each particular stream. In the 'Results' section the following abbreviations will be used: DC stands for Dry Creek, CLC stands for Cloud Creek, CHC stands for Cherokee Creek and CH stands for Columbia Hollow.

Water Chemistry and Benthic Sediment Composition

Stream water composition and conductivity are displayed in Table 2. NH_4-N was generally below the detection limit except in Columbia Hollow, a PS impacted stream, where NH_4-N ranged from 0.01 to 1.2 mg/L. Conversely, NO_3-N concentrations were significantly different among streams (CH>CHC=CLC>DC, ANOVA, Fisher's LSD, α=0.05). SRP concentrations were greatest in the PS impacted stream then decreased in proportion with agricultural land use in the upland. Chloride concentrations were also greater in Columbia Hollow than in the NPS impacted streams, whereas the other three streams had

similar concentrations (α=0.05). The stream water conductivity increased with an increase in percent agriculture.

Benthic sediment particle size distribution was similar across streams and seasons (α=0.05) (Table 3). After the sediment samples were sieved through a 4.75-mm mesh, the dominant fraction of the remaining sediments was sand, representing 73-92% of the total sample. Thus, the finer particles represented the smallest fraction of the benthic sediments in these streams. Percent organic matter content in all streams ranged from 0.8 to 3.0% (Table 4). Dry Creek had the lowest OM content, followed by Cloud Creek and Cherokee Creek (α=0.05). The highest organic matter measurement was in Columbia Hollow.

EPC_0 via $CaCl_2$ Solution Method

In all seasons, 0.03 M $CaCl_2$ solution was diluted to match stream water conductivity and used in the laboratory as a substitute for stream water. A statistical analysis using a completely randomized block design (CRBD) showed that EPC_0 obtained by this method was significantly higher in Columbia Hollow than in any of the other NPS impacted stream across all seasons (ANOVA, $p<0.0001$, α=0.05) (Table 4; Figure 2). Among NPS impacted streams, Cherokee Creek was significantly higher than Dry and Cloud Creeks in summer of 2000. EPC_0 remained homogeneous across all seasons for each creek with the exception of Cherokee Creek being higher in summer of 2000 than in all other seasons (Table 5).

When all the data for Columbia Hollow and NPS impacted streams were grouped together, there was a significant positive correlation between stream

water column SRP and EPC_0 (R=0.99, α=0.05) (Figure 3). This high correlation is probably due to the data grouping (SRP ranged from 13-80 μg/L in NPS impacted streams to 2200-3200 μg/L in Columbia Hollow and EPC_0 ranged from 5-30 μg/L in NPS impacted streams to 1000-1100 μg/L in Columbia Hollow). Therefore, there were two groups of data, one was at the low end and another one was at the upper end. However, a relatively low but significantly positive correlation (R=0.6, α=0.05) between these variables was observed for NPS impacted streams only (Figure 4). Moreover, benthic sediment EPC_0 was not related to water column SRP (R=0.11, α=0.05) when the data were plotted only for Columbia Hollow (Figure 5). These observations suggest that EPC_0 may peak at extremely high SRP concentrations in these streams.

Benthic sediment EPC_0 obtained by the $CaCl_2$ solution method was lower than stream water SRP, being about 35-60% of the SRP (Table 6). P-values for the difference between water column SRP and benthic sediment EPC_0 and percent EPC_0 calculated as SRP are listed in Table 6. There was no significant correlation between EPC_0 and the benthic sediment sand, clay, silt and clay+silt fractions, and organic matter content in any of theses streams (Table 7-11).

EPC_0 via Stream Water Method

In summer 2000, filtered stream water was used to determine if the differences between EPC_0 and water column SRP resulted from using a $CaCl_2$ solution to stimulate the stream water conductivity. As was determined for the $CaCl_2$ method, the highest EPC_0 measurement obtained using the stream water method was recorded for Columbia Hollow ($p<0.0001$, $\alpha<0.05$) (Table 4). Among

solution and found a positive difference between water column SRP and EPC_0 only at Council Creek, a negative difference between the variables at Little Stillwater Creek and approximately no difference at Feather Creek. However, when I used stream water collected directly from the streams in summer of 2000, EPC_0 was not significantly different from stream water column SRP in Dry Creek and Columbia Hollow, and lower than stream water SRP in Cloud and Cherokee Creeks.

When an equilibrium exists between stream water SRP and benthic sediment EPC_0, then sorption/desorption processes by the benthic sediment may play a dominant role in the P dynamics in the stream. When there is no such equilibrium, benthic sediments might not be a dominant factor controlling stream water column SRP (Haggard *et al.*, 1999). However, the rates of sorption/desorption by the benthic sediments might still be significant. Assuming that the first method of EPC_0 determination using $CaCl_2$ solution is accurate, benthic sediments were not in equilibrium with the stream water column SRP and benthic sediments acted as a P sink.

There is reason to believe that the stream water method may be more representative. Although 0.03 M $CaCl_2$ solution was diluted to match stream water conductivity, it might have overestimated the amount of Ca^{2+} in the solution. Klotz (1988) used several solutions of different $CaCl_2$ concentrations; the higher the concentration of Ca^{2+} in the solution and the ionic strength of the solution, the lower the EPC_0. This might explain such low EPC_0 values in my streams. However, Klotz (1988) did not evaluate differences in EPC_0 using

(Table 10), although there was a significant but low positive correlation between SBAP in Cherokee Creek and the clay fraction of the benthic sediment (R=0.53, α=0.05) (Table 9).

$MgCl_2$-extractable P (Exchangeable P) in Columbia Hollow, a PS impacted stream, was significantly greater than in the NPS impacted streams at α=0.05 (Table 4). In summer of 1999 ExP in Cherokee Creek was significantly higher than in Dry and Cloud Creeks, but the amount of ExP in the benthic sediments was similar during the other sampling dates (Table 4). Also, ExP varied across seasons. In Dry, Cloud and Cherokee Creeks the highest measurement was taken in summer of 1999 and in Columbia Hollow the highest measurement was recorded in summer of 2000 (Table 5). The amount of ExP in Columbia Hollow was positively correlated with the percent organic matter (R=0.58, α=0.05) (Table 11). However, there was no relationship between particle size distribution and ExP. Although there was a relatively high positive correlation between ExP and SBAP in Cherokee Creek (R=0.45, α=0.05) (Table 9) and in the combination of all NPS impacted streams (R=0.32, α=0.05) (Table10), ExP represented 8% of SBAP in Dry Creek, 5% in Cloud Creek, 10% in Cherokee Creek and 13% in Columbia Hollow.

KCl-extractable NH_4-N did not differ across all streams in summer of 1999, was significantly higher in Cherokee Creek than in any other stream in winter of 2000, and varied dramatically in summer of 2000 (CLC>CHC=DC>CH ANOVA, Fisher's LSD, α=0.05) (Table 4). There was a significant difference across the seasons for each stream, with summer of 2000 measurements being the highest

(Table 5). Also, there was no significant correlation between KCl-extractable NH_4-N and stream water NO_3 at α=0.05. In Columbia Hollow, KCl-extractable NH_4-N was positively correlated with the percent organic matter content (R=0.52, α=0.05).

Benthic Sediment Buffering Capacity

PSI of the 'live' benthic sediments, although low, varied across streams with Cherokee Creek having the highest sediment P buffering capacity in all three seasons and Columbia Hollow having the lowest sediment P buffering capacity (Table 4, Figure 8). Moreover, each stream had seasonal variations with winter samples having the highest sediment buffering capacity across all streams (Table 5). In contrast to PSI of the 'live' sediments, PSI of the 'dead' (autoclaved) sediments did not differ across streams except for summer of 2000 and there was no seasonal difference for each stream.

An analysis of variance between 'live' and 'dead' sediment PSI revealed that there was no significant difference between the two variables in Dry Creek ($p<0.72$, α=0.05) and in Cloud Creek ($p<0.13$, α=0.05). In Cherokee Creek PSI of the 'live' benthic sediments was significantly higher than PSI of the 'dead' sediments ($p<0.00043$, α=0.05), and in Columbia Hollow PSI of the 'dead' sediments was significantly higher than PSI of the 'live' sediments ($p<0.0001$, α=0.05).

CHAPTER VI

DISCUSSION

P and N Pools

Similar to findings of Haggard *et al.* (1999), the statistical analysis of the data showed that benthic sediment P attributes measured in this study were not correlated with sediment organic matter content or sediment particle size distribution. This is an unusual finding because many researchers have found the opposite; a strong correlation between sediment P attributes and sediment particle size distribution (Klotz, 1985; Meyer, 1979; Hill, 1982) and sediment P attributes and sediment organic matter content (Meyer, 1979).

Benthic sediments from all four selected streams used in my experiment had sand as the dominant fraction of the fine sediment content, representing on average 83% of the total sample. The pooled samples from all streams were not significantly different in their sand, silt and clay fractions (ANOVA, α=0.05). In contrast, Duffin Creek and Nottawasaga River in the study of Hill (1982) had a six fold difference in the clay content (25% and 4%, respectively), which might have influenced the difference in the sediment P sorption capacity. So, absence of correlation between benthic sediment P and the sediment particle size distribution might be a direct result of the similarity of the benthic sediment

particle size distribution among streams and the low sediment silt and clay content of the samples. Among NPS impacted streams, sediment organic matter content was the lowest in Dry Creek, and the highest in Cherokee Creek. Low organic matter content in Dry Creek could be explained by the low in-stream productivity. Relatively high organic matter content in Cherokee Creek could be a direct result of manure from cattle that have direct access to the stream. Although organic matter content varied among streams, the range of variation may not have been significant enough to influence benthic sediment P interactions, which may explain the absence of correlation between organic matter content and benthic sediment P.

The amount of SBAP increased with increased water column SRP concentration in each stream; the greater the amount of P in the stream water column, the greater the amount of P potentially available for algal and macrophyte growth. The ratio of the P distribution between the benthic sediment and the water column indicated that there is more SRP present in 1 g of the benthic sediments than in 1 g of the water column in each stream (Figure 7).

Also, the amount of Exchangeable P ($MgCl_2$-Exctractable P) in Columbia Hollow, a PS impacted stream, was significantly higher than in NPS impacted streams which indicates that more P is involved in the exchange reactions between water column and benthic sediments in the highly impacted system. Similar results were obtained by Gonsiorczyk *et al.* (1998) when the amount of exchangeable P was higher in eutrophic than in oligotrophic lakes. There was 5-10% of the ExP represented as SBAP in NPS impacted streams and 13% in

Columbia Hollow. Increases in the fraction of exchangeable P in SBAP form from NPS impacted streams to Columbia Hollow could be explained by the increasing concentration of SBAP from the least to the most impacted stream. However, the easily exchangeable P represented only a small part of the SBAP in these streams.

In Columbia Hollow the amount of KCl-extractable NH_4-N was about two times lower than the amount of $MgCl_2$-extractable P. There is probably not much benthic sediment adsorptive capacity for NH_4-N when there is an excess of P. However, in Dry, Cloud and Cherokee Creeks, the amount of readily exchangeable P was low, ranging from 0.03 to 0.27 μg/g, which might be the reason why KCl-extractable NH_4-N level is higher in these streams. Relatively high concentration of KCl-extractable NH_4-N in Columbia Hollow might be a *direct result of a high positive correlation* of KCl-extractable NH_4-N with organic matter content. Similar findings were observed in the study of Richey *et al.* (1985). He observed that the sediment organic matter content could retain inputs of dissolved nitrogen However, the mechanism of nitrogen retention in NPS impacted streams remains unclear.

Control of P by Benthic Sediments

When I used 0.03 M $CaCl_2$ solution diluted to the conductivity level of the stream water on the sampling date, at all sites water column SRP was greater than EPC_0 by 2-3 times. Similar results were observed by Klotz (1988), when he tested six sites along Hoxie Gorge Creek using $CaCl_2$ solution. Haggard *et al.* (1999), in his study of three northcentral Oklahoma streams, also used $CaCl_2$

solution and found a positive difference between water column SRP and EPC_0 only at Council Creek, a negative difference between the variables at Little Stillwater Creek and approximately no difference at Feather Creek. However, when I used stream water collected directly from the streams in summer of 2000, EPC_0 was not significantly different from stream water column SRP in Dry Creek and Columbia Hollow, and lower than stream water SRP in Cloud and Cherokee Creeks.

When an equilibrium exists between stream water SRP and benthic sediment EPC_0, then sorption/desorption processes by the benthic sediment may play a dominant role in the P dynamics in the stream. When there is no such equilibrium, benthic sediments might not be a dominant factor controlling stream water column SRP (Haggard *et al.*, 1999). However, the rates of sorption/desorption by the benthic sediments might still be significant. Assuming that the first method of EPC_0 determination using $CaCl_2$ solution is accurate, benthic sediments were not in equilibrium with the stream water column SRP and benthic sediments acted as a P sink.

There is reason to believe that the stream water method may be more representative. Although 0.03 M $CaCl_2$ solution was diluted to match stream water conductivity, it might have overestimated the amount of Ca^{2+} in the solution. Klotz (1988) used several solutions of different $CaCl_2$ concentrations; the higher the concentration of Ca^{2+} in the solution and the ionic strength of the solution, the lower the EPC_0. This might explain such low EPC_0 values in my streams. However, Klotz (1988) did not evaluate differences in EPC_0 using

$CaCl_2$ solution and stream water. Since the two methods were applied simultaneously only in summer of 2000, there is not enough evidence to draw a definitive conclusion. Further investigation is required to determine the appropriate methodology.

Assuming that the stream water method is more accurate, then benthic sediment EPC_0 in Dry Creek and Columbia Hollow were in equilibrium with water column SRP. In addition, based on the stream water method, benthic sediments from Cloud and Cherokee Creeks are not in equilibrium with the water column SRP and act as a P sink.

House *et al.* (1995) suggested that during large storm events suspended sediment can sorb P from the water column, reducing SRP and thus create an imbalance between these two parameters. However, benthic sediments in Dry Creek and Columbia Hollow were sampled only during base flow events, when suspended sediment is least available in the water column. Thus, this factor could not have a significant effect on the equilibrium between water column SRP and sediment EPC_0 in these streams. In summary, the two laboratory procedures used for EPC_0 determination showed that benthic sediments act as a P sink in Cloud Creek and Cherokee Creek only, however, further research is required to determine the role of benthic sediments in Dry Creek and Columbia Hollow.

The Role of Benthic Sediment in P Dynamics

Based on results obtained using the two EPC_0 methods, it is difficult to determine if benthic sediments act as a P sink for the stream water column SRP

or if benthic sediments are the only controller of the stream water column SRP in all four selected streams. However, it is clear that benthic sediments play a very important role in P dynamics in all selected streams. As anticipated, the PS impact had the greatest effect on the benthic sediment P sorption ability compared to the NPS impact. The P sorption indices show that Dry, Cloud and Cherokee Creeks have potentially more capacity to sorb SRP from the water column than Columbia Hollow. P sorption indices varied from summer to winter for all streams, being the highest in winter of 2000. This is a surprising finding, because Klotz (1991) in his study of the Hoxie Gorge Creek over an annual cycle observed higher EPC_0 and sediment buffering capacity during the base summer flow conditions. He explained it by increased sediment sorption ability in the summertime which in turn can potentially lead to increases in EPC_0.

If biological factors play a significant role in the P removal from the water column, then PSI of the 'live' sediments should be higher than PSI of the 'dead' sediments (Haggard *et al.*, 1999). If biological factors play a minor part in this process, then PSI of the 'live' sediments should be approximately the same as PSI of 'dead' sediments (Klotz, 1985; Meyer, 1979). When benthic sediments were autoclaved to eliminate the impact of biological activity, abiotic control was the same across all seasons and streams. In Dry and Cloud Creeks the 'dead' (autoclaved) sediments showed the same P buffering capacity as 'live' sediments proving that the biotic factors are not significant in the P dynamics in these streams. Conversely, in Cherokee Creek biotic sorption was greater than abiotic suggesting that there was a substantial contribution of the biological community,

which could be a direct result of the manure from cattle that had an access to the sampling reach used in the experiment.

In Columbia Hollow PSI of the 'live' sediments was lower than PSI of the dead sediments. This is a conflicting finding, because many researchers observed the opposite. Such inconsistency could be explained by several factors. First, the autoclaving used in this experiment might have changed the sediments physical characteristics, thus allowing greater surface to volume ratio and higher sediment buffering capacity of the 'dead' sediments from Columbia Hollow. Secondly, autoclaving might have destroyed the cells of the biocommunity in the sediment samples, which in turn triggered the release of P and increased the sediment P buffering capacity. Thirdly, the time period between 'dead' and 'live' sediments PSI determination might have had an impact on the results in Columbia Hollow. In this experiment, due to logistical constraints, PSI of the 'dead' sediments was determined a few weeks after the sample collection. Despite the above mentioned possible explanations for such difference between 'live' and 'dead' sediments PSI, the results of this experiment should be interpreted cautiously.

CHAPTER VII

CONCLUSIONS

Two separate opinions regarding the transport and transformation of DIP in aquatic systems exist in this area. First of all, some investigators demonstrated that benthic sediments alone control P dynamics in streams (Meyer, 1979; McLaughlin et al., 1981; Klotz, 1988) and the influence of the biological community is not significant. In the study conducted by Haggard *et al.* (1999), benthic biological activity has a substantial influence on the P sorption rate by the sediments. However, many researchers agree that benthic sediments play an important part in the sorption/desorption processes that occur in aquatic ecosystems.

Limitations of the methodology used in my experiment influenced the results of the experiment and prevented me from drawing definite conclusions about the degree of significance of the biological input to the P sorption in Columbia Hollow. However, it is clear that natural benthic sediment buffering capacity, although significant, is relatively low in all selected streams.

Assuming that stream water method is the most accurate for EPCo determination, then benthic sediments in Cloud and Cherokee Creeks acted as a P sink to the stream water SRP in summer of 2000. Benthic sediments in Dry Creek and Columbia Hollow were in equilibrium with

stream water SRP. Assuming that the $CaCl_2$ solution method for EPCo determination is the most representative, then benthic sediments acted as P sink for water column SRP in all streams in summer of 1999 and in summer of 2000. However, it is also clear that benthic sediments in Columbia Hollow, a PS impacted stream, are less able to control water column P and buffer increasing P concentrations compared to Dry Creek, Cloud Creek and Cherokee Creek.

CHAPTER VIII

SUGGESTIONS FOR FURTHER RESEARCH

I would like to make several suggestions for future researchers in this area concerning some difficulties that I have encountered in the course of my research project. First of all, I was not able to determine the appropriate method for EPC_0 determination; whether diluted 0.03 M $CaCl_2$ solution gives a fair representation of the in-stream conditions, or just an approximate one and stream water should be used instead. I suggest performing several experiments for EPC_0 determination using both methods and compare the results.

Secondly, I did not determine the appropriate time period between field sediment collection and laboratory analysis. To ascertain the difference between PSI for 'live' and 'dead' sediments, I suggest performing the extraction on 'live' and autoclaved sediment samples simultaneously directly following sample collection, and then every other day for a certain period of time to determine when the indices start to change and by how much. I would replicate this experiment several times

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Table 1. Land use practices and Universal Transverse Mercator (UTM) coordinates for four northeastern Oklahoma and northwestern Arkansas watersheds.

	Urban, %	Forest, %	Agriculture, %	X Coordinate	Y Coordinate
Dry Creek	<1	76	24	335,203	4,020,509
Cloud Creek	1	36	63	342,111	4,020,753
Cherokee Creek	2	32	66	351,278	4,017,510
Columbia Hollow	4	23	73	365,232	4,022,690

Table 2. Mean ambient NO_3-N, NH_4-N, Cl^-, Soluble Reactive Phosphorus (SRP) concentrations and conductivity in four northeastern Oklahoma and northwestern Arkansas streams.

Date	NO_3-N, mg/L	NH_4-N, mg/L	Cl^-, mg/L	SRP, mg/L	Conductivity, µs/cm
Dry Creek					
Summer (7-27-1999)	0.5	<0.03	7.2	0.013	130
Winter (12-14-1999)	1.0	<0.03	9.3	0.016	117
Summer (6-19-2000)	0.8	<0.03	25	0.020	120
Cloud Creek					
Summer (8-03-1999)	1.5	<0.03	7.3	0.035	130
Winter (12-14-1999)	2.4	<0.03	4.5	0.020	150
Summer (7-18-2000)	1.4	<0.03	17	0.042	145
Cherokee Creek					
Summer (7-21-1999)	2.7	<0.03	6.8	0.031	211
Winter (12-14-1999)	2.3	<0.03	9.2	0.020	285
Summer (7-31-2000)	2.8	<0.03	18	0.080	267
Columbia Hollow					
Summer (8-11-1999)	6.4	0.06	29	2.6	370
Winter (1-06-2000)	13.0	1.20	56	2.2	445
Summer (8-16-2000)	6.8	0.01	190	3.2	330

Table 3. Mean particle size distribution and organic matter content (OM) of benthic sediments from four northeastern Oklahoma and northwestern Arkansas streams (percent by weight for dry samples).

Date	Sand[1], %	Silt[2], %	Clay[3], %	OM, %
Dry Creek				
Summer (7-27-1999)	87	8	5	1.0
Winter (12-14-1999)	88	7	5	0.9
Summer (6-19-2000)	92	4	4	0.9
Cloud Creek				
Summer (8-03-1999)	77	16	7	1.6
Winter (12-14-1999)	84	11	5	0.8
Summer (7-18-2000)	84	12	4	1.1
Cherokee Creek				
Summer (7-21-1999)	85	9	6	1.4
Winter (12-14-1999)	73	20	7	1.3
Summer (7-31-2000)	86	7	7	1.3
Columbia Hollow				
Summer (8-11-1999)	81	10	9	1.8
Winter (1-06-2000)	88	7	5	1.4
Summer (8-16-2000)	83	9	8	3.0

([1] 2-0.05 mm, [2] 0.05-0.002 mm, [3] <0.002 mm)

Table 4. Means and differences among streams for EPC_0, SBAP, ExN, ExP, OM and 'live' PSI (values in a row with the same letter are not significantly different, values in a row with different letters are significantly different from each other at α=0.05).

Variable	Dry Creek	Cloud Creek	Cherokee Creek	Columbia Hollow
Equilibrium Phosphorus Concentration (EPC_0), µg/L, $CaCl_2$ method				
Summer'99	5.4**a**	10.5**a**	11.2**a**	1103**b**
Winter'00	n/a	18.3**a**	11.9**a**	n/a
Summer'00	11.6**a**	14.6**a**	30.7**b**	1090**c**
Equilibrium Phosphorus Concentration (EPC_0), µg/L, stream water method				
Summer'00	17**b**	8.4**a**	31**c**	3330**d**
Benthic sediment bioavailable Phosphorus (SBAP), µg/g				
Summer'99	0.4**a**	0.6**b**	2.2**c**	25**d**
Winter'00	0.6**a**	2.3**b**	2.3**b**	40**c**
Summer'00	0.3**a**	1.1**b**	0.3**a**	23**c**
Exchangeable NH_4-N (KCl-extractable NH_4-N) (ExN), µg/g				
Summer'99	1.0**a**	0.8**a**	1.7**a**	1.4**a**
Winter'00	1.4**a**	1.7**a**	5.0**b**	1.8**a**
Summer'00	4.0**b**	5.2**c**	4.6**c**	2.7**a**
Exchangeable Phosphorus ($MgCl_2$-Exctractable P) (ExP), µg/g				
Summer'99	0.13**a**	0.13**a**	0.27**b**	2.8**c**
Winter'00	0.04**a**	0.05**a**	0.07**a**	2.6**b**
Summer'00	0.03**a**	0.04**a**	0.04**a**	4.6**b**
Organic Matter Content (OM), %				
Summer'99	1.0**a**	1.6**b**	1.4**b**	1.8**b**
Winter'00	0.9**a**	0.8**a**	1.3**b**	1.4**b**
Summer'00	0.9**a**	1.1**ab**	1.3**b**	3.0**c**
Phosphorus Sorption Index (PSI) for 'live' sediments				
Summer'99	3.4**c**	2.1**b**	3.6**c**	0.4**a**
Winter'00	4.1**c**	3.5**b**	4.4**c**	1.4**a**
Summer'00	3.7**b**	3.4**b**	4.5**c**	1.1**a**

Table 5. Means and differences across seasons for EPC_0, SBAP, ExN, ExP, OM, and 'live' PSI (values in a row with the same letter are not significantly different, values in a row with different letters are significantly different from each other at α=0.05).

Variable	Summer'99	Winter'00	Summer'00
Equilibrium Phosphorus Concentration (EPC_0), μg/L			
Dry Creek	5.4a	n/a	11.6a
Cloud Creek	10.5a	18.3a	14.6a
Cherokee Creek	11.2a	11.9a	30.7b
Columbia Hollow	1103a	n/a	1090a
Benthic sediment bioavailable Phosphorus (BAP), μg/g			
Dry Creek	0.4a	0.6a	0.3a
Cloud Creek	1.6b	2.3c	1.1a
Cherokee Creek	2.2b	2.3b	0.3a
Columbia Hollow	25a	40b	23a
Exchangeable NH_4-N (KCl-extractable NH_4-N) (ExN), μg/g			
Dry Creek	1.0a	1.4a	4.0b
Cloud Creek	0.8a	1.7a	5.2b
Cherokee Creek	1.7a	5.0b	4.6b
Columbia Hollow	1.4a	1.8a	2.7b
Exchangeable Phosphorus ($MgCl_2$-Exctractable P) (ExP), μg/g			
Dry Creek	0.13b	0.04a	0.03a
Cloud Creek	0.13b	0.05a	0.04a
Cherokee Creek	0.27b	0.07a	0.04a
Columbia Hollow	2.8a	2.6a	4.6b
Organic Matter Content (OM), %			
Dry Creek	1.0a	0.9a	0.9a
Cloud Creek	1.6b	0.8a	1.1a
Cherokee Creek	1.4a	1.3a	1.3a
Columbia Hollow	1.8a	1.4a	3.0b
Phosphorus Sorption Index (PSI) for 'live' sediments			
Dry Creek	3.4a	4.1b	3.7a
Cloud Creek	2.1a	3.5b	3.4b
Cherokee Creek	3.6a	4.4b	4.5b
Columbia Hollow	0.4a	1.4c	1.1b

Table 6. ANOVA p-values for the difference between stream water Soluble Reactive Phosphorus (SRP) and benthic sediment Equilibrium Phosphorus Concentration (EPC_0) obtained by the $CaCl_2$ method in summer of 1999 and summer of 2000 and obtained by the stream water method in summer of 2000. EPC_0as a fraction of SRP, calculated as *EPC_0/SRP*. DC – Dry Creek, CC – Cloud Creek, CHC – Cherokee Creek, CH – Columbia Hollow.

Season	Parameter	DC	CLC	CHC	CH
		$CaCl_2$ Solution Method			
Summer'99	p-value	0.0054	0.0262	<0.0001	<0.0001
	SRP/EPC_0 Ratio	0.42	0.34	0.36	0.42
Summer'00	p-value	<0.0001	<0.0001	<0.0001	<0.0001
	SRP/EPC_0 Ratio	0.57	0.34	0.36	0.34
		Stream Water Method			
Summer'00	p-value	0.73	<0.0001	<0.0001	0.032
	SRP/EPC_0 Ratio	0.92	0.20	0.36	1.04

Table 7. Pearson Correlation matrix (Prob > |r| under H_0: Slope=0) for Dry Creek across all seasons.

	'Live' PSI	'Dead' PSI	ExP	ExN	OM	BAP	EPC_0	Sand	Silt	Clay	Clay+Silt
'Live' PSI	1										
'Dead' PSI	0.207	1									
ExP	-0.236	-0.249	1								
ExN	0.179	0.275	-0.385	1							
BAP	0.122	-0.13	-0.309	-0.405*	1						
OM	0.154	0.075	0.148	0.047	-0.235	1					
EPC_0	0.055	-0.189	-0.669*	0.339	0.141	-0.188	1				
Sand	0.08	-0.06	-0.13	-0.100	-0.64	0.357	0.278	1			
Silt	-0.11	0.000	0.159	0.066	0.59	-0.35	-0.31	-0.98	1		
Clay	-0.02	0.17	0.057	0.136	0.66	-0.32	-0.18	-0.93	0.83	1	
Clay+Silt	-0.08	0.06	0.127	0.096	0.64	-0.36	-0.28	-1.00	0.98	0.93	1

**Significant at α=0.05.*

Table 8. Pearson Correlation matrix (Prob > |r| under H_0: Slope=0) for Cloud Creek across all seasons.

	'Live' PSI	'Dead' PSI	ExP	ExN	OM	BAP	EPC_0	Sand	Silt	Clay	Clay+Silt
'Live' PSI	1										
'Dead' PSI	0.417*	1									
ExP	-0.573*	-0.231	1								
ExN	0.603*	0.121	-0.381*	1							
BAP	-0.053	0.303	0.036	-0.546*	1						
OM	-0.235	-0.132	0.385*	-0.014	-0.322	1					
EPC_0	0.236	0.312	0.347	0.064	0.286	0.142	1				
Sand	0.15	-0.08	-0.21	0.026	-0.48	-0.06	-0.02	1			
Silt	-0.17	0.066	0.189	-0.09	0.49	0.12	0.041	-0.99	1		
Clay	-0.06	0.117	0.219	0.156	0.36	-0.11	-0.06	-0.85	0.75	1	
Clay+Silt	-0.15	0.083	0.206	-0.03	0.48	0.06	0.018	-1.00	0.99	0.85	1

**Significant at α=0.05.*

Table 9. Pearson Correlation matrix (Prob > |r| under H_0: Slope=0) for Cherokee Creek across all seasons.

	'Live' PSI	'Dead' PSI	ExP	ExN	OM	BAP	EPC_0	Sand	Silt	Clay	Clay+Silt
'Live' PSI	1										
'Dead' PSI	0.238	1									
ExP	-0.412*	0.049	1								
ExN	0.409*	0.155	-0.707*	1							
OM	0.072	0.117	0.177	-0.125	1						
BAP	0.119	0.267	0.452*	-0.252	0.334	1					
EPC_0	0.469*	0.133	-0.353	0.266	-0.212	-0.559*	1				
Sand	-0.30	-0.[illegible]	0.08	-0.15	0.124	-0.18	-0.28	1			
Silt	0.273	0.[illegible]92	-0.17	0.188	-0.23	0.067	0.321	-0.98	1		
Clay	0.292	0.[illegible]21	0.255	-0.04	0.296	0.525*	0.057	-0.75	0.61	1	
Clay+Silt	0.297	0.[illegible]92	-0.08	0.149	-0.12	0.177	0.284	-1.00	0.98	0.75	1

**Significant at α=0.05.*

Table 10. Pearson Correlation matrix (Prob > |r| under H_0: Slope=0) for all nonpoint source impacted streams across all seasons.

	'Live' PSI	'Dead' PSI	ExP	ExN	OM	BAP	EPC_0	Sand	Silt	Clay	Clay+Silt
'Live' PSI	1										
'Dead' PSI	0.253*	1									
ExP	-0.213	-0.134	1								
ExN	0.429*	0.081	-0.346*	1							
OM	-0.005	-0.085	0.295*	0.077	1						
BAP	-0.029	-0.096	0.317*	0.135	0.2	1					
EPC_0	0.347*	-0.029	-0.134	0.240*	0.128	-0.019	1				
Sand	-0.13	0.03	-0.05	-0.07	-0.37	-0.24	0.128	1			
Silt	0.122	-0.05	0.034	0.07	0.321	0.228	-0.12	-0.98	1		
Clay	0.128	0.05	0.072	0.074	0.43	0.223	-0.11	-0.83	0.71	1	
Clay+Silt	0.131	-0.03	0.046	0.075	0.368	0.24	-0.13	-1.00	0.98	0.83	1

**Significant at α=0.05.*

Table 11. Pearson Correlation matrix (Prob > |r| under H_0: Slope=0) for Columbia Hollow across summer of 1999 and summer of 2000.

	'Live' PSI	'Dead' PSI	ExP	ExN	OM	BAP	EPC_0	Sand	Silt	Clay	Clay+Silt
'Live' PSI	1										
'Dead' PSI	0.246	1									
ExP	0.123	0.136	1								
ExN	0.255	-0.235	0.513*	1							
OM	-0.248	-0.194	0.581*	0.515*	1						
BAP	0.453*	0.231	-0.436*	-0.215	-0.385*	1					
EPC_0	-0.019	-0.131	-0.144	-0.073	-0.181	-0.04	1				
Sand	0.23	0.468	0.182	0.064	-0.11	0.301	0.217	1			
Silt	-0.09	-0.29	-0.08	0.103	0.08	-0.33	0.035	-0.78	1		
Clay	-0.15	-0.43	-0.09	-0.12	0.2	-0.11	-0.24	-0.78	0.31	1	
Clay+Silt	-0.15	-0.44	-0.11	-0.01	0.172	-0.27	-0.12	-0.96	0.82	0.8	1

**Significant at α=0.05.*

Table 12. Analysis of variance, p-value for the difference* between two methods of EPC_0 determination: $CaCl_2$ solution vs. stream water.

Source of Var	SS	df	MS	F	P-value	F crit
Between Groups	1852988	1	1852988	1.49	0.2350	5.38
Within Groups	27347932	22	1243088			

** H_0: There is no difference between two methods of EPC_0 determination. H_A: There is a difference between two methods of EPC_0 determination.*

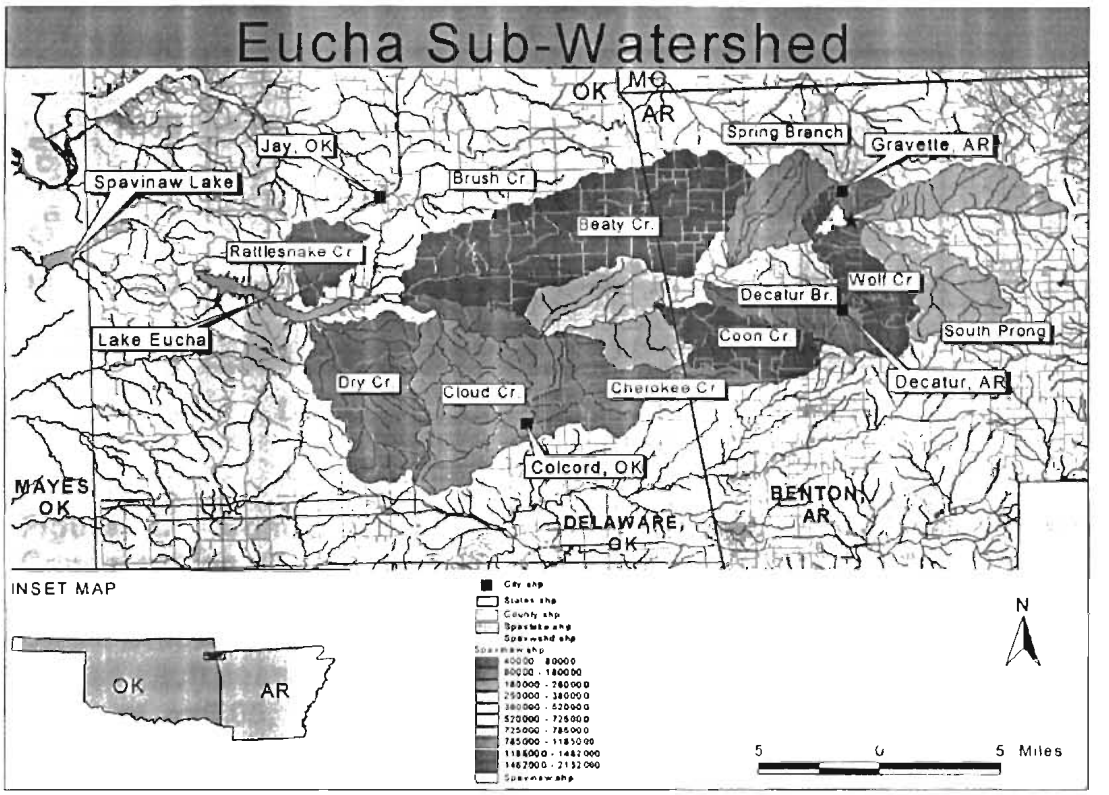

Figure 1. Lake Eucha basin and its tributaries.

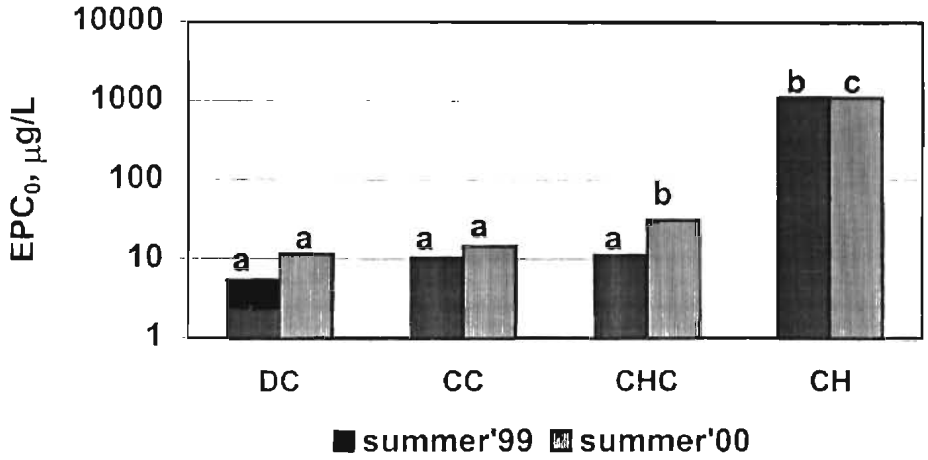

Figure 2. Comparing stream water column Equilibrium Phosphorus Concentration (EPC_0) in four northeastern Oklahoma and northwestern Arkansas streams obtained by the $CaCl_2$ method (DC – Dry Creek, CC – Cloud Creek, CHC – Cherokee Creek, CH – Columbia Hollow). Same letters across each season represent streams not significantly different from each other at α=0.05, different letters across each season represent streams significantly different from each other at α=0.05.

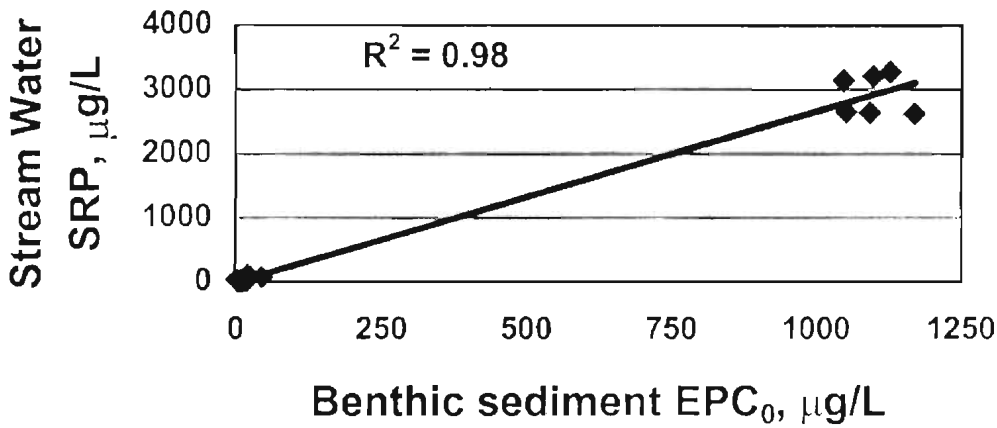

Figure 3. Stream water column Soluble Reactive Phosphorus (SRP) versus benthic sediment Equilibrium Phosphorus Concentration (EPC_0) obtained by the $CaCl_2$ method for Columbia Hollow and three nonpoint source impacted streams (Dry Creek, Cloud Creek, Cherokee Creek) for summer of 1999 and summer of 2000.

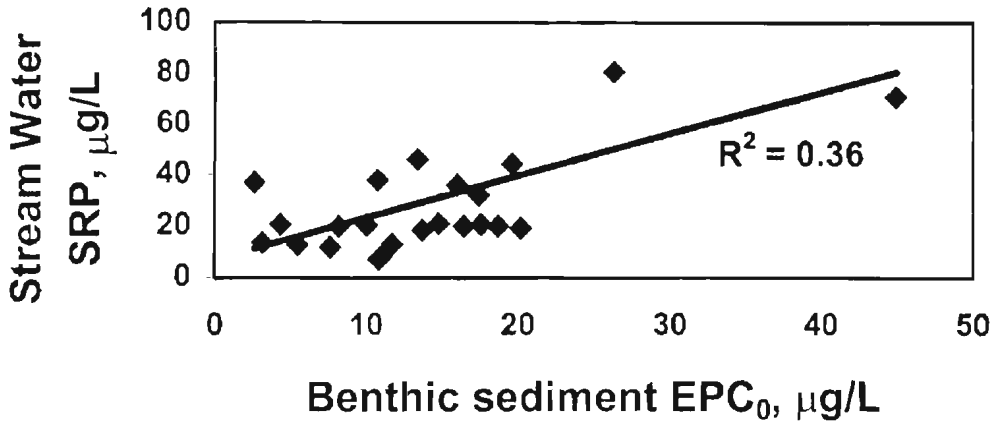

Figure 4. Stream water column Soluble Reactive Phosphorus (SRP) versus benthic sediment Equilibrium Phosphorus Concentration (EPC_0) obtained by the $CaCl_2$ method for three nonpoint source impacted streams (Dry Creek, Cloud Creek, Cherokee Creek) for summer of 1999 and summer of 2000.

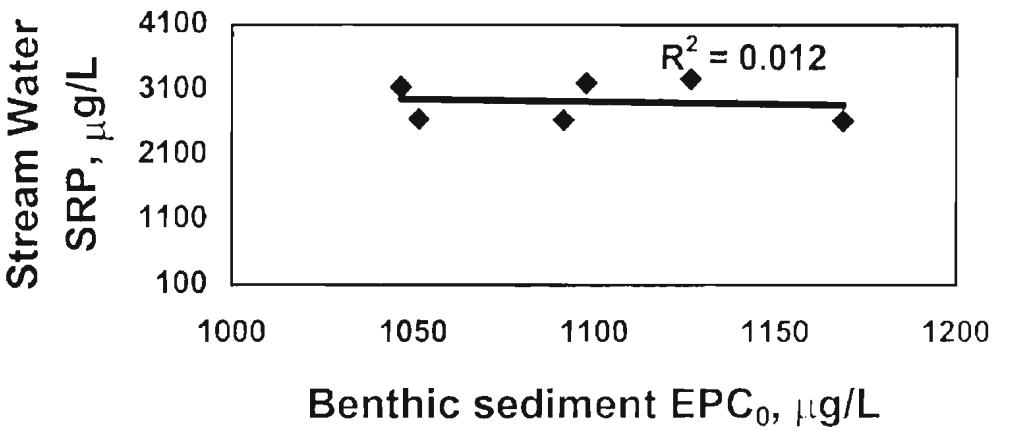

Figure 5. Stream water column Soluble Reactive Phosphorus (SRP) versus benthic sediment Equilibrium Phosphorus Concentration (EPC_0) obtained by the $CaCl_2$ method for Columbia Hollow, a point source impacted stream, for summer of 1999 and summer of 2000.

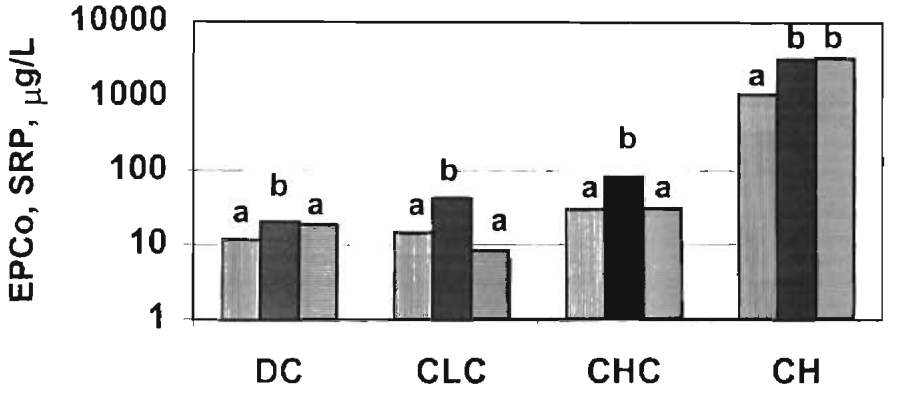

Figure 6. Comparing benthic sediment Equilibrium Phosphorus Concentration (EPC_0) obtained by $CaCl_2$ solution method and stream water method, and stream water Soluble Reactive Phosphorus (SRP) in summer of 2000 for four northeastern Oklahoma and northwestern Arkansas streams (DC – Dry Creek, CC – Cloud Creek, CHC – Cherokee Creek, CH – Columbia Hollow). Same letters across each creek represent phosphorus concentrations not significantly different from each other at α=0.05, different letters across each creek represent phosphorus concentrations significantly different from each other at α=0.05).

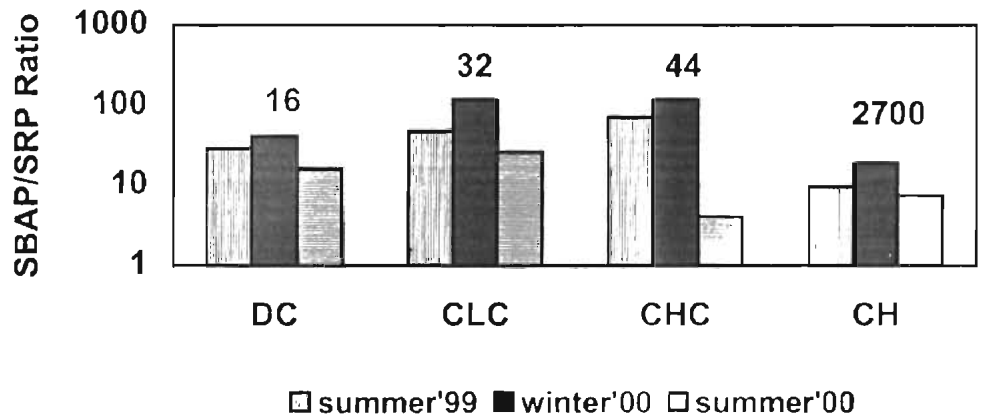

Figure 7. Benthic sediment bioavailable Phosphorus, SBAP, to stream water Soluble Reactive Phosphorus, SRP, ratio (DC – Dry Creek, CC – Cloud Creek, CHC – Cherokee Creek, CH – Columbia Hollow). Numbers above the bars represent mean SRP in µg/L concentration in the stream water column on the sampling dates.

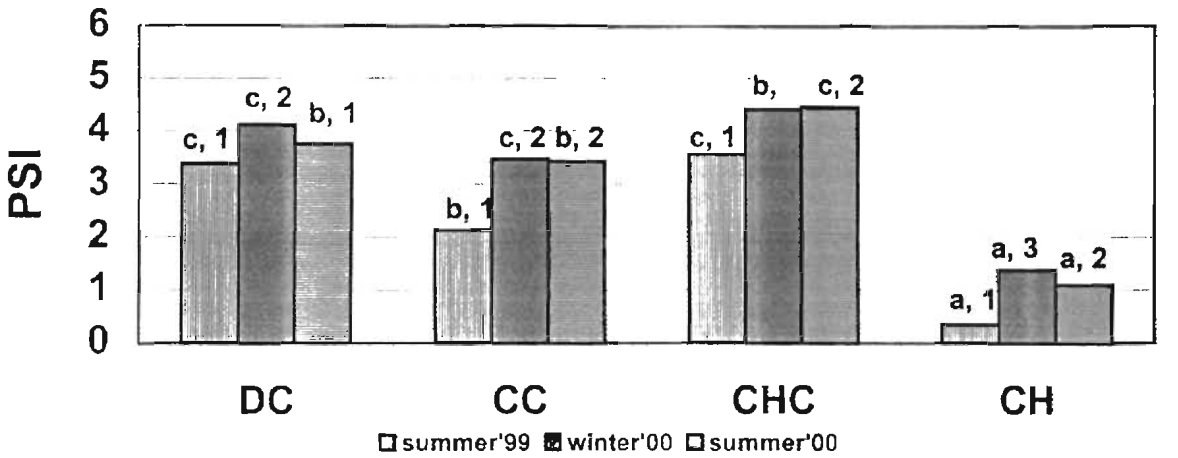

Figure 8. Comparing Phosphorus Sorption Index (PSI) for 'live' sediments in four northeastern Oklahoma and northwestern Arkansas streams (DC – Dry Creek, CC – Cloud Creek, CHC – Cherokee Creek, CH – Columbia Hollow). Same letters across each season represent streams not significantly different in their sediment buffering capacity at α=0.05, different letters across each season represent streams significantly different in their sediment buffering capacity at α=0.05. Same numbers within each stream represent PSI not different on a seasonal scale, different numbers within each streams represent PSI different on a seasonal scale.

APPENDIX A

Original data for Dry Creek, Cloud Creek, Cherokee Creek and Columbia Hollow for all parameters and all seasons

Dry Creek	Rep		Live' PSI	Dead' PSI	ExP	BAP	ExN	OM	EPC_0	Cl^-	NO_3-N	NH_4-N	P	Sand	Silt	Clay
					µg/g	µg/g	µg/g	%	µg/L	µg/L	µg/L	mg/L	µg/L	%	%	%
slow run	1	summer'99	2.95	3.20	0.185	0.220	1.578	1.3	1.2	7.2	0.55	0.005	14	90.83	4.37	4.80
slow run	2	summer'99	3.35	3.07	0.262	0.307	1.176	0.9	4.4					80.58	12.64	6.78
slow run	3	summer'99	3.63	3.72	0.188	0.288	0.788	1.1	3.9					82.97	9.96	7.07
fast run	1	summer'99	3.12	3.27	0.051	0.367	0.942	0.8	5.1	7.2	0.55	0.012	13	90.83	4.37	4.80
fast run	2	summer'99	3.51	3.36	0.021	0.498	0.682	1.0	9.6					90.83	4.37	4.80
fast run	3	summer'99	3.45	3.22	0.179	0.512	0.681	0.7	1.7					89.65	5.57	4.78
riffle	1	summer'99	3.40	3.98	0.131	0.512	1.756	0.9	2.1	7.1	0.54	0.003	12	97.79	1.77	0.44
riffle	2	summer'99	3.57	3.52	0.087	0.260	1.105	1.2	8.1					78.01	14.60	7.38
riffle	3	summer'99	3.55	3.61	0.076	0.384	0.683	1.1	12.5					77.25	15.34	7.40
		average	**3.39**	**3.44**	**0.131**	**0.372**	**1.043**	**1.0**	**5.4**	**7.2**	**0.55**	**0.007**	**13**	**86.53**	**8.11**	**5.36**
slow run	1	winter'00	3.96	4.27	0.017	0.732	1.055	1.1	n/a	9.3	1.03	0.000	18	91.25	4.69	4.05
slow run	2	winter'00	3.55	5.72	0.035	0.566	0.909	0.7	n/a					92.13	4.66	3.21
slow run	3	winter'00	3.41	3.14	0.032	0.843	0.602	0.5	n/a					92.92	3.06	4.02
fast run	1	winter'00	4.61	4.33	0.027	0.524	2.261	1.7	n/a	9.3	1.05	0.000	14	88.32	8.37	3.31
fast run	2	winter'00	4.45	3.26	0.019	0.543	2.520	0.7	n/a					86.70	5.24	8.06
fast run	3	winter'00	3.72	2.99	0.037	0.737	4.377	0.7	n/a					83.39	11.85	4.75
riffle	1	winter'00	5.14	4.13	0.078	0.685	0.616	n/a	n/a	9.4	1.04	0.000	16	83.79	9.32	6.89
riffle	2	winter'00	4.16	3.52	0.078	0.538	0.347	0.7	n/a					87.29	7.20	5.52
riffle	3	winter'00	3.93	2.64	0.039	0.564	0.234	0.8	n/a					86.42	7.55	6.03
		average	**4.10**	**3.78**	**0.040**	**0.637**	**1.436**	**0.9**	**n/a**	**9.3**	**1.04**	**0.000**	**16**	**88.02**	**6.88**	**5.09**
slow run	1	summer'00	4.59	4.56	n/a	0.157	6.087	1.1	7.2	3.9	0.78	0.000	20	93.85	3.20	2.96
slow run	2	summer'00	3.47	5.30	0.003	0.237	3.492	0.6	6.9					94.84	2.57	2.59
slow run	3	summer'00	3.91	3.17	0.084	0.223	3.602	0.9	10.5					94.05	2.91	3.05
fast run	1	summer'00	4.23	4.38	0.026	0.436	3.705	0.7	11.5	5.4	0.71	0.000	21	67.63	18.28	14.10
fast run	2	summer'00	4.16	7.07	0.037	0.202	4.342	0.8	5.6					95.48	0.79	3.72
fast run	3	summer'00	3.75	2.97	0.023	0.291	4.632	0.8	13.0					94.71	1.98	3.31
riffle	1	summer'00	3.14	4.63	0.015	0.528	3.849	1.4	11.2	65.7	0.87	0.000	20	96.98	1.18	1.83
riffle	2	summer'00	3.02	4.16	0.017	0.539	2.554	0.6	17.7					98.65	1.00	0.35
riffle	3	summer'00	3.51	2.20	0.020	0.290	3.335	0.8	20.6					95.83	1.79	2.38
		average	**3.75**	**4.27**	**0.028**	**0.322**	**3.955**	**0.9**	**11.6**	**25.0**	**0.79**	**0.000**	**20**	**92.45**	**3.74**	**3.81**

Cloud Creek	Rep		Live' PSI	Dead' PSI	ExP	BAP	ExN	OM	EPC_0	Cl^-	NO_3-N	NH_4-N	P	Sand	Silt	Clay
					µg/g	µg/g	µg/g	%	µg/L	µg/L	µg/L	mg/L	µg/L	%	%	%
slow run	1	summer'99	2.15	3.12	0.137	1.544	0.826	2.6	n/a	7.3	1.49	0.006	32	68.23	18.67	13.10
slow run	2	summer'99	2.24	3.93	0.077	1.576	1.133	1.5	n/a					52.79	36.11	11.10
slow run	3	summer'99	2.48	n/a	0.116	1.727	0.854	2.9	17.43					28.67	58.32	13.01
fast run	1	summer'99	2.05	2.96	0.328	1.724	0.768	1.9	42.06	7.3	1.53	0.005	36	90.75	6.28	2.97
fast run	2	summer'99	2.18	2.64	0.074	1.676	0.600	0.9	0.47					94.03	2.81	3.16
fast run	3	summer'99	2.17	2.65	0.075	1.891	0.587	1.4	5.45					92.87	4.37	2.76
riffle	1	summer'99	2.08	3.47	0.086	1.344	0.860	1.2	2.07	7.3	1.49	0.000	37	87.69	8.11	4.20
riffle	2	summer'99	1.91	3.00	0.144	1.699	0.824	0.9	4.51					88.21	6.40	5.39
riffle	3	summer'99	1.97	2.73	0.133	1.623	0.574	0.9	1.23					88.35	6.57	5.08
		average	**2.14**	**3.06**	**0.130**	**1.645**	**0.781**	**1.6**	**10.46**	**7.3**	**1.50**	**0.004**	**35**	**76.84**	**16.41**	**6.75**
slow run	1	winter'00	3.15	3.62	0.093	2.400	3.484	0.9	n/a	4.5	2.37	0.000	21	70.20	20.82	8.98
slow run	2	winter'00	4.20	3.73	0.087	1.934	1.111	1.4	13.62					84.13	9.92	5.95
slow run	3	winter'00	3.08	2.51	0.073	2.720	1.105	0.6	15.94					89.28	6.80	3.91
fast run	1	winter'00	3.64	4.66	0.025	3.206	3.152	0.7	26.49	4.5	2.34	0.000	19	76.58	17.97	5.45
fast run	2	winter'00	3.41	3.35	0.031	1.942	2.236	0.6	19.79					81.36	13.36	5.28
fast run	3	winter'00	3.60	4.18	0.054	2.361	0.888	0.6	14.33					88.92	6.26	4.82
riffle	1	winter'00	3.57	3.21	0.033	2.662	0.325	0.7	17.92	4.5	2.44	0.000	20	91.78	3.94	4.28
riffle	2	winter'00	3.49	3.29	0.031	1.124	1.541	0.8	15.80					89.05	7.27	3.68
riffle	3	winter'00	3.06	3.15	0.036	2.188	0.994	1.3	22.38					88.01	7.81	4.18
		average	**3.47**	**3.52**	**0.051**	**2.282**	**1.648**	**0.8**	**18.28**	**4.5**	**2.38**	**0.000**	**20**	**84.37**	**10.46**	**5.17**
slow run	1	summer'00	3.85	3.30	0.038	0.612	5.745	1.4	8.41	12.4	1.38	0.001	38	86.95	6.25	6.80
slow run	2	summer'00	4.26	3.18	0.006	0.568	9.161	1.7	8.07					92.86	3.39	3.75
slow run	3	summer'00	3.24	2.95	0.021	0.965	4.768	1.0	15.85					91.59	4.30	4.12
fast run	1	summer'00	3.31	3.01	0.080	0.741	3.996	1.2	15.80	21.2	1.40	0.003	46	96.27	1.18	2.55
fast run	2	summer'00	3.22	3.21	0.002	1.038	3.940	1.4	9.35					94.83	1.67	3.50
fast run	3	summer'00	2.94	3.44	0.008	1.587	3.409	0.8	15.06					95.39	1.67	2.94
riffle	1	summer'00	3.23	3.33	0.123	0.961	5.845	0.9	17.81	17.1	1.40	0.002	44	51.12	28.15	20.72
riffle	2	summer'00	3.79	3.55	0.057	1.475	6.223	1.3	27.42					78.10	13.09	8.80
riffle	3	summer'00	2.94	3.09	0.028	1.802	3.990	0.6	13.77					n/a	n/a	n/a
		average	**3.42**	**3.23**	**0.040**	**1.083**	**5.231**	**1.1**	**14.62**	**16.9**	**1.39**	**0.002**	**43**	**85.89**	**7.46**	**6.65**

Cherokee Creek	Rep		Live' PSI	Dead' PSI	ExP	BAP	ExN	OM	EPC_0	Cl^-	NO_3-N	NH_4-N	P	Sand	Silt	Clay
					µg/g	µg/g	µg/g	%	µg/L	µg/L	µg/L	mg/L	µg/L	%	%	%
slow run	1	summer'99	3.51	3.22	0.093	1.961	2.949	1.3	10.67	6.9	2.73	0.007	7	87.08	8.57	4.34
slow run	2	summer'99	3.64	3.10	0.175	1.699	1.260	1.3	7.95					88.64	8.76	2.60
slow run	3	summer'99	3.65	3.03	0.206	1.910	1.317	1.9	13.90					87.17	7.08	5.75
fast run	1	summer'99	3.37	3.44	0.186	2.389	0.884	1.5	7.65	6.8	2.74	0.008	8	89.61	5.64	4.75
fast run	2	summer'99	3.44	3.62	0.264	2.172	2.208	1.2	8.88					89.30	5.40	5.30
fast run	3	summer'99	3.55	3.40	0.370	2.395	1.547	1.2	16.34					91.47	4.16	4.37
riffle	1	summer'99	3.85	3.82	0.297	2.273	1.349	1.6	9.41	6.8	2.83	0.013	13	71.29	15.89	12.83
riffle	2	summer'99	3.49	3.44	0.463	2.487	0.924	1.4	14.55					80.73	11.00	8.27
riffle	3	summer'99	3.50	3.20	0.369	2.434	2.493	1.4	11.17					76.40	14.55	9.05
		average	**3.55**	**3.36**	**0.269**	**2.191**	**1.659**	**1.4**	**11.17**	**6.8**	**2.77**	**0.009**	**9**	**84.63**	**9.01**	**6.36**
slow run	1	winter'00	7.21	4.22	0.052	3.820	n/a	1.8	22.33	9.3	2.33	0.000	21	71.91	17.40	10.69
slow run	2	winter'00	4.34	3.73	0.079	2.912	6.861	1.4	15.34					71.34	17.25	11.41
slow run	3	winter'00	5.75	3.17	0.059	3.512	6.043	1.4	15.07					75.51	16.22	8.26
fast run	1	winter'00	3.90	2.59	0.048	1.773	2.814	0.8	3.09	9.3	2.29	0.000	21	85.11	11.09	3.80
fast run	2	winter'00	3.68	2.61	0.103	1.707	3.616	1.0	5.40					84.35	11.41	4.24
fast run	3	winter'00	3.88	3.10	0.086	1.466	4.195	n/a	4.50					82.62	12.08	5.30
riffle	1	winter'00	3.80	4.57	0.071	1.682	n/a	1.1	16.53	9.1	2.43	0.000	19	53.87	37.32	8.81
riffle	2	winter'00	3.38	4.40	0.086	1.880	5.827	1.4	12.50					55.30	36.19	8.51
riffle	3	winter'00	3.70	3.47	0.066	1.980	5.731	n/a	12.16					73.24	21.38	5.38
		average	**4.41**	**3.54**	**0.072**	**2.304**	**5.012**	**1.3**	**11.88**	**9.2**	**2.35**	**0.000**	**20**	**72.58**	**20.04**	**7.38**
slow run	1	summer'00	5.92	3.72	0.055	0.344	3.769	0.7	41.26	15.3	2.83	0.009	71	65.09	29.80	5.11
slow run	2	summer'00	5.06	3.81	0.052	0.173	3.969	1.2	52.75					48.34	40.65	11.01
slow run	3	summer'00	n/a	2.75	0.031	0.310	2.928	n/a	40.86					82.76	12.87	4.37
fast run	1	summer'00	4.85	2.93	0.053	0.176	5.271	1.5	22.13	12.5	2.88	0.040	102	92.03	3.87	4.10
fast run	2	summer'00	3.80	3.10	0.028	0.226	5.195	1.0	30.18					90.90	6.15	2.95
fast run	3	summer'00	4.53	3.31	0.012	0.261	4.276	1.6	9.94					91.54	4.83	3.63
riffle	1	summer'00	3.90	3.00	0.012	0.412	4.958	1.6	28.74	24.8	2.95	0.000	81	95.67	1.00	3.33
riffle	2	summer'00	3.99	3.48	0.016	0.454	7.114	1.2	27.83					93.04	3.68	3.28
riffle	3	summer'00	3.59	3.40	0.115	0.589	3.746	1.3	22.44					92.91	3.97	3.12
		average	**4.45**	**3.28**	**0.041**	**0.327**	**4.581**	**1.3**	**30.68**	**17.5**	**2.89**	**0.016**	**84**	**83.59**	**11.87**	**4.54**

Columbia Hollow	Rep		Live' PSI	Dead' PSI	ExP	BAP	ExN	OM	EPC_0	Cl^-	NO_3-N	NH_4-N	P	Sand	Silt	Clay
					µg/g	µg/g	µg/g	%	µg/L	µg/L	µg/L	mg/L	µg/L	%	%	%
slow run	1	summer'99	0.34	3.22	3.265	13.567	1.931	2.2	784	28.3	6.34	0.071	2619	65.67	20.79	13.54
slow run	2	summer'99	0.20	3.44	2.752	15.258	1.276	1.8	1327					71.55	14.77	13.68
slow run	3	summer'99	0.26	3.07	2.381	27.392	1.327	1.8	1396					78.84	12.81	8.35
fast run	1	summer'99	0.37	3.88	2.556	22.101	1.526	1.6	1073	29.1	6.44	0.043	2632	79.19	11.50	9.31
fast run	2	summer'99	0.35	3.20	2.722	31.898	1.173	1.8	1170					82.38	9.97	7.65
fast run	3	summer'99	0.39	3.11	2.463	31.515	1.211	1.9	1032					82.06	10.17	7.77
riffle	1	summer'99	0.51	4.51	3.257	30.867	1.411	1.6	1082	29.6	6.34	0.073	2647	91.32	4.06	4.62
riffle	2	summer'99	0.44	3.67	2.796	27.721	1.047	1.8	1138					92.47	2.97	4.56
riffle	3	summer'99	0.37	3.67	2.556	25.014	1.432	1.6	935					89.54	0.46	1.00
		average	**0.36**	**3.53**	**2.750**	**25.037**	**1.371**	**1.8**	**1104**	**29.0**	**6.37**	**0.062**	**2633**	**81.45**	**9.72**	**7.83**
slow run	1	winter'00	1.45	3.17	2.692	39.746	1.542	1.5	n/a	69.0	17.00	1.190	2420	90.40	5.78	3.82
slow run	2	winter'00	0.96	3.66	2.732	43.769	2.075	1.4	n/a					86.53	8.61	4.86
slow run	3	winter'00	1.12	3.67	3.162	30.354	2.214	1.7	n/a					89.40	6.52	4.08
fast run	1	winter'00	3.14	4.03	2.264	46.562	1.343	1.2	n/a	50.0	12.00	1.150	2150	86.43	8.73	4.84
fast run	2	winter'00	1.13	4.19	2.334	43.764	0.598	1.1	n/a					82.28	11.15	6.58
fast run	3	winter'00	1.08	3.90	2.821	36.138	0.932	1.2	n/a					84.25	9.84	5.91
riffle	1	winter'00	1.26	3.32	2.688	43.823	3.750	1.1	n/a	50.0	10.00	1.330	2120	90.26	4.02	5.72
riffle	2	winter'00	1.24	3.65	2.260	37.821	1.749	1.3	n/a					90.79	5.39	3.82
riffle	3	winter'00	1.13	3.54	2.553	45.614	2.318	2.3	n/a					93.48	3.94	2.58
		average	**1.39**	**3.68**	**2.612**	**40.843**	**1.836**	**1.4**	**n/a**	**56.3**	**13.00**	**1.223**	**2230**	**88.20**	**7.11**	**4.69**
slow run	1	summer'00	1.68	3.53	4.602	19.362	3.673	2.7	1190	46.7	7.15	0.025	3203	87.76	7.47	4.77
slow run	2	summer'00	1.52	3.55	5.349	25.354	2.200	2.4	1109					80.92	12.63	6.45
slow run	3	summer'00	1.07	3.38	4.546	22.692	4.191	3.3	995					80.15	13.36	6.49
fast run	1	summer'00	0.73	3.72	5.550	19.827	2.327	2.2	1044	137.3	6.50	0.009	3268	87.35	7.59	5.06
fast run	2	summer'00	1.25	4.17	7.754	19.856	2.868	3.5	1084					86.63	7.39	5.98
fast run	3	summer'00	0.93	3.02	2.473	12.758	2.584	2.4	1252					84.17	8.82	7.01
riffle	1	summer'00	0.90	3.09	4.290	31.402	2.803	3.4	1238	388.6	6.72	0.000	3140	85.04	8.11	6.86
riffle	2	summer'00	0.98	3.82	2.580	36.579	1.981	4.1	1033					79.48	12.04	8.48
riffle	3	summer'00	0.87	3.02	4.117	27.661	2.004	3.2	868					74.59	3.17	22.24
		average	**1.10**	**3.48**	**4.585**	**23.943**	**2.737**	**3.0**	**1090**	**190.9**	**6.79**	**0.011**	**3204**	**82.90**	**8.95**	**8.15**

APPENDIX B

Quality Assurance and Quality Control of the sample analysis

Date	Sample #	Nutrient	Sample Estimate, ppm	Replicate Estimate, ppm	% Difference ±10%	Accept	Reject > ±10%
01-12-00	1	NH_4-N	0.00	0.00	0	X	
01-12-00	1	NO_3-N*	2.33	2.44	5	X	
01-12-00	1	P*	1.03	1.04	1	X	
01-31-00	10	P	0.06	0.05	17		X
01-31-00	20	P	0.02	0.02	0	X	
06-21-00	1	NH_4-N	0.00	0.00	0	X	
06-21-00	1	NO_3-N	0.78	0.74	5	X	
06-21-00	35	NH_4-N	0.49	0.51	4	X	
06-21-00	35	NO_3-N	0.14	0.12	15		X
08-08-00	1	P	0.07	0.07	0	X	
08-08-00	35	NH_4-N	0.87	0.87	0	X	
08-08-00	1	Cl^-*	15.28	16.3	7	X	
08-24-00	1	P	3.20	3.25	2	X	
08-24-00	1	NH_4-N	0.02	0.02	0	X	
08-24-00	1	NO_3-N	7.15	6.91	3	X	
08-24-00	19	P	1.07	1.12	5	X	
08-24-00	37	P	3.82	3.94	3	X	
08-24-00	1	Cl^-	46.67	48.73	4	X	
12-21-00	5	NH_4-N*	0.23	0.24	4	X	
12-21-00	15	NH_4-N	0.16	0.16	0	X	

NH_3-N detection level is 0.03 mg/L*
NO_3-N detection level is 0.01 mg/L*
P detection level is 0.05 mg/L*
Cl^- detection level is 0.1 mg/L

Date	Nutrient	Blank, ppm	EPA
01-12-00	Cl^-	0.28	9.99
01-12-00	Cl^-	0.28	
01-12-00	Cl^-	0.28	
01-12-00	Cl^-	0.42	
01-31-00	P	0.03	0.25
01-31-00	P	0.03	
01-31-00	P	0.02	
01-31-00	P	0.02	
01-31-00	P	0.02	
06-21-00	P	0.03	0.25
06-21-00	P	0.03	
06-21-00	P	0.02	
06-21-00	Cl^-	0.00	10.6
06-21-00	Cl^-	0.00	
06-21-00	Cl^-	0.00	
07-21-00	P	0.15	0.31
07-21-00	P	0.11	
07-21-00	P	0.11	
07-21-00	P	0.11	
07-21-00	Cl^-	1.90	4.90
07-21-00	Cl^-	1.90	
07-21-00	Cl^-	1.90	
07-21-00	Cl^-	1.90	
08-08-00	NO_3-N	0.12	1.27
08-08-00	NO_3-N	0.15	
08-08-00	NO_3-N	0.17	
08-08-00	NO_3-N	0.13	
08-08-00	P	0.04	0.28
08-08-00	P	0.07	
08-08-00	P	0.08	
08-08-00	P	0.04	
08-08-00	NH_4-N	0.00	0.80
08-08-00	NH_4-N	0.00	
08-08-00	NH_4-N	0.00	
08-08-00	NH_4-N	0.00	
08-08-00	Cl	1.67	11.12
08-08-00	Cl	1.67	
08-08-00	Cl^-	1.67	

08-08-00	Cl^-	1.67	
08-24-00	NH_4-N	0.06	4.78
08-24-00	NH_4-N	0.06	
08-24-00	NH_4-N	0.00	
08-24-00	NH_4-N	0.00	
08-24-00	NO_3-N	0.00	11.41
08-24-00	NO_3-N	0.00	
08-24-00	NO_3-N	0.00	
08-24-00	NO_3-N	0.00	
08-24-00	Cl^-	1.00	11
08-24-00	Cl^-	1.00	
08-24-00	Cl^-	1.00	
08-24-00	Cl^-	1.00	
08-24-00	P	0.13	0.65
08-24-00	P	0.13	
08-24-00	P	0.13	
08-24-00	P	0.13	
12-21-00	NH_4-N	0.03	0.79
12-21-00	NH_4-N	0.00	
12-21-00	NH_4-N	0.03	

VITA

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Master of Science

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