

## Memorandum

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**DATE: July 25, 2011**

**SUBJECT: Response to the Oklahoma Scenic River Technical Advisory Group Call for Data**

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**Purpose:** The objective of the Oklahoma Scenic River Technical Advisory Group (OSRTAG) is to “re-evaluate the Oklahoma Scenic River phosphorus criterion to reaffirm its appropriateness or to recommend if a revised phosphorous (sic) criterion might better serve to restore and protect the integrity of Oklahoma’s Scenic Rivers.” The purpose of the review of the Illinois River nutrient criteria for phosphorus is to insure that the numeric standard is informed by the most current data and methods for protecting water quality. The Advisory Group requested submission of “best scientific information contributions regarding phosphorus criteria that will protect the natural scenic beauty, water conservation, fish, wildlife and outdoor recreational values of Oklahoma’s six Scenic Rivers.” This memorandum provides the assessment of Drs. Matlock, Haggard and Sharpley of the information that is available and appropriate to consider, as well as supporting information through attachments.

**Recommendations:** Our recommendations for the OSRTAG include 1) Review of the procedure for developing nutrient criteria for phosphorus in Oklahoma, 2) clarification of the impacts and water quality characteristics of greatest concern in the Illinois River, and 3) revision of the monitoring and assessment procedures to evaluate attainment levels of water quality in the Illinois River. These recommendations and citations to the associated literature to support them are provided below.

**Recommendation 1: Review of the procedure for developing nutrient criteria for phosphorus in Oklahoma.** The US EPA recommends three scientifically defensible approaches for nutrient criteria development: 1) reference condition approaches, 2) mechanistic modeling, and 3) stressor-response analysis. The initial water quality standard for phosphorus was established using the first approach based largely on the work of Clark et al. (2000). Nutrient concentrations from “relatively un-impacted basins” were analyzed, and the third quartile distribution (75% exceedance level) was selected as the numeric criteria for the Illinois River Basin (0.0375 mg/l total phosphorus). The first procedure (using reference conditions) does not consider current catchment land use and land cover of streams when developing nutrient criteria. It is our assessment that the third method, the stressor-response analysis, is most appropriate for assessing impacts on complex stream systems with multiple stressors and changing conditions. The stressor-response criteria method published by EPA (USEPA, 2010a) is applied in the site-specific alternative criteria method adopted by USEPA Region 4 for Florida (FDEP, 2011). It is our belief that this method represents the most robust method for development of nutrient criteria of which the goal is to protect the designated uses of Oklahoma Scenic Rivers. This approach is consistent with the goals and intentions of the Task Force. This approach allows stakeholders to develop site-specific alternative criteria (SSAC) for waterbodies. These SSACs replace numeric nutrient criteria where data suggests designated uses are more protected by alternative metrics, are technically sound, and detailed compliance criteria are presented.

This recommendation is consistent with recent independent Scientific Advisory Board Panel’s (SAB) “Review of Empirical Approaches for Nutrient Criteria Derivation” (USEPA, 2010b), which stated that “the stressor-response approach is a legitimate, scientifically based method for developing numeric nutrient criteria if the approach is appropriately applied (i.e., not used in isolation but as part of a weight-of-evidence approach).” Further, the Panel suggested that the stressor-response approach be used with other available methodologies in the context of a

tiered approach where uncertainties in different approaches are recognized, and weight of evidence is used to establish the likelihood of causal relationships between nutrients and their effects for criteria derivation (USEPA, 2010b). A more recent SAB report reviewing “EPA's draft Approaches for Deriving Numeric Nutrient Criteria for Florida's Estuaries, Coastal Waters, and Southern Inland Flowing Waters” came to the same weight-of-evidence approach to developing numeric nutrient criteria (USEPA, 2011).

**Recommendation 2: Clarification of impacts and water quality characteristics of greatest concern in the Illinois River.** The current numeric phosphorus criterion was developed to “assure that water quality better than that necessary to support beneficial uses is achieved” (OWRB, 2011). The objective of the numeric phosphorus criterion was to “restore and protect the integrity of Oklahoma’s Scenic Rivers” (OWRB, 2011). The impact of concern was “...nutrients – primarily phosphorus – were seen to be causing accelerated primary productivity in the Illinois River, resulting in significant growths of both attached algae (periphyton) and suspended algae (phytoplankton). As a consequence, historical river clarity and substrate quality were being adversely affected to such an extent that, without intervention, the Illinois River’s exceptional ecological and recreational significance were in jeopardy” (OWRB, 2011). There are a number of concerns and associated assumptions raised in this statement. The “integrity of Oklahoma’s Scenic Rivers” was implied to be defined as the “exceptional ecological and recreational significance”. The presumption seems to be that algal growth from phosphorus was the primary cause of this threat or impairment.

Much of the data collected and analyzed in the basin over the past 20 years was summarized in Haggard et al. (2010). This report summarized the data and results of over 30 contemporary assessments of water quality and ecosystem condition in the Upper Illinois River Basin (i.e., that portion of the Basin in Arkansas); this report provides a comprehensive listing of the papers relevant to the Illinois River including 2010 and prior years. Haggard (2010) showed that total phosphorus loads in the Upper Illinois River began to decrease in 2002. Phosphorus concentrations in the Upper Illinois River have been declining for almost a decade. Scott et al. (2011) showed similar decreases in phosphorus concentrations of the Lower Illinois River, especially at the Illinois River near Watts, Oklahoma. No assessments have been conducted on the Lower Illinois River (i.e., that portion of the River in Oklahoma) by OWRB to evaluate if the “exceptional ecological and recreational significance” have improved or changed as a result of a decade of decreasing phosphorus. Without these data there is no credible way to correlate phosphorus loads to the water quality objectives described by the OWRB standard.

Matlock et al. (2009) demonstrated that the aquatic ecosystem condition (fish, benthic macro-invertebrate and algae) were less impacted by phosphorus than by other land use impacts such as hydrologic regime alteration, bank erosion, and riparian cover loss (Matlock et al., 2009). Ecological metrics suggested that in-stream characteristics might have improved in these streams over the past 10 years. The data are not adequately resolved to identify proximal causes of impact or improvement, but the role of phosphorus was not the sole driver in ecosystem structure.

**Recommendation 3: Revision of the monitoring and assessment procedures to evaluate water quality in the Illinois River.** The current approach to monitoring water quality in the Illinois River will not measure success at meeting the criteria described by OWRB. The most appropriate method to measure the “exceptional ecological and recreational significance” of the Illinois River is to assess key ecological characteristics that define “exceptional ecological...significance” and identify water quality characteristics that define “exceptional...recreational significance.” These are not difficult to monitor; they are the same characteristics monitored by Matlock et al. (2009) in Spring and Osage Creeks in the Upper Illinois River in 2007-2009. A basin-level assessment strategy should include water quality, ecosystem characteristics, river reach characteristics, and watershed land use characteristics. This assessment would support Recommendation 1. A five-year assessment, in conjunction with current comprehensive phosphorus emission reduction strategies, would provide the resolution of data to characterize and prioritize causal agents for remaining ecological and recreational impacts from water quality.

#### **Related Land management and stream information gathered by the Division of Agriculture University of Arkansas**

Related information on land management and in-stream concentration of P, along with potential legacy effects of phosphorus stored in the Illinois River Basin from prior discharges and management include:

1. The recent thesis of Rogers (2010), which evaluated the P retention capabilities of stream sediments with varying land use in the Illinois River Watershed. The main findings of which were; “Results showed that streams in the Upper Illinois River Watershed are comprised of a mix of substrate sizes, a large portion of which are > 20-mm where P reactions are mainly biologically driven. Fine sediments which were approximately 15% of bed sediment influenced chemically driven P reactions. Based on fluvium experiments, sediments in the watershed have a high affinity to adsorb P (86 - 96%), with varying amounts of P subsequently desorbed (1 - 7 %). This implies that prior land use management of the watershed has affected sediment properties, which continue to influence DRP levels of streams. Thus, a lack of decrease in P loads in streams of the Upper Illinois River Watershed is not indicative of a lack of effectiveness of recently implemented management strategies, rather it is likely a lack of sufficient time for reduction in both soil P levels, through adoption of agricultural and urban BMPs, and stream sediment-bound P acting as continued regulators of stream DRP levels.”
2. Fact Sheets documenting the revised Arkansas P Index, which was adopted for use in the Illinois River Watershed at the beginning of 2010 (Sharpley et al., 2010a, b, and 2011).
3. A peer-reviewed paper documenting the change in litter application rates with use of ESPI in the Eucha-Spavinaw Watershed (Sharpley et al. 2009). Given the basic similarity in the AR PI and ESPI, application rates in the Illinois River Watershed will be similar (i.e., ~1.3 tons poultry litter/acre) when following a risk-based nutrient management plan. Given, the loss

of P in runoff is close to linearly related to litter application rate (currently ~1.3 tons poultry litter/acre), the potential decrease in P runoff since adoption of ESPI (and Arkansas P Index), is estimated to be about one third of pre-ESPI application rates (3 to 5 tons poultry litter/acre), if all other conditions were to remain constant.

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THE ROLE OF FLUVIAL SEDIMENTS IN MODIFYING PHOSPHORUS EXPORT  
FROM THE UPPER ILLINOIS RIVER WATERSHED, ARKANSAS



THE ROLE OF FLUVIAL SEDIMENTS IN MODIFYING PHOSPHORUS EXPORT  
FROM THE UPPER ILLINOIS RIVER WATERSHED, ARKANSAS

A thesis submitted in partial  
fulfillment of the requirements for the degree of  
Master of Science in Crop, Soil, and Environmental Sciences

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## ABSTRACT

Anthropogenic phosphorus (P) loading to freshwaters is a key concern facing Northwest Arkansas and the Upper Illinois River Watershed (UIRW), the focus of this study. Inputs of P to surface waters are cited as a key contributor to accelerated eutrophication. Subsequent reductions in overall water quality due to diverse inputs from both urban and agricultural sources have been researched, and measures have been implemented to reduce P loads. While strategies have been put in place, stream sediments are a critical, while less understood, link in the fate and transport of P from the landscape to overlying waterbodies and represent a potential source of a legacy effect in which prior management strategies continue to influence stream dissolved reactive P (DRP) concentrations. Thus, a comprehensive study of stream sediments within the region is necessary to understand whether or not bed sediment is still potentially a key regulator of DRP in the region. A three-fold approach was implemented; classification of physical and chemical properties of bed sediments, evaluation of extracting solutions for use in P-sorption isotherm experiments to replicate stream water, and P uptake and release in a simulated stream channel utilizing a high P poultry litter source to evaluate typical agricultural practices of the region. Five sites were selected in the UIRW representing agricultural, forest, and urban sites. Sediment was collected and analyzed for a myriad of factors for each experiment. Results showed that streams in the UIRW are comprised of a mix of substrate sizes, a large portion of which are > 20-mm where P reactions are mainly biologically driven. Fine sediments which were approximately 15 % of bed sediment influenced chemically driven P reactions. Within the region DI water is most comparable to stream water and thus the most appropriate equilibrating solution to characterize P sorption and desorption properties of sediments. Based on fluvium

experiments, sediments in the watershed have a high affinity to sorb P (86 – 96%), with varying amounts of P subsequently desorbed (1 – 7 %). Across studies, sites showed a strong relationship to modified P saturation ratio ( $PSR_{mod}$ ). This implies that prior land use management of the watershed has affected sediment properties, which continue to influence DRP levels of streams. Thus, a lack of decrease in P loads in streams of the UIRW is not indicative of a lack of effectiveness of recently implemented management strategies, rather it is likely a lack of sufficient time for reduction in both soil P levels, through adoption of agricultural and urban best management practices (BMPs), and stream sediment bound P acting as continued regulators of stream DRP levels.

This thesis is approved for recommendation to the Graduate Council

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## **DEDICATION**

I dedicate this thesis to my mother and father who have supported and encouraged me throughout my graduate work. Without them, none of this would have been possible.

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**CHAPTER 1**  
**INTRODUCTION**

## INTRODUCTION

The 1972 Clean Water Act is the foundation of surface water quality conservation in the United States. Ground breaking legislation when enacted, it set the stage for future guidance and laws that were put in place to protect the valuable water resources of the United States. The Act initially focused on point sources; however, later amendments would bring lawmakers attention to other areas including waste water treatment plants (WWTP) and nonpoint sources, such as agriculture and urban storm water runoff. In effect, the Clean Water Act created the framework for improving water quality throughout the country (USEPA, 2008). This Act, more than any other legislation, was pivotal in changing the paradigm and advancing water quality conservation through measures to research, monitor, and protect this most valuable and life sustaining resource.

Many of the nation's current concerns related to water resources and accelerated freshwater eutrophication stem from excessive loading of phosphorus (P) into streams and lakes. While P is needed by both aquatic plants and animals for growth and biological productivity, amounts in excess of optimal levels can lead to accelerated eutrophication (Carpenter et al. 1998; Schindler, 1977; Sharpley et al., 2003). This is particularly well documented in whole lake studies which have shown P as the major cause of eutrophication in freshwater lakes (Howarth and Paerl, 2008; Schindler et al., 2008). Trophic status of lakes is particularly important, as highly eutrophic lakes are more likely to have algal blooms which can lead to decreases in oxygen levels, fish kills, loss of biodiversity, loss of aquatic plant beds, and impairment of water resources for drinking and recreational use (Howarth et al., 2000).

The general indicator of balanced algal growth is described by the Redfield Ratio which describes the molecular ratio of carbon (C), nitrogen (N), and phosphorus (P) in aquatic primary producers at 40:7:1 (Redfield, 1958). However, a 30 year study of freshwater lakes in Canada reported that regardless of N:P ratios, algal biomass remained proportional to P inputs (Schindler et al., 2008). This phenomenon was explained by the fact that atmospheric N fixation was sufficient to allow biomass accumulation to be proportional to P inputs (Schindler et al., 2008). Thus, an understanding of the fate and transport of P in the environment is critical to effectively manage water quality.

Northwest Arkansas has a large network of freshwater streams and lakes. These water bodies are adjacent to a growing urban community and one of the largest poultry production regions in the United States with a finite landmass available for litter application (Slaton et al., 2004). This interconnectedness has led to a region that is sensitive to issues related to water quality response to land use and management.

A large body of research exists on the impacts of agricultural land use on nutrient runoff from small plot and edge of field studies, both regionally and nationally (Edwards and Daniel, 1993; Moore et al., 2000; Sharpley et al., 2003). However, there is less information on P transformations that occur between the edge of the field and point of impact in receiving water bodies, even though we know this to be critical in determining water quality response to land management and land-based remedial measures (Haggard and Sharpley, 2007; McDowell et al., 2004). This research measured in-stream processes of P uptake and release by sediments within the Upper Illinois River Watershed (UIRW) to more accurately assess the transport mechanisms which occur after leaving the terrestrial environment and upon entrance into the fluvial system. Quantification of these

in-stream processes was accomplished through experiments based on the following research objectives.

### **RESEARCH OBJECTIVES**

1. To quantify stream bed makeup of select streams within the UIRW and the landuses draining these sub-basins.
2. To determine which background solution used in P-sorption isotherms was most similar and thus replicable as compared to stream water.
3. To determine the uptake and release characteristics of fine-sized stream sediments in a simulated stream.

### **OVERVIEW OF THE STUDY**

Chapter 2 examines literature associated with P source management and biogeochemistry in soil, sediment, and water environments. Chapter 3 focuses on determining the composition of stream beds of representative streams in the UIRW and measuring physical as well as chemical parameters within the stream. This establishes relative amounts of different sizes of sediment as well as chemical parameters associated with the fine-sized fraction (< 2-mm) and their influence on water column P levels. Chapter 4 focuses on establishing a routine procedure for determination of P-sorption isotherms and associated parameters for use in streams within the watershed. In this Chapter, we will establish the method which most closely mimics stream water as an extracting solution for use in subsequent chapters. In Chapter 5, we measure in-stream conditions and subsequently conduct a set of experiments including P-isotherms based on

the results of Chapter 4. Furthermore, an experiment utilizing a simulated stream environment to measure uptake and release of P from a poultry litter source is utilized. This fluvarium experiment measures P uptake and release in an environment more similar to in-stream conditions than isotherm procedures. Based on these experiments, overall conclusions are drawn in Chapter 6 concerning in-stream P dynamics within the UIRW.

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**CHAPTER 2**  
**LITERATURE REVIEW**

## **LITERATURE REVIEW**

### **TERMINOLOGY**

In this research, the following terminology for P forms in soil, sediment, and water will be used, as detailed in Table 1. Dissolved reactive P (DRP) will be used to represent inorganic orthophosphate dissolved in water, which is measured as that P reacting with the molybdate reagent during standard colorimetric determination. Dissolved reactive P is operationally analogous to the terms soluble reactive P and molybdate reactive P used by other researchers. Total dissolved P (TDP) represents both inorganic and organic P in solution of a sample of water or extract that has been filtered (< 0.45- $\mu\text{m}$ ) and digested. Total P (TP) is the total amount of inorganic and organic P in a sample after digestion to convert all forms to inorganic P; the measured form. Particulate P (PP) represents P associated with sediment or other particulate material, which is not in solution and is calculated as the difference between total and total dissolved P. Methods to determine these various forms are detailed in the individual Materials and Methods sections.

### **REGIONAL DESCRIPTION AND CURRENT CONDITIONS**

The Upper Illinois River Watershed (UIRW) of Northwest Arkansas is the focus of this study and is located within Benton, Washington, and a small portion of Crawford Counties. The UIRW is a source of a large amount of research concerning the fate and transport of P from the landscape to surface waters. This is largely due to the regions rapid urban population growth and predominance in poultry production paired with a large surface network of streams and rivers.

Washington and Benton counties have seen some of the most prolific population growth the state has witnessed in the past two decades. The population in Northwest Arkansas increased 48% between 1990 and 2000 and increased another 20% from 2000 to 2005 (Kemper et al., 2006). This is partly due to the emergence of the area as the headquarters for several large companies – including large poultry integrators (Kemper et al., 2006). The area still retains a strong agricultural economy and is centered within the largest poultry producing region in the state and one of the largest producing regions in the country (USDA Economic Research Service, 2008; USDA National Agricultural Statistics Service, 2004; Slaton et al., 2004).

Overabundance of nutrients moving from poultry litter to water sources has been cited as a source of water quality concerns in the Ozark region in which the UIRW is located (Sauer et al., 2002). Other studies have found significant sources from WWTP and urban runoff (Ekka et al., 2006). To address this, increased measures have been taken to reduce the output from WWTPs, and best management practices (BMPs) have been implemented as a means of minimizing agricultural transport of essential nutrients to surface and ground waters. BMPs include such measures as feed management, riparian buffer zones, and nutrient management planning (Sharpley et al., 2005). However, these measures are part of a long term sustainability plan and even when these measures are implemented and P losses are reduced, little response may be seen in actual stream loads when the timeframe is not of sufficient scale (Sharpley et al., 2009).

A broad approach to watershed management is necessary and a knowledge of the pathways in which nutrients move and the mechanisms that facilitate this movement are critical as part of an effective watershed management plan. Multiple sources and

mechanisms of nutrient transport need to be understood though research at various scales to target water quality impairments and subsequently, remedial efforts within a watershed.

## **PHOSPHORUS DYNAMICS IN SOIL AND WATER SYSTEMS**

Submerged plant communities in aquatic systems are vital to the biological diversity of rivers providing essential food-chain resources for healthy and viable aquatic systems (Mainstone and Parr, 2002). Plants and animals both need P for growth; however, increased inputs of P to surface waters can increase biological productivity and accelerate eutrophication (Sharpley et al., 2003). Eutrophication is accelerated by P, which is generally in shortest supply and thus, most frequently the limiting nutrient in fresh waters (Mainstone and Parr, 2002; Schindler et al., 2008). Accelerated eutrophication leads to increased biological production which can have a wide range of problems in aquatic ecosystems including decreases in oxygen, fish kills, loss of biodiversity, loss of aquatic plant beds in coral reefs, and impairment of water resources for drinking and recreational use (Carpenter et al., 1998; Howarth et al., 2000). The effect of nutrient enrichment, particularly P, in freshwater aquatic systems is one of the primary concerns of current research involving water quality parameters.

Acceleration of freshwater eutrophication by P is well documented in the literature (Carpenter et al., 1998; Howarth and Paerl, 2008; Mainstone and Parr, 2002; Schindler, 1977; Schindler et al., 2008; Sharpley et al., 1994). Other nutrients needed for aquatic bioproductivity, nitrogen (N) and carbon (C), can freely exchange between the atmosphere and water body, whereas P has no significant mechanism for exchange with

the atmosphere. Nitrogen fixation in aquatic systems is primarily carried out by cyanobacteria which are particularly important in eutrophic lakes where research has shown they may account for 6 to 82% of the N inputs into the lake (Howarth et al., 1988). Furthermore, N fixing bacteria appear to be able to overcome N deficits through atmospheric fixation, retaining limitation by P as it has no comparable fixation mechanism (Howarth et al., 1988; Schindler, 1977; Schindler, 2008). However, estuarine and saline systems present different dynamics from freshwater systems. These systems are likely to be N-limited as N-fixing bacteria are exceedingly limited in saline systems (> 6 - 8%) (Howarth and Paerl, 2008). Thus, decrease of N inputs into freshwater lakes is purported to have negligible effect as N-fixing bacteria become increasingly favored and are able to make up the N deficit of the lake, while decreased P inputs to freshwaters will depress algal production (Schindler et al., 2008).

As an example, the Chesapeake Bay was one of the first areas to be managed for P and nutrient loading to prevent accelerated eutrophication. The Bay presented one of the best opportunities for research on both N and P inputs from various land uses as the drainage basin has large inputs from agriculture and urban land uses (Sharpley, 2000). The fact that the Bay is an estuary also improves the ability of researchers to understand the dynamic differences in nutrient limitation that occur in fresh water, saline, and estuary settings. Isolated outbreaks of dinoflagellate (*Pfiesteria piscicida*) led researchers to look at diverse sources of nutrients in the environment (Boesch et al., 2001; Burkloder and Glasgow, 1997).

## PHOSPHORUS SOURCES

Point sources of P have been much easier to control and regulate than nonpoint sources, and thus, nonpoint sources are often the dominant inputs of P to surface waters in the United States (Carpenter et al., 1998; Sharpley et al., 2007). Therefore, management of nutrients in agricultural nonpoint systems is of increasing concern. One of the primary reasons for this is that it has been shown in many instances to be a more cost-effective strategy than remediating the impaired waters. In the 1990's for example, the New York metropolitan area determined that a targeted nutrient management strategy costing approximately \$10 million was more economical than building an \$8 billion water treatment facility (Howarth et al., 2000; National Research Council, 2000).

Phosphorus is of significant concern in pasture and confined animal feeding operations - especially poultry (*Gallus domesticus*), as crops take up P and N in the ratio of about 1:8, while the ratio of P:N in manures ranges from 1:2 to 4 (Sharpley and Moyer, 2000). Thus, continued land application of manure at rates to meet the N needs of a crop can lead to a buildup of P in soil, increasing the potential for P loss in runoff (Carpenter et al., 1998; Maguire et al., 2005). In this regard, the land application of poultry litter as a fertilizer is of particular concern, as it typically contains two to four times more P relative to N compared to other animal manures (Kleinman et al., 2005; Sims and Sharpley, 2005). The linkage of field P inputs relative to outputs relating to eutrophication has been shown in surface waters in the United States, and in many areas of intensive animal production with limited land for manure application P is in excess of crop or pasture needs (Fluck et al., 1992; Kellogg et al., 2000; Lander et al., 1998; Sharpley et al., 1981; Sharpley et al., 2007; Slaton et al., 2004).

In large scale poultry production areas buildup of nutrients is a concern for the environment, and sustainable P management must begin with sound animal nutrition and feeding decisions (Sharpley et al., 2007). One main reason for this is that poultry only utilize approximately 1/3 of the P in the feed that is brought onto the farm with the other two-thirds being excreted and subsequently land applied (Maguire et al., 2005; Patterson et al., 2005). Thus, research has been conducted to find ways of reducing the amount of P in feed including enzymes and crop hybrids that contain lower levels of phytate-P (Sharpley et al., 2007). Also, additions of phytase and amino acids to laying hen diets can decrease P in excretion by 50%, however, feed cost for this type of ration nearly tripled, decreasing the feasibility of implementation (Keshavarz and Austic, 2003). However, it is still uncertain if phytase-litter actually decreases P in runoff if litter is not applied on a P-based nutrient scheme (DeLaune et al., 2004; Penn et al., 2004).

The effect of poultry litter application on P runoff is influenced by several factors; the most important are rate, method, and timing of application relative to the first runoff event (Edwards and Daniel, 1993). An intense rainfall event shortly after application is likely to have significantly higher nutrient losses than later events (Edwards and Daniel, 1993). This is of particular concern, as most P transported from overland flow (> 80%) is concentrated in small areas (< 20%) and takes place during relatively few large storm flow events (Pionke et al., 1997).

In urban areas, > 50% of the P reaching rivers generally comes from point sources (Carpenter et al., 1998). However, point sources have been more easily targeted and controlled than nonpoint; thus, nonpoint sources have become an increasing concern. For instance, urban and suburban construction has increased in Northwest Arkansas and with

this comes increased risk of runoff from exposed construction sites (Kemper et al., 2006). Also, runoff from lawns and streets in urban and suburban settings can be enriched with nutrients that have the potential of entering local water bodies (USEPA, 2005a).

The EPA (2005a) established Phase I of the National Pollutant Discharge Elimination System (NPDES) stormwater program. This program requires operators of medium and large Municipal Separate Stormwater Systems (MS4s - separate stormwater and municipal water facilities owned by a public entity serving 100,000 plus people) to implement a stormwater management program. Phase II expands the program to include small MS4s or those in urban areas. Phase II also requires MS4s to implement strategies to deal with construction sites including erosion and sediment controls (USEPA, 2005b). These programs are an attempt to control urban sources, which are still key contributors to surface water nutrient loading (Carpenter et al., 1998; Ekka et al., 2006).

Pollutant discharges from municipal WWTPs tend to be consistent and can be monitored by measuring discharge (Carpenter et al., 1998). A recent study by Ekka et al. (2006) found that WWTPs still had a profound impact on the streams within the Ozark watershed of the study. The study showed that mean DRP concentrations were significantly greater in selected streams downstream from effluent discharge. Also, the sediment-bound P was increased and in P-enriched streams it was postulated that effluent P discharges regulated sediment and aqueous phase P equilibrium (Ekka et al., 2006). Another study by Migliaccio et al. (2007), further supported the idea that stream samples below WWTP have higher concentrations of P, and sediment water concentrations are more controlled by discharge from WWTP's than by the inherent properties associated with the benthic sediments.

## SOIL PROCESSES

Sorption is the main mechanism of P retention in soils in the approximate 4 to 7.5 pH range, above and below this range calcium (Ca) and metal-complexing (Fe, Al) reactions become more important (Heathwaite, 1997). In a simulated stream environment in the pH range 5.2 to 5.4, uptake of P was associated with Al and Fe hydrous oxides and Ca complexing became predominant at 6.5 to 7.2 (McDowell and Sharpley, 2003). This is in contrast to other important nutrients (i.e. nitrate) that do not act as strongly with solid surfaces and cations in organic matter (House et al., 1994).

The main mechanism of P loss from agricultural land is by surface runoff and erosion (Sharpley et al., 1994). Studies have shown that transport of P in subsurface or baseflow is generally lower than in surface runoff due to sorption of P during movement through the soil profile. Exceptions can occur in sandy or organic soils, with low sorption capacity and in soils with extensive preferential flow pathways (Bengston et al., 1988; Sharpley and Syers, 1979; Sims et al., 1998). Of this runoff, the two primary forms of P are DRP and particulate (PP). The first step in DRP's movement to surface waters is the desorption, dissolution, and extraction of P from soil and vegetative cover. Dissolved reactive P is comprised mostly of orthophosphate which is immediately available for algal uptake.

Particulate P can contribute a variable portion of bioavailable P (10-90%) depending on agricultural management (Sharpley et al., 1994). The type of P entering the aquatic system is important as not all P is immediately available to aquatic biota and thereby potential water quality problems; bioavailability of the inflow P depends on its chemical form and the nature of the receiving waters (Pionke et al., 1997). Of note is

research that showed more organic P is present in solution of manured soils than soils that receive the same quantity of inorganic fertilizer (McDowell and Sharpley, 2001a). This difference is important to consider as overland flow entering streams containing higher organic P levels associated with manure application will undergo different reactions and transformations once in the aquatic system compared to inputs as inorganic P (McDowell and Sharpley, 2003).

The forms of P in agricultural runoff are dependent on the initial sources of P and the hydrologic pathway followed from land to stream (Heathwaite, 1997). This includes land use, topography, parent material, and soil test P. Both PP and DRP may be transported in surface runoff, although PP usually dominates, especially in cultivated landscapes (Heathwaite, 1997; Sharpley et al., 1995). Particulate P includes P sorbed by soil particles and organic matter that was eroded during runoff and varies from 10 to 90 % bioavailable (Sharpley et al., 1992; Sharpley et al., 1994). Runoff from grass or forested lands typically carry little sediment, but increasing amounts of erosion can increase the PP concentration (Sharpley et al., 1994).

Soil chemistry is known to play an influential role in P uptake in stream systems (McDowell and Sharpley, 2003). Multiple factors have been studied that influence characteristics of the fate and transport of P. A study by McDowell and Trudgill (2000) in the United Kingdom showed seasonal variations of P loss were apparent, with maximum concentrations in late summer and minimum in late winter. Wetting and drying cycles can change P from water-soluble easily exchangeable pools to pools that are not easily water soluble (McDowell et al., 2002; Watts, 2000). These studies show some of the

varying aspects of the environment that can affect P availability and mobility in the ecosystem.

When P is added to soil either as mineral fertilizer or as manure it generally accumulates at the surface (Kingery et al., 1994; Sharpley et al., 2003). The effective depth of interaction (EDI) is defined as that portion of soil in which P and other sorbed chemicals react with runoff and are released from a thin layer of surface soil (Sharpley, 1985). Thus, EDI (0 – 5-cm) between runoff water and surface soil is important in determining the release of P from soil and thereby P loss in runoff. The EDI between the soil surface and runoff becomes deeper with an increase in rainfall intensity, soil slope, and vegetative cover and thus, varies across a field, landscape, and hillslope (Sharpley, 1985).

Research conducted at the University of Arkansas on a Captina silt loam showed that soil P saturation was highly correlated to bioavailable P in runoff ( $R^2 = 0.77$ ) (Pote et al., 1996). The study also found that water extractable P of surface soil was highly correlated to surface runoff ( $R^2 = 0.82$ ). However, other factors such as climate, topography, land use, and water flow (transport) pathways must also be taken into consideration (Sharpley et al., 2003).

Generally, soils with a higher percentage of clay content will contain more P than those with a larger percentage of coarser materials (McDowell and Sharpley, 2003). Eroded soil typically has a higher content of P than source soil due to erosion of finer-sized soil particles – termed enrichment (Sharpley et al., 1994). Phosphorus losses are related to soil concentration and sorption and desorption of P by colloids can be greatly affected by the amendment rate (McDowell and Sharpley, 2001a).

Phosphorus's role in the environment is diverse, and each step of P movement within the environment poses new questions and opportunities for better understanding of the biogeochemical mechanisms controlling transport from land to water. Of primary interest to this study is P transported from poultry litter sources that have entered Ozark streams within the UIRW. However, a complete understanding of the processes that occur between the edge of a field and receiving waters is still lacking and complicates the process of precisely explaining how applied nutrients affect aquatic systems (Haggard and Sharpley, 2007; Sharpley et al., 2005).

## **FLUVIAL PROCESSES**

Sediments within the fluvial environment tend to have different sorption properties than when in their original land environment and thus, should be studied while actually in an aquatic environment to most closely simulate the properties they would demonstrate in the real world (McCallister and Logan, 1978). Once P leaves a field and enters a stream, different mechanisms occur compared to the terrestrial environment, largely due to differences in soil-atmosphere exchange compared to soil-water column atmosphere exchange. As P reacts strongly with sediments, the sorption and desorption of P by stream sediments are two of the main processes which regulate behavior and concentration of P in streams (McDowell et al., 2004; Sharpley et al., 2005). For instance, McDowell et al. (2002) studied a watershed in Vermont, results showed that sediments in streams draining agricultural land had a significantly greater concentration of fine sediments (< 63- $\mu\text{m}$ ) than those draining other land uses and sediment Mehlich-3

extractable P was on average twice that of forested and urban sites, although not statistically significant.

In a study conducted in a Pennsylvania watershed, McDowell and Sharpley (2001b), found that total P concentrations were greater in bank sediments ( $417 \text{ mg P kg}^{-1}$ ) than in bed sediments ( $281 \text{ mg P kg}^{-1}$ ); however, bed sediments were composed of a greater percentage of sand-sized material and thus would release more P and support a greater DRP concentration in stream flow. Furthermore, the researchers estimated that resuspension of bed sediments would contribute more P to the aquatic system than bank sediments because of the availability of the P to transfer to and from the water column (McDowell and Sharpley, 2001b).

Within the stream environment, base and stormflow conditions have different fluvial processes controlling uptake and release of P. Baseflow conditions related to sediments are less controlled by suspended sediments compared to storm flow which is greatly influenced by the sediment loads (McDowell and Sharpley, 2001b). During storm flow, research has shown that P concentrations decrease due to sediment depositions, resorption of P by sediment, and dilution by low P baseflow (McDowell and Sharpley, 2001b). In streams with lateral channel movement and size sorting as an important characteristic, sediments on the river bed may be a net source of P even during baseflow conditions (McDowell et al., 2002). Other research has shown that sediments in river beds that have high inputs of P can possibly act as reservoirs of P influencing the stream mechanisms controlling P uptake and release (Mainstone and Parr, 2002). These sediments essentially act as buffers minimizing the measurable effects of accelerated eutrophication in downstream waterbodies.

Benthic sediments have the ability to buffer P in aquatic systems and successful environmental management must not only include P inputs but also the transformations occurring within the fluvial system (McDowell and Sharpley, 2003). The form and mobility of land-applied P is of critical importance once in the fluvial system (McDowell and Sharpley, 2003). Percent sand in sediments was shown to be related to the decay rate for PP and TP, indicating that the decrease in PP and TP with time increased with the proportion of sand particles in the sediment (McDowell and Sharpley, 2003). Also, increasing stream velocity has been shown to increase the influx of DRP into the water column (House et al. 1994).

Sediment equilibrium P concentration ( $EPC_0$ ) is the concentration of P in water at which there is no net sorption or desorption of P (Haggard et al., 2007; Klotz, 1988; Taylor and Kunishi, 1971). Sediment  $EPC_0$  is often used to determine if sediments are a source or sink of P to the overlying waters in streams (Haggard et al., 2007). In fluvial systems,  $EPC_0$  has a major influence on the P concentration in solution. For instance, if P in stream flow is less than  $EPC_0$  then P will desorb from sediment and vice versa (Kunishi et al., 1972; McDowell et al., 2002; Taylor and Kunishi, 1971). Some work has shown particle size is positively related to  $EPC_0$  and increasing amounts of fine sediment appear to increase P buffering capacity (Haggard et al., 2007; McDowell et al., 2002). Even though sand-sized particles ( $> 2 - 0.05$ -mm) contain less P than clays ( $< 0.002$  mm), research suggests that P is less sorbed in the sand and thus is more easily released into the water column (McDowell et al., 2002).

An array of abiotic and biotic processes influence the DRP equilibrium concentration between water and sediments (Haggard et al., 2007). Sediments in streams

play a key role in the fate and transport of DRP in stream systems, and equilibrium P ( $EPC_0$ ) of benthic sediments are often related to stream DRP concentrations ( $r = 0.51$ ) (Haggard et al., 2007). The researchers also correlated Mehlich-3 P levels to DRP levels ( $r = 0.50$ ). Modified P saturation ratio was another important parameter determined to be influential in predicting water column DRP levels in Ozark streams and is defined as  $PSR_{mod} = M3P / [M3Fe + M3Mg + M3Mn]$ . This is a modification of Sims et al. (2002) and was determined within Ozark streams and was related to the overlying DRP concentration within the stream ( $r = 0.71$ ).

## **BIOTIC PROCESSES**

Geochemical processes have been cited as the primary regulators of dissolved P of stream water (Klotz, 1988). However, research by Haggard et al. (1999) reported that geochemical processes are only part of the elaborate process controlling P concentrations in aquatic systems, biological processes also play an important role. The classical model of microbial interaction with P in aquatic systems is as catalysts that aid uptake or release by abiotic processes; however, it was theorized that it is more likely that the microbes depend on P as a nutrient and that net release of P is controlled by their demands for the nutrient (Gachter and Meyer, 1993).

Sediment microorganisms have been researched as a mechanism of P movement in fluvial systems with varying degrees of importance attributed to them in the literature (Haggard et al., 1999; Klotz, 1988; McDowell and Sharpley, 2003). Specifically, McDowell and Sharpley (2003) reported that 34 to 43% of sediment P uptake from manure-rich overland flow was accounted for by microbial biomass. Sediment with a

higher initial TP concentration exhibited a greater uptake of P into the microbial biomass (McDowell and Sharpley, 2003). Haggard et al. (1999) found that biotic processes accounted for approximately 38% of P uptake in their sample streams within the Ozarks. Similarly, Khoshmanesh et al. (1999) found that aquatic biota accounted for 30 to 40% of sediment P uptake and release in a wetland sediment. In contrast, other work has suggested that the microbial community associated with stream sediments played only a small role in P sorption and buffering capacity (Klotz, 1988; Meyer, 1979). Clearly, the temporary storage of P from biotic in-channel processes does alter the transport characteristics of P from different landscape positions through streams to a given outlet within a catchment.

Phosphorus uptake is influenced by biological processes such as assimilation by bacteria, and biofilms (Mainstone and Parr, 2002). A recent study by Gainswin et al. (2006) conducted in the United Kingdom, found that in a system with a biofilm appearing on the larger size fractions the sediments particulate material results in a greater flux of dissolved P than fine sediment.

## **SEDIMENT SIZE DEPENDENCY**

Recent work has shown that sediment sizes play a key role in determining whether abiotic or biotic processes play the primary role in the uptake and release of P. For larger sediments with a developed biofilm, biotic factors are likely the primary factor controlling P dynamics on these substrates (Gainswin et al., 2006). Gainswin et al. (2006), also found that the role of fine sediments was primarily through abiotic processes. Similarly, Lottig and Stanely (2007) attributed P retention in a Wisconsin headwater stream to the presence of fine sediments (< 2-mm). Also in this study, it was found that

relatively coarse fine sediment (2 – 0.05-mm), which typically is relatively unreactive was able to support substantial abiotic uptake of P. Thus, P sorption may be linked to the size of sediments but is not a necessary dependency. It was also concluded that high amounts of sand-size fraction in sediments may be able to act as P-buffering mechanism better than silt or clay as they are frequently replenished and transported, thus avoiding becoming sinks of P (Lottig and Stanley, 2007).

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**TABLE**

Table 2.1. Terminology of phosphorus extractions and forms in water and sediment

<b>Name</b>	<b>Abbr.</b>	<b>Description</b>	<b>Methodology</b>
<b>Water Terms</b>			
Dissolved Reactive Phosphate	DRP	“Reactive” does not refer to behaviour in the environment, but rather to the reaction with molybdate in colorimetric analysis. Some organic P may be hydrolyzed to ortho P during colorimetric analysis	Murphy and Riley colorimetric analysis
Particulate P	PP	Inorganic and organic P associated with or bound to particles in water column	By difference = [TP - TDP]
Total Dissolved P	TDP	All P remaining in a sample after filtration; includes all inorganic and organic P forms	Potassium persulfate autoclave digestion subsequent Murphy and Riley colorimetric analysis
Total P in Water (Total P unfiltered)	TP	Total amount in dissolved and particulate phases. Full water column sample including algal cells and particulates	Potassium persulfate autoclave digestion subsequent Murphy and Riley colorimetric analysis
<b>Sediment</b>			
Mehlich-3 P	M3P	Labile-P subsequently correlated to plant availability of soil P	Mehlich-3 extractant
Microbial P		P contained within microbial communities	One sample sterilized (chloroform) and unsterilized. Subsequent extraction via NaHCO <sub>3</sub> . By difference = [Unsterilized-sterilized]
Modified P Sorption Ratio	PSR <sub>mod</sub>	A calculated parameter utilizing M3 extractable nutrients to account for P binding with various trace metals which decrease availability	M3P/ [M3 Fe + M3Mg + M3Mn]
Water Extractable P	WEP	Labile P which is displaced by distilled water	Distilled water extraction
<b>Sorption Properties using the Langmuir Isotherm</b>			
Binding Energy	<i>k</i>	Constant related to binding energy between P and sediment	Batch spiking procedures
Equilibrium P Concentration	EPC <sub>0</sub>	Concentration at which there is no net uptake or release of P between sediment and water column	Batch spiking procedures
P Sorption Maximum	P <sub>max</sub>	Maximum amount of P a sediment can sorb	Batch spiking procedures

## **CHAPTER 3**

### **SEDIMENT DISTRIBUTION CHARACTERISTICS OF SELECT STREAMS WITHIN THE UPPER ILLINOIS RIVER WATERSHED**

## ABSTRACT

To better understand the relationship between P inputs and water quality response in the Upper Illinois River Watershed (UIRW) information is needed on the fate and transport of phosphorus (P) and the role of stream sediment in regulating transient P. Prior studies indicate that P uptake and release for fine- (< 2-mm) and larger- (> 2-mm) sized sediments are primarily driven by abiotic and biotic mechanisms, respectively. Fine-sized sediments play a pivotal role in P storage via sorption and burial, which can be released back to stream water. Algae attached to larger-sediments (periphyton) can consume and store large amounts of P. This study investigated the relative size distribution of bed sediment and specific chemical and physical properties of the fine-sediment as potential sinks and sources of P in five streams draining watersheds of differing land use. Watersheds had mixed land use with 3 predominately agriculture, 1 forest, and 1 urban. Stream substrate was variable within specific sites but across sites, 2 to 20 and 20 to 75-mm size classes dominated. The < 2-mm sediment contributed 9 to 18% of total bed substrate, while the >2-mm fraction dominated at over 80%. Along with this, the modified P saturation ratio of < 2-mm sediment was correlated to stream water DRP levels ( $r = 0.96$ ). An inverse correlation existed between stream water DRP and TP levels compared to > 75-mm sediment, a possible sink via periphyton uptake. In the UIRW, stream beds are comprised of a wide range of sediment sizes, leading to a need for both abiotic and biotic research to understand the effect stream substrate has on transient-P storage.

## INTRODUCTION

Increased public awareness in the 1970's concerning the degradation of surface waters led to the enactment of the Federal Water Pollution Control Act of 1972 (USEPA, 2008). The Clean Water Act as it is more commonly known established basic parameters around which water quality regulations and guidelines are set for the federal government and for which most states have followed.

Accelerated eutrophication of freshwaters is identified as the leading impairment of water quality in the United States (USEPA, 1996). In freshwaters, P is linked to increased algal productivity, as it is the most common limiting nutrient for algal growth (Howarth and Paerl, 2008; Schindler et al., 2008). Stream characteristics influence P types and amounts transported from the landscape to lakes and reservoirs. Within the fluvial system, abiotic and biotic processes at the sediment-water interface occur simultaneously and both play important roles in the transport and storage of P within stream systems (Haggard and Sharpley, 2007). Sediments act as either sinks or sources of P and thus, may be influential in determining the time frame over which changes occur in watersheds after management strategies have been implemented (Haggard and Sharpley, 2007).

Sediment size fractions have important impacts on determining dominate processes controlling P-dynamics in streams. Phosphorus interaction with fine-sized sediments (< 2-mm) are typically regulated by chemical reactions, and with increasing size, biological control associated with algal periphyton growth becomes the dominate P uptake mechanism (Fig. 3.1; Lottig and Stanley, 2007). Work in the United Kingdom reported P release from algal-biofilms on large-sized sediments (> 20-mm) to stream

water was greater than release from fine sediments (< 2-mm) (Gainswin et al., 2006). However, Lottig and Stanley (2007) showed that fine-sediments (< 2-mm) had a greater capacity to adsorb P than larger sediments and thus, had a greater capacity to act as buffers of P entering from storm-flow runoff events (Fig. 3.1).

Agricultural land use in Northwest Arkansas is often cited as a leading contributor to increased inputs of P into the waters of the region (Sauer et al., 2002). This is in part due to the rapid increase in population growth over the last 20 years and the area's large number of poultry production operations and associated litter, which is often spread on local pastures (Sharpley et al. 2007; Slaton et al., 2004). With continued application of litter at rates to meet forage nitrogen (N) requirements, soil P can accumulate to levels that increase the risk of P enrichment of runoff (Sharpley et al., 2007). Urban areas in the region are also important sources of P, as they have large amounts of impervious surfaces, inputs from lawns, and human waste inputs (Ekka et al., 2006). For instance, research has shown when 10 to 15% of a watershed is comprised of impervious surfaces a strong correlation is apparent in the aquatic ecosystems drained from these areas (Kleine, 1979; Wang et al., 2000).

## **OBJECTIVES**

This study strove to determine the relative size distributions of bed sediments of five selected streams within the UIRW, determine the dominate land uses draining into them, and study sediment interactions with the overlying stream-water column.

## **MATERIALS AND METHODS**

### **STUDY SITES**

Five streams draining into the Illinois River were selected to represent agricultural, forested, and urban land uses. Subwatersheds were delineated by sampling sites using a digital elevation model and land use / land cover data in ArcGIS 9.2 (CAST, 2006; ESRI, 2006; ASLIB, 2007). Land use / land cover was aggregated into agriculture, urban, and forested land uses. The delineated subwatersheds were determined using the ArcHydro tool within ArcGIS and proportion land use was calculated as percentages of total land area within each subwatershed.

### **SAMPLE COLLECTION AND ANALYSIS TECHNIQUES**

A representative reach (riffle and pool) was established at each of the 5 streams and samples collected in August, 2008 across the reach at equal distances (Photos 3.1-3.5). Reaches were measured at 7 to 10 equally spaced intervals and transects determined, and used as sampling locations for this study. Transect width was measured and stream velocity measured using a Flo-Mate 2000 (Marsh-McBirney, Inc., Frederick, MD) at 10 equally spaced points across the transect upstream at each sampling site during baseflow conditions. Width and velocities were used to calculate flow rate and average velocity across each transect within the reach.

Stream water samples were collected at the time of sediment sampling. A subsample was filtered (0.45- $\mu$ m), acidified to pH 2 (HCl) in-field, and transported to the laboratory and stored at 4 °C until analysis. An unfiltered water sample was also acidified

(pH 2) and stored at 4 °C until analysis. Filtered samples were analyzed using the automated ascorbic acid method on a Skalar San Plus Wet Chemistry Autoanalyzer (Skalar, the Netherlands) (APHA, 1998). Unfiltered samples were digested via an alkaline persulphate method (Hosomi and Sudo 1986; Lambert and Maher, 1995).

A 2 L sample of sediment was collected from a 0- to 3-cm depth at five locations across each transect with a spade and composited to create a representative sample. Samples from the transect were sieved to size classes of > 75, 75 to 20, 20 to 2, and < 2-mm within 24 h after sampling. A < 2-mm sample was also collected at each transect for particle size analysis, and a sub-sample air dried prior to Mehlich-3 extraction (Arshad et al., 1996; Mehlich, 1984).

Each size fraction of sediment was air dried. After drying, size classes were measured using a standard water displacement procedure, where water (6 L) was added to a container and the volume of water displaced measured when each size class was added. Total displacement of all size classes was determined along each transect and each size class divided by this total to determine relative proportion of each size class within the stream transect.

Fine-fraction sediment (< 2-mm) was used for particle size analysis. Sediments were added at 50 g dry weight to a 1 L cylinder with 50 mL of sodium hexametaphosphate and brought to volume (Arshad et al., 1996). Three hydrometer readings were taken and averaged at the 40 s mark, and one 2 h reading was taken. These readings were then used to calculate the relative proportion of sand (2 - 0.05-mm), silt (0.05 - 0.002-mm), and clay (<0.002-mm) at each transect within each stream (Arshad et

al., 1996). A sub-sample of the fine-fraction was air dried and used for Mehlich-3 extraction (Mehlich, 1984).

### **MODIFIED PHOSPHORUS SATURATION RATIO**

Mehlich-3 P (M3P) has been used as an indicator to estimate environmental susceptibility to P loss in runoff (Sharpley et al., 1996; Sims et al., 2002). In Sims et al. (2002), M3P saturation ratio was calculated using M3 extractable nutrients as  $PSR = [M3P / M3Al + M3 Fe]$ . This ratio includes P-reactive trace elements and improves upon the relationship between soil test P measures and subsequent DRP concentrations of surface runoff, as increases in these trace elements decrease the movement of P into the water column. For calcareous soils, inclusion of M3Ca and M3Mg improved the relationship between PSR and runoff DRP (Ige et al., 2005). Based on this, work in UIRW streams by Haggard et al. (2007) modified the P saturation ratio ( $PSR_{mod}$ ) to  $[M3P / M3Fe + M3Mg + M3Mn]$ . Modified P saturation ratio was found to be statistically more closely correlated to in-stream DRP levels ( $r = 0.71$ ) and will be utilized in this study to investigate relationships among bed sediment extractable nutrients and stream water DRP.

### **STATISTICAL ANALYSIS**

Linear regressions were performed in SigmaPlot with significance levels of  $\alpha < 0.05$ . Relationship strength between parameters within the text is discussed in terms of correlation coefficients ( $r$ ). When regression models are presented in figures coefficients of determination ( $R^2$ ) are reported.

A one-way analysis of variance (ANOVA) was performed in SAS 9.2 where streams were treated as a fixed factor and the four size classes were tested separately.

When stream effect was significant, means were separated using Fisher's protected least significant difference (LSD).

## **RESULTS AND DISCUSSION**

### **LAND USE AND LANDCOVER**

Stream sites within the region represented varying land uses and within each site agricultural, forested, and urban activities were present (Fig. 3.2). Delineation and calculation of land use land cover resulted in 1 primarily forested (> 50%), 3 agricultural, and 1 urban dominated subbasins (Table 3.1). Agricultural land is dominated by pasture systems with both warm and cool season grasses often accompanied by beef cattle production. Mud Creek Tributary was the most urbanized stream sampled with 68% of the drainage land dominated by this land use and only 7% composed of agricultural land. Wildcat Creek in contrast was nearly 70% agriculture and 4% urban. Chamber Springs with 61% forest was the only primarily forested landscape; however, the subbasin is also comprised of 38% agriculture much of which is directly adjacent to the stream (Table 3.1).

### **WATER COLUMN**

Average stream velocity at the time of sediment sampling was variable across sites ranging from 0.06 to 0.26 m s<sup>-1</sup> (Table 3.2). Flow rates also varied across sites at baseflow conditions ranging from 0.02 to 0.20 m<sup>3</sup> s<sup>-1</sup>. Clearly, water was flowing at different rates and in different amounts across the selected sites at the time of sampling. This results in varying transient storage times across sites, which could lead to differences in P uptake due to residence time differences.

Dissolved reactive P concentrations at the time of sediment sampling, varied across sites with Moore's Creek having the highest value  $0.067 \text{ mg P L}^{-1}$  and Mud Creek Tributary the lowest  $0.034 \text{ mg P L}^{-1}$  (Table 3.2). Total P across sites ranged from  $0.035 \text{ mg P L}^{-1}$  at Mud Creek Tributary to  $0.104 \text{ mg P L}^{-1}$  at Moore's Creek. Previous work within the region observed trends based on linear regressions between land use and stream DRP levels (Haggard et al., 2007; Popova et al., 2006). Within our dataset no linear relationship between DRP and land use was found; however, land use is still important in determining the loading of P to these waters in both dissolved and particulate forms.

## **SEDIMENT DISTRIBUTIONS**

The relative size distribution of sediments was similar across sites. Sediment  $> 20\text{-mm}$  accounted for roughly 50% of bed sediment across all sites with the remaining  $< 20\text{-mm}$ , with relatively large variability within sites as shown by the standard errors (Fig. 3.3). Gainswin et al. (2006) reported chlorophyll-a concentrations of  $2$  to  $20\text{-mm}$  size fraction sediment at two sampled sites in the United Kingdom ( $6.4$  and  $8.6 \text{ mg m}^{-2}$ ) was appreciably lower than  $> 20\text{-mm}$  sediment ( $22.8$  and  $62.7 \text{ mg m}^{-2}$ ). Sediment of  $2\text{-}$  to  $20\text{-mm}$  was more similar to fine sediments which had chlorophyll-a concentrations of  $3.0$  and  $2.3 \text{ mg m}^{-2}$ , respectively (Gainswin et al., 2006). The  $2\text{-}$  to  $20\text{-mm}$  size fraction is the least reactive size class as it does not have a substantial chemical charge like the  $< 2\text{-mm}$  size fraction and is not able to form as significant amounts of biofilm as the  $> 20\text{-mm}$  size class. This is critical, as the intersection of these size classes likely represent an important transition from abiotic to biotic dominance of P reactions and transformations (Fig. 3.1).

Thus, bed sediments of streams in the UIRW represent a system in which there are large portions of sediment where P reactions are predominately biologically and abiotically driven.

Further separating the size classes, the > 75-mm sediments comprised the lowest percentage across sites, ranging from 0.3 to 11 % of the bed sediment (Table 3.3). The < 2-mm sediments were the second lowest, ranging from 9 to 18% of streambed composition. However, the < 2-mm sediments are likely to have the largest surface area per unit weight of any sediment size class and thus, greatest chemical reactivity. The 75 to 20-mm and 20- to 2-mm classes represented roughly 80 to 90% of the total bed material across sites and ranged from 35 to 48 and 36 to 46% of fluvial sediment, respectively. Within sites, large variation within a reach was observed within sediment size fractions (Fig. 3.3). However, no significant relationship for any size class was observed across streams; *p*-values ranged from 0.19 (20- - 2-mm) to 0.54 (< 2-mm), and thus, means were not separated by LSD (Table 3.3). Thus, stream size classes of the selected streams are comparable in their bed sediment makeup and differences in P-chemistry across streams is likely due to other factors such as, periphyton growth, clay type, sediment P concentrations, and P inputs to the stream from the landscape.

At the time of sampling, in-stream concentrations of DRP decreased as the percentage of > 75-mm sediment increased (Fig. 3.4). Total P concentrations also steadily decreased when the percentage of >75-mm sediment increased (Fig. 3.5). This is likely related to associated periphyton growth on large sediments (> 20-mm) acting as sinks of P during growth and uptake. However, upon death and decomposition, periphyton biomass could become sources of P to overlying waters (McCormick et al., 2006).

Periphyton, upon becoming unattached and subsequently transported, may also act as a P source to downstream lakes and reservoirs.

### **FINE-FRACTION SEDIMENTS**

The < 2-mm size fraction at Moore's Creek was greatest at 17.9% with Little Wildcat Creek the least at 8.6%. Across streams there was no significant stream effect on the mean < 2-mm percentage (Table 3.3). Sand (> 2- - 0.05-mm) was the most predominant fraction of < 2-mm sediment, comprising over 80% of the fine sediment at each site (Table 3.3). Differences existed between streams for the sand fraction with Mud Creek Tributary having a significantly greater mean sand content than either Chamber Springs or Wildcat Creek (Table 3.3). This fraction is often linked to highly available P-fractions which are less tightly sorbed than on clay sized fractions.

The silt-sized fraction was also variable within site and across streams, Wildcat Creek and Chamber Springs had a statistically greater mean than the other sampled sites which were statistically similar (Table 3.3). The clay-fraction was not statistically different across streams as analyzed by ANOVA analysis ( $\alpha = 0.05$ ), but within sites ranged from 2.1 to 5.4% with relatively large standard errors within sites (Table 3.3; Fig. 3.6).

Mean clay content of all sites did not differ statistically across streams (Table 3.3). While clay-fractions typically can hold the most P, this is also contingent on the extent and duration of P inputs to the stream. Similar to results from McDowell and Sharpley (2003), our forested site (Chamber Springs) had relatively high clay content (Table 3.3) and a relatively low M3P concentration (Table 3.4), likely due to a lack of

inputs and subsequent runoff to the stream. Also, P held by sand-sized particles is generally more easily released to water, as it is less tightly adsorbed (Lottig and Stanley, 2007). As there were few differences in sand content and the mean clay content across sites was statistically similar, and typically, this is the largest area of P-storage no trends between < 2-mm fractions and M3P concentrations were found.

The continued replenishment of fine-sized sediment from the landscape in turn acts as a renewal mechanism for P within these stream sites. For example, Mud Creek Tributary, which drains a highly urbanized area, experiences rapid influxes of water during storm events, thus, sediments may be more rapidly transported within this stream than those draining dominantly agricultural or forested areas. Subsequently, these large loads can continually replenish its sand-sized fraction (94.8 %) and the remainder of the < 2-mm size fraction of bed sediment with eroded soil (enrichment) estimated at 2 times the concentration of the initial soil P level (Brady and Weil, 2008; Sharpley et al., 1994).

### **MEHLICH-3 VALUES**

The M3P concentrations of < 2-mm sediments ranged from 12 to 37 mg P kg<sup>-1</sup> (Table 3.4). Calculated PSR<sub>mod</sub> ranged from 3 to 8 % across sites and may be a better indicator of P availability as it takes into account trace elements (Fe, Mg, Mn), which are reactive with P (Table 3.4). Along with this, M3Ca ranged from 737 to 2428 mg Ca kg<sup>-1</sup>, M3Cu from 3 to 8 mg Cu kg<sup>-1</sup>, M3Fe from 133 to 337 mg Fe kg<sup>-1</sup>, and M3Zn from 4 to 6 mg Zn kg<sup>-1</sup> (Table 3.5). Sediment M3P was related to M3Fe ( $r = 0.79$ ) for all stream transects (Fig. 3.7), suggesting that much of the P is bound with Fe in these sediments.

Sediment M3P was also highly correlated to DRP ( $r = 0.89$ ) with increased streambed M3P content leading to greater stream DRP concentrations (Fig. 3.8). This relationship is driven by one high-P site (Moore's Creek) and as P availability is highly linked trace elements,  $PSR_{mod}$  as described by Haggard et al. (2007) was utilized (Table 3.4). Modified P saturation ratio showed a stronger correlation with stream DRP concentrations ( $r = 0.96$ ) (Fig. 3.9). Based on the work of Lottig and Stanley (2007) and our results, it is probable that  $PSR_{mod}$  decreases with increased amounts of larger-sized sediments and may be representative of a shift in the buffering mechanisms from abiotic to biotic control. Thus, in terms of P transformations between stream sediments and the water column, it is important to consider the concentrations of trace elements as well as P.

## CONCLUSIONS

It is apparent that many variables contribute to determining the DRP concentration of stream waters at any given time they are measured. Simple land use characterization of streams may not always show conclusive relationships in determining stream DRP concentrations, particularly with a small sample size of five sampled streams; previous research by Haggard et al., 2007 utilized approximately 20 sites and found a relatively small relationship ( $r^2 = 0.31$ ). However, land use is nonetheless important, as the characteristics and transport mechanisms within the watershed will determine the sediment and nutrient loading within. Large-sized sediments ( $> 20$ -mm) and subsequent biofilm growth can act as temporary P storage mechanisms. As these sampled sites have a large portion of the substrate composed of larger-size fractions,

biofilm growth is probably a key regulator of DRP during their growing seasons. However, a large portion of the sediment is comprised of the < 20-mm sediment leading to a large portion of sediment that is driven by chemical reactions, with both < 2-mm sediments and associated trace elements associated with this size fraction. Thus, in the UIRW stream sediment uptake and release of P is intrinsically intertwined between abiotic and biotic processes.

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**TABLES**

Table 3.1. Percentage of watershed in agriculture, forest, and urban land use categories for five selected streams in the Upper Illinois River Watershed, AR.

Stream	Urban	Agriculture	Forest
	----- % -----		
Chamber Springs	1.2	37.7	<b>61.0*</b>
Little Wildcat Creek	18.5	<b>61.2</b>	20.2
Mud Creek Tributary	<b>67.9</b>	6.7	25.4
Moore's Creek	5.5	<b>55.9</b>	38.7
Wildcat Creek	4.0	<b>70.0</b>	26.0

\* Bold numbers represent dominant land use within a given watershed.

Table 3.2. Water column parameters including dissolved reactive P (DRP) and total P (TP) concentrations for five selected streams in the Upper Illinois River Watershed, AR.

<b>Stream</b>	<b>Velocity</b>	<b>Flow rate</b>	<b>DRP</b>	<b>TP</b>
	$\text{m s}^{-1}$	$\text{m}^3 \text{s}^{-1}$	----- $\text{mg P L}^{-1}$ -----	
Chamber Springs	0.20	0.08	0.046	0.048
Little Wildcat	0.26	0.16	0.038	0.038
Moore's Creek	0.12	0.20	0.067	0.104
Mud Creek Tributary	0.06	0.02	0.034	0.035
Wildcat Creek	0.20	0.19	0.041	0.046

Table 3.3. Sediment size classifications and < 2-mm particle size analysis for five selected streams in the Upper Illinois River Watershed, AR.

Stream	Total Sediment				< 2-mm particle size		
	> 75	75-20	20-2	< 2	Sand	Silt	Clay
	-----mm-----				-----%-----		
Chamber Springs	5.7	45.5	36.6	12.2	85.5b*	9.2a	5.3
Little Wildcat Creek	10.8	40.4	40.3	8.6	92.0ab	5.6ab	2.4
Moore's Creek	0.3	35.0	46.2	17.9	90.9ab	3.8b	5.3
Mud Creek Tributary	12.2	40.4	36.2	11.2	94.8a	3.1b	2.1
Wildcat Creek	7.4	48.7	35.7	14.3	84.7b	9.8a	5.4
<i>p</i> -value	0.200**	0.220	0.188	0.534	0.048	0.008	0.145

\* Means in the same column followed by the same letter are not statistically different based on Fisher's protected LSD

\*\* Size classes without a significant stream effect were not separated by Fisher's protected LSD

Table 3.4. Mehlich-3 P (M3P), modified P saturation ratio (PSR<sub>mod</sub>), and pH of sediments from five selected streams in the Upper Illinois River Watershed, AR.

Stream	pH	M3P	PSR <sub>mod</sub>
		mg P kg <sup>-1</sup>	%
Chamber Springs	7.5c*	11.5c	5.1b
Little Wildcat Creek	7.9b	16.9b	5.0b
Moore's Creek	7.4c	37.0a	7.9a
Mud Creek Tributary	8.3a	13.7bc	3.3c
Wildcat Creek	8.1ab	15.6	4.0bc
<i>p</i> -value	<0.0001	<0.0001	<0.0001

\* Means in the same column followed by the same letter are not statistically different based on Fisher's protected LSD

Table 3.5. Mehlich-3 (M3) trace element concentrations of sediments at 5 selected streams in the Upper Illinois River Watershed, AR.

Stream	Ca	Cu	Fe	Mg	Mn	Zn
	-----mg kg <sup>-1</sup> -----					
Chamber Springs	1113c*	7.0ab	134b	34c	63c	3.7
Little Wildcat Creek	943c	5.6b	176b	34c	132b	5.8
Moore's Creek	738c	3.0c	337a	39c	103bc	5.4
Mud Creek Tributary	1861b	5.3bc	133b	79a	203a	5.7
Wildcat Creek	2428a	8.4a	153b	51b	219a	4.5
<i>p</i> -value	<0.0001	0.001	<0.0001	<0.0001	<0.0001	0.063**

\* Means in the same column followed by the same letter are not statistically different based on Fisher's protected LSD

\*\* Nutrients without a significant stream effect were not separated by Fisher's protected LSD

FIGURES

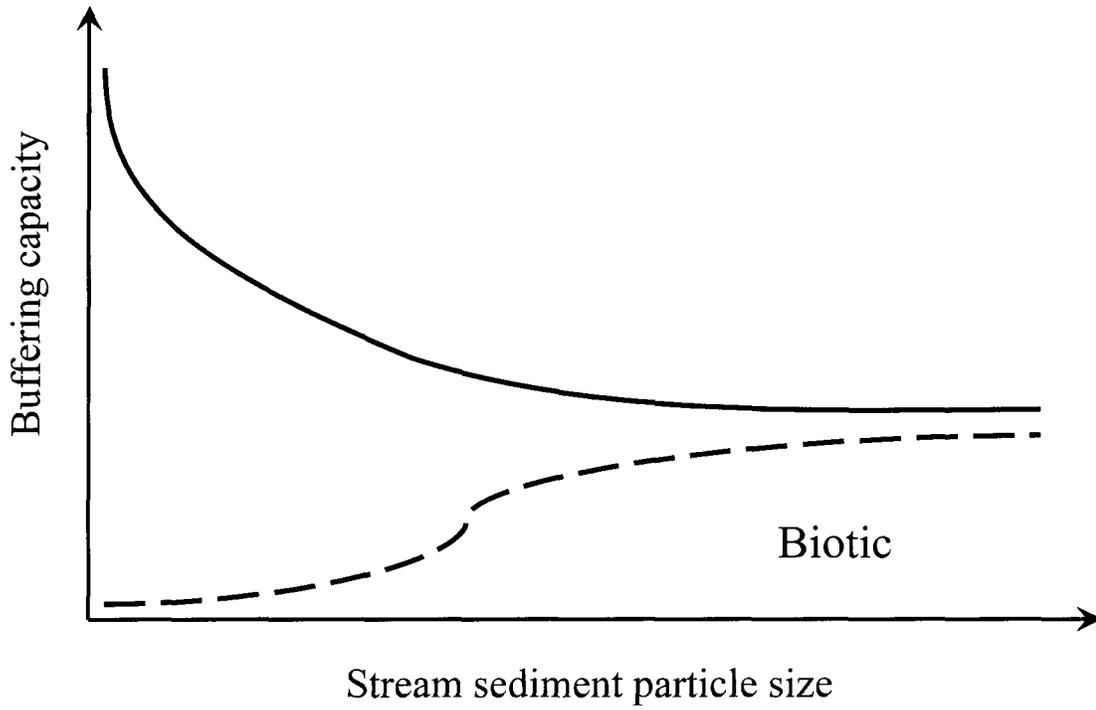


Figure 3.1. Conceptual framework for controlling mechanism of P buffering for stream sediments (Lottig and Stanley, 2007).

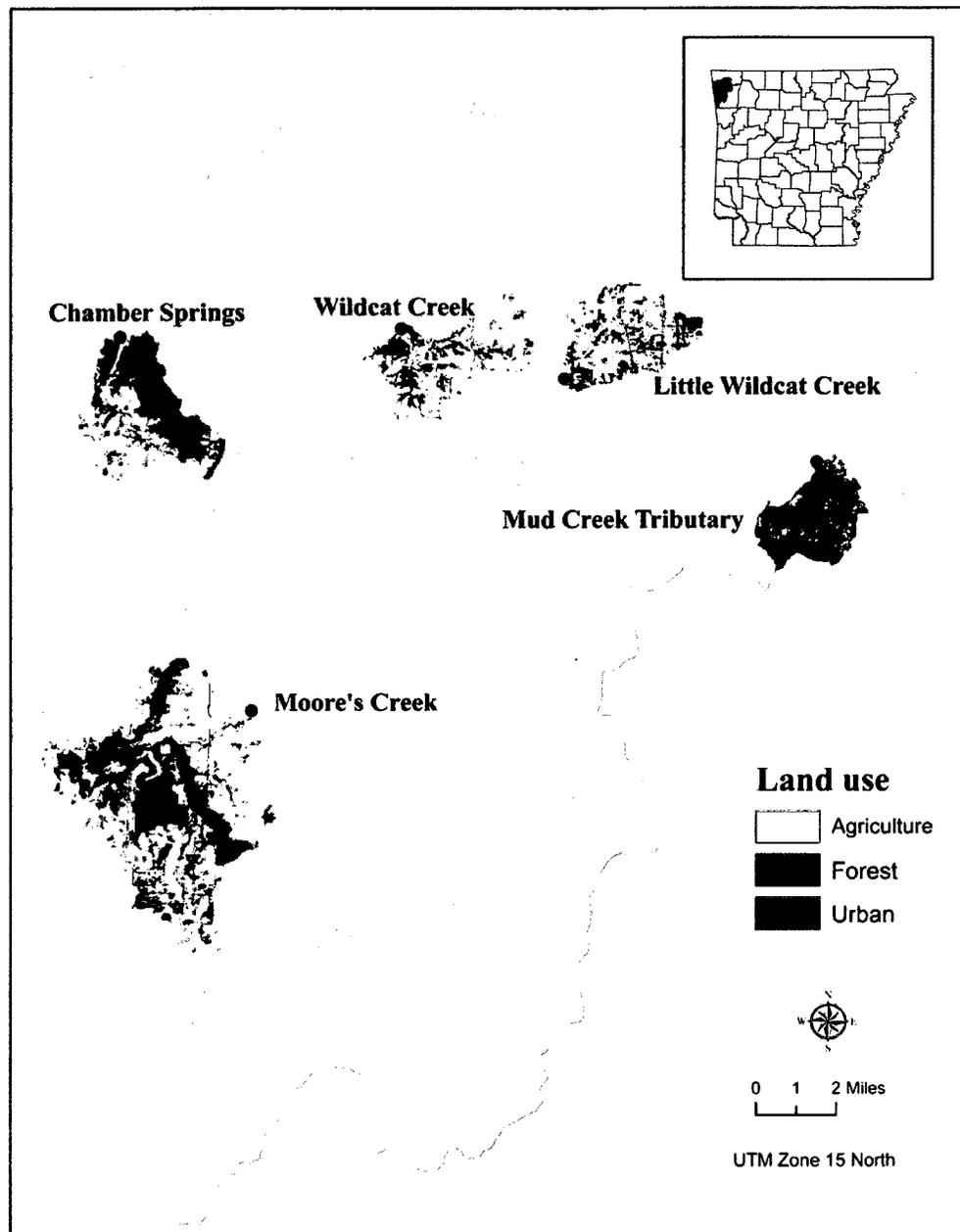
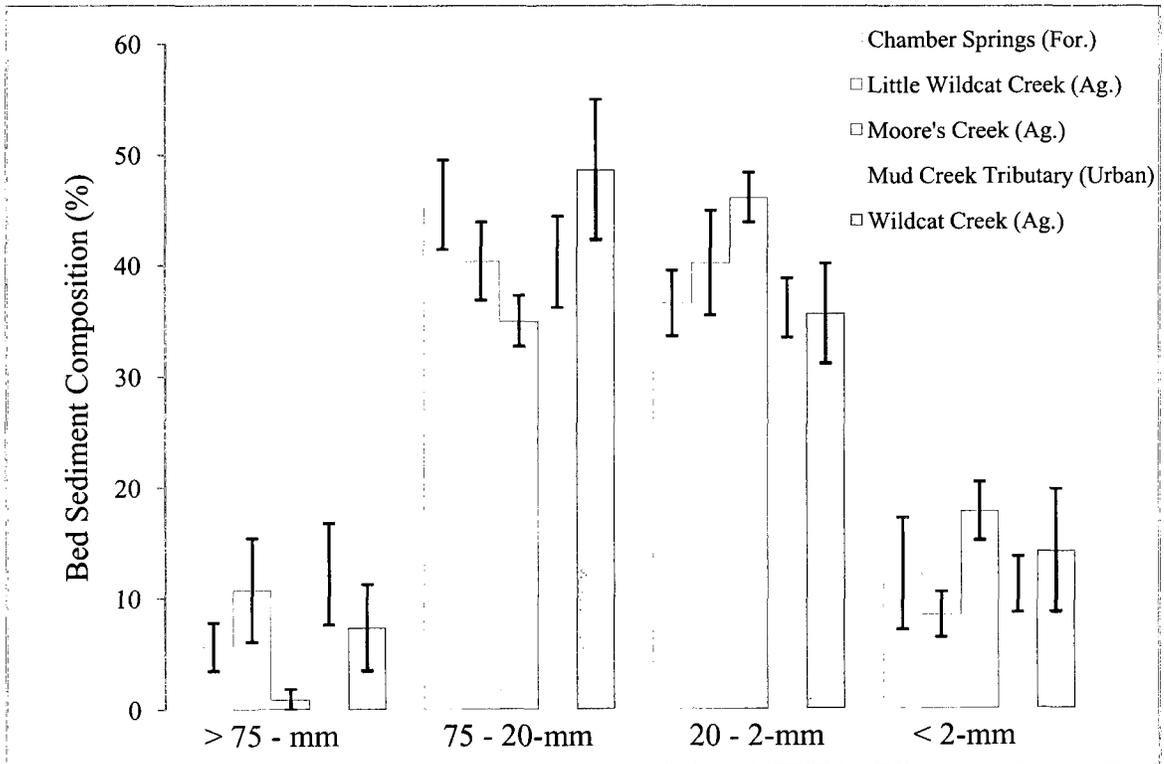


Figure 3.2. Map of delineated research site drainage basins with land use land classification (agriculture, forest, urban) for five streams in the Upper Illinois River Watershed, AR.



\* Streams did not have significantly different means for any of the particle size classes ( $\alpha = 0.05$ )

Figure 3.3. Bed sediment distribution for four size classes for five selected streams in the Upper Illinois River Watershed, AR (standard errors presented for within stream variation)

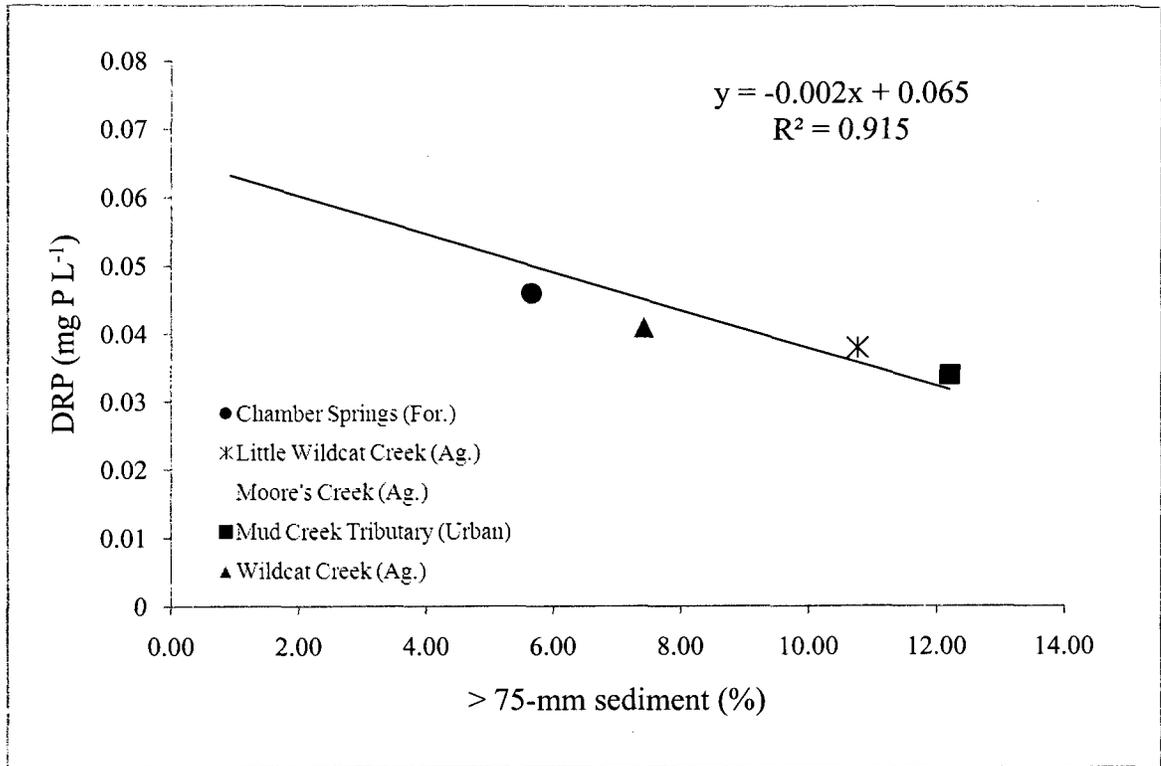


Figure 3.4. Relationship between dissolved reactive P concentration (DRP) and average percent > 75- $\mu$ m sediment at five streams in the Upper Illinois River Watershed, AR.

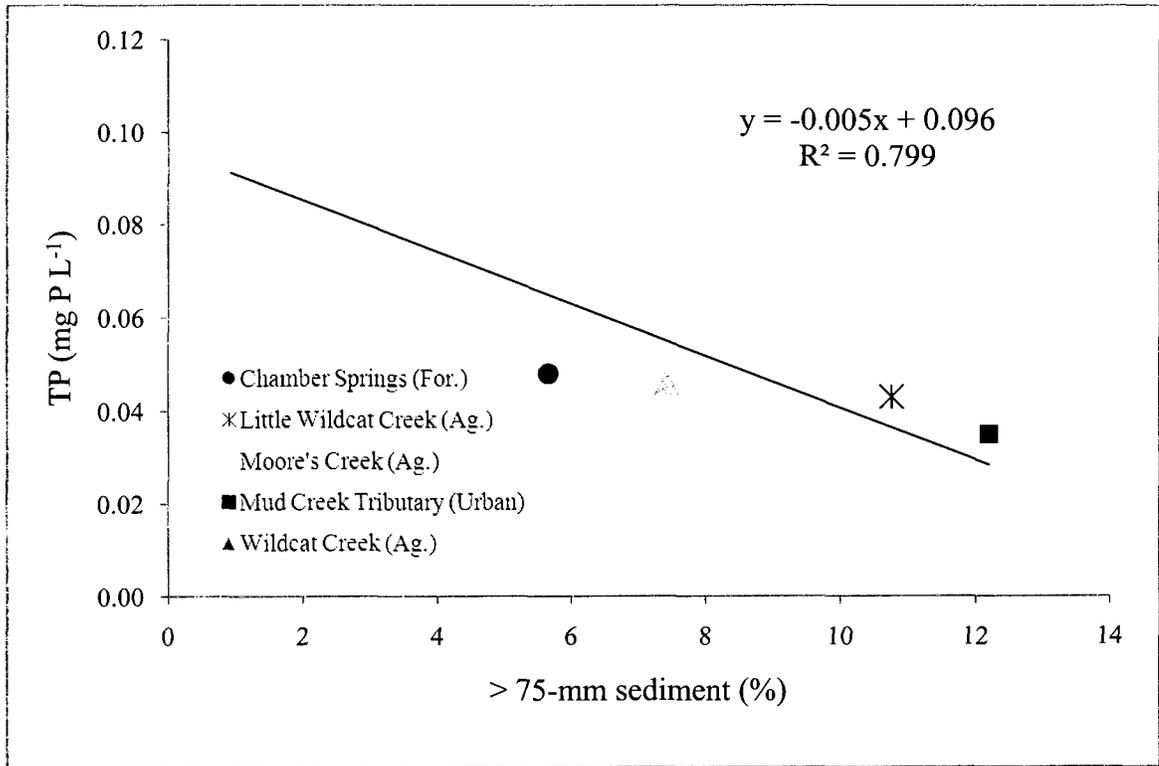
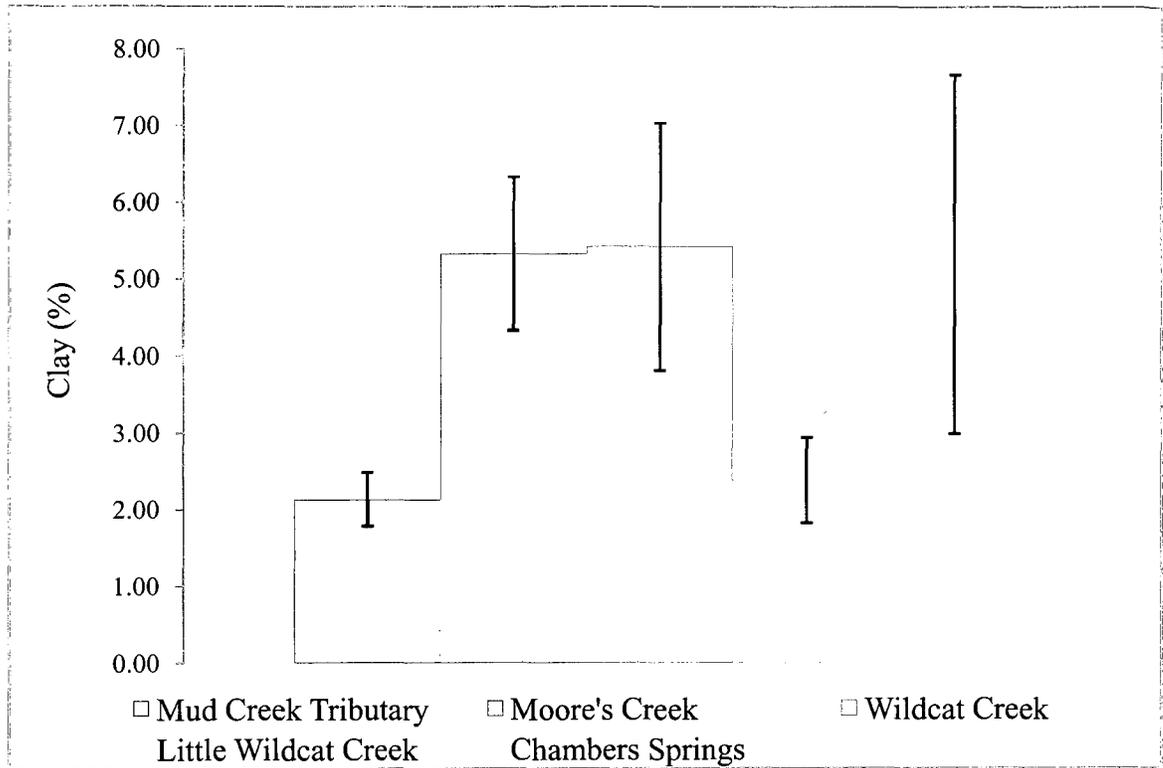


Figure 3.5. Relationship between total P concentration (TP) and average percent > 75-mm sediment at five streams in the Upper Illinois River Watershed, AR.



\*Mean clay content was not statistically different across streams ( $\alpha = 0.05$ )

Figure 3.6. Mean clay (< 0.002-mm) content for five streams in the Upper Illinois River Watershed, AR (standard errors presented).

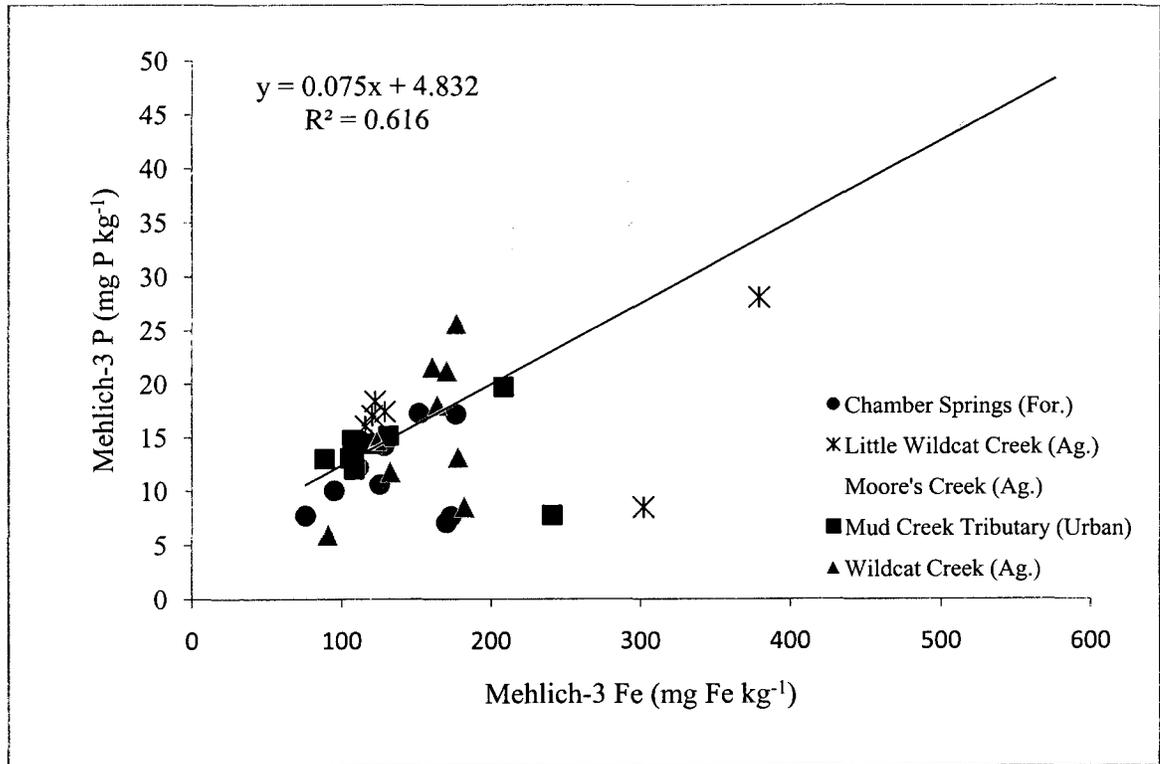


Figure 3.7. Relationship between Mehlich-3 P (M3P) and Mehlich-3 Fe (M3Fe) at all transects for five streams in the Upper Illinois River Watershed, AR.

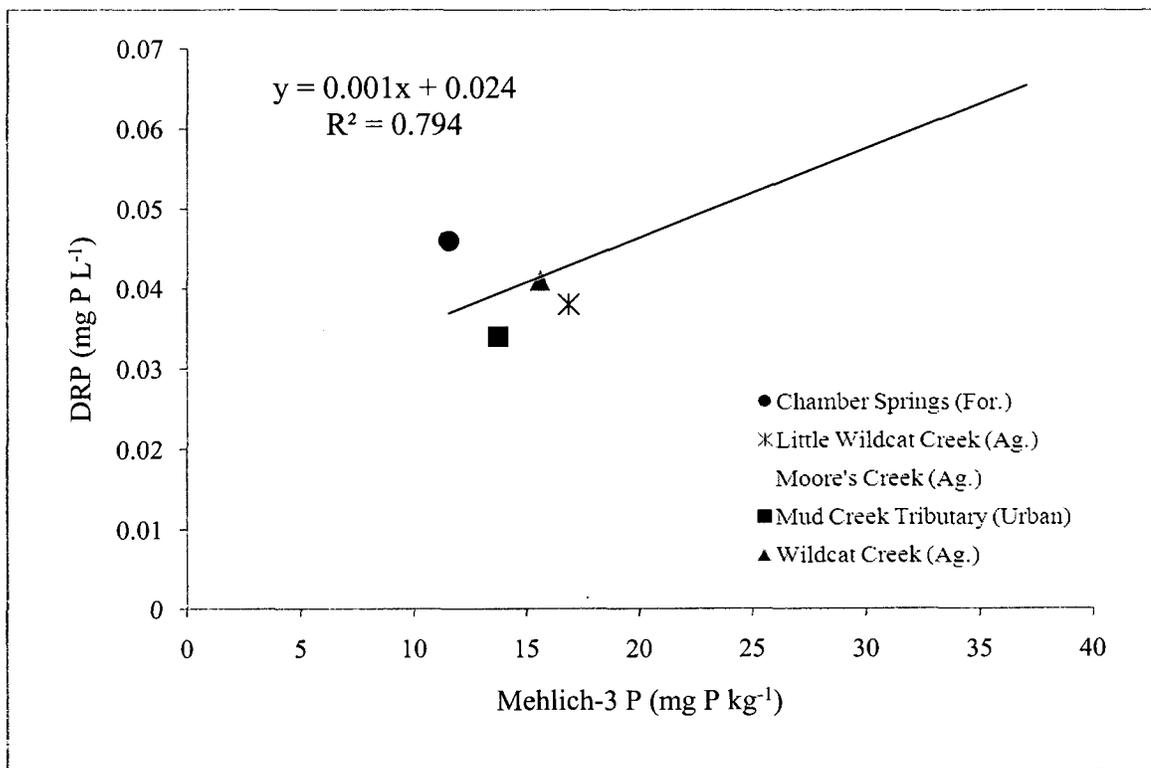


Figure 3.8. Relationship between average Mehlich-3 P (M3P) and dissolved reactive P (DRP) for five streams in the Upper Illinois River Watershed, AR.

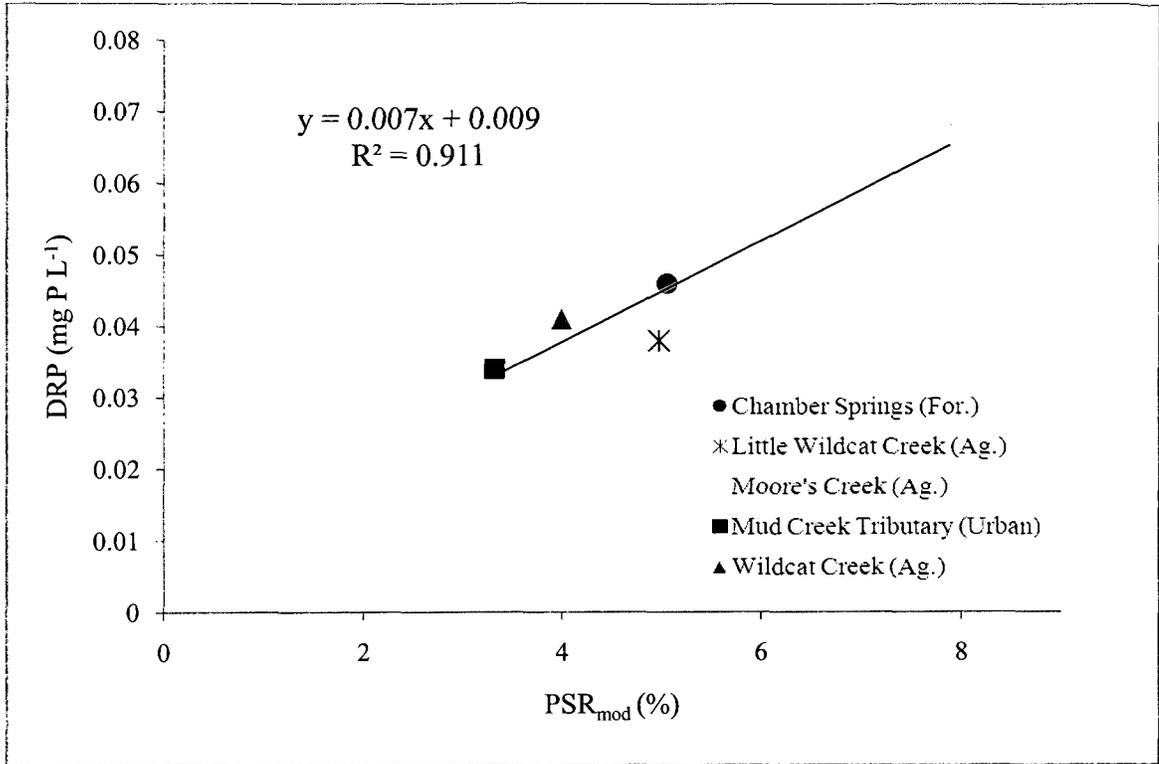


Figure 3.9. Relationship between modified P saturation ratio ( $PSR_{mod}$ ) of sediments and dissolved reactive P concentrations (DRP) for five streams in the Upper Illinois River Watershed, AR.

## PHOTOS



Photo 3.1. Chamber Springs, Upper Illinois River Watershed, AR



Photo 3.2. Little Wildcat Creek, Upper Illinois River Watershed, AR



Photo 3.3. Moore's Creek, Upper Illinois River Watershed, AR



Photo 3.4. Mud Creek Tributary, Upper Illinois River Watershed, AR



Photo 3.5. Wildcat Creek, Upper Illinois River Watershed, AR

## **CHAPTER 4**

### **ANALYSIS OF VARIOUS BACKGROUND ELECTROLYTE VIABLITIES FOR USE IN P-SORPTION BATCH EXPERIMENTS USING LANGMUIR ISOTHERMS**

## ABSTRACT

Phosphorus (P) has a high affinity for soil and sediment and is bound tightly to the < 2-mm fraction. Important parameters concerning the forms and fate of P can be determined by sorption experiments. Standard P sorption methodologies exist for soil, which have been adapted for use with stream sediments. This Chapter evaluates prior research and investigates the effects of extracting solutions on P sorption and desorption properties. Sediments (< 2-mm) were collected from five streams in the Upper Illinois River Watershed (UIRW) and extracted within 12 h of collection. Wet sediment was equilibrated for 24 h with varying P concentrations in the following solutions; filtered stream water, deionized water (DI), 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub>, and 0.01 Mol L<sup>-1</sup> KCl. We believe filtered stream water represents the best approximation of real-world conditions but imposes limitations on standardized methodology, due to its variable chemical composition. Measured P sorption parameters were compared by analysis of covariance (ANCOVA) and statistical differences in maximum P sorption ( $P_{\max}$ ) existed between DI and 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub>. This is possibly due to Ca phosphate formation, which at measured stream sediment pH (7.3 - 8.3) may occur due to low solubility. Equilibrium P concentration ( $EPC_0$ ) from isotherms, is an important sediment property, as it represents a transitioning point for sediment acting as sinks or sources of P. No equilibrating solution was statistically different from stream water for  $EPC_0$  or any of the calculated isotherm parameters. Thus, of tested solutions, there is no solution which is clearly a better choice for extracting and calculating parameters from P sorption isotherms.

## INTRODUCTION

Concerns of phosphorus (P) loading into streams have resulted in a need for an understanding of the dynamic exchange of P occurring at the sediment water interface. This can largely be determined by studying a sediment's ability to uptake P in batch sorption experiments, in which sediment is equilibrated with varying P concentrations and subsequently extracted. From this, P sorption isotherms can be constructed from which several parameters can be calculated; P sorption maximum ( $P_{\max}$ ), equilibrium P concentration ( $EPC_0$ ), and binding energy (k) (Graetz and Nair, 2009; Syers et al., 1973). Of particular importance is  $EPC_0$ , which when compared with stream water dissolved reactive P (DRP) concentration, represents whether stream sediments are acting as a source or sink of P and  $P_{\max}$ , which estimates the potential size of the sediments capacity to adsorb P (Haggard and Stoner, 2009; McDowell and Sharpley, 2001). The technique is advantageous because it allows easy soil / sediment and solution separation, a relatively large volume of sample is produced, and methodology can be standardized for use across laboratories (Graetz and Nair, 2009). However, disadvantages of the technique are the difficulties in measuring the kinetics of the reaction, and optimizing the mixing without particle breakdown (Burgoa, et al. 1990; Graetz and Nair, 2009).

Research and proposed methods for soil and sediment are outlined below; however, standardized techniques specifically designed for sediments are not available. While methods for soil have been adapted for P-sorption extraction, this research sought to refine methods based on previous literature and current research in an attempt to design a more repeatable procedure for stream sediments that more closely reflects the physio-chemical conditions of fluvial systems.

One of the earliest published studies on stream sediments was Taylor and Kunishi (1971), who extracted sediments determining  $EPC_0$  and its relation to stream water in the Mahantango Creek Watershed, PA. In this study, samples were air dried and stored at 25 °C. A 1:10 sediment to solution ratio was used with 2.5 g dry-weight sediment and 25 mL of 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub> spiking solution with varying P concentrations. Samples were shaken via a vortex mixer at 15 min intervals. A 1 h equilibrium was used to limit microbial activity and to more closely reflect the relatively short interaction time between water and sediment in flowing stream environments. When the equilibration time was increased to 4 h, Taylor and Kunishi (1971) found that  $EPC_0$  was relatively unchanged, but P sorption at higher solution P levels increased. Although  $P_{max}$  was not determined by Taylor and Kunishi (1971), a longer equilibration than 1 h would be needed to ensure complete sorption of P by the sediment, particularly at higher P concentrations. For instance, samples with varying sediment to solution ratio and 1 and 4 h equilibration times showed that at a sediment to solution ratio of 1:100 sorption occurred for about 2 h, while at an approximate 1:7 ratio the sediment continued to sorb P for at least 4 h. Taylor and Kunishi (1971) concluded that in streams where sediment P is close to being in equilibrium with stream DRP, sediment to solution ratio is likely unimportant but with sediment recently inundated with a high P source, a higher sediment to solution ratio may be required.

Further research on P sorption / desorption by sediments used a 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub> solution and 1:10 sediment to solution ratio, but sediments were wet sieved to < 2-mm and stored at 4 °C until analysis rather than air-dried (McCallister and Logan, 1978). Toluene was also added to minimize microbial activity. Sediments were shaken end-over-

end on a rotary shaker for 24 h, centrifuged, filtered, and P determined colorimetrically (McCalliseter and Logan, 1978).

A standard P-sorption procedure was proposed by Nair et al. (1984) for soil samples. This standardization attempted to address interlaboratory differences in determining the P sorption parameters of the same soils (Rao et al., 1980). The procedure proposed was for 0.5 to 1.0 g soil at a 1:25 ratio with 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub> as the equilibrating solution in a 50 mL centrifuge tube, with 20 g L<sup>-1</sup> of chloroform added. Samples were shaken-end-over end for 24 h filtered (.45µm), and analyzed colorimetrically.

Klotz (1988) outlined improved procedures to be used for determining EPC<sub>0</sub> of stream sediments. Outlined in this study, is the need for use of an equilibrating solution that mimics the ionic strength of the stream, preventing excessively high Ca levels and thus precipitation of the P from solution. The study used a very low ionic strength solution (0.005 Mol L<sup>-1</sup>; 20 mg Ca L<sup>-1</sup>) as CaCl<sub>2</sub> to represent stream water ionic strength. Calcium concentrations influenced measured EPC<sub>0</sub> values with EPC<sub>0</sub> decreasing as Ca increased. Also included, is the recommendation to use fresh wet sediments, as it was shown that air-dried sediments had nearly twice the EPC<sub>0</sub> of fresh sediments (Klotz, 1988).

More recent studies of stream sediments have further modified equilibration methods. For example, House and Denison (2000; 2002) used a dilute CaCl<sub>2</sub> solution to mimic stream water Ca levels. McDowell and Sharpley (2001) calculated P sorption properties of sediments from a stream draining an agricultural watershed using deionized water as the equilibrating solution and a 1:20 sediment to solution ratio.

Recently, however, Haggard et al. (2007) used filtered stream water as the equilibrating solution. Use of stream water by Haggard et al. (2007) was an effort to minimize the influence of dissolved cations on the measured  $EPC_0$  value. While several of the studies discussed above alluded to this influence (House and Denison, 2000; Klotz, 1988), the research of Haggard et al. (2007) was one of the first to directly demonstrate the influence of stream water as an extracting solution on  $EPC_0$  determination.

A study in Ozark streams (Arkansas) used fresh wet sediments,  $CaCl_2$  diluted to the ionic strength of stream water, along with stream water as equilibrating solution (Popova et al., 2006). The researchers reported lower  $EPC_0$  values when sediment was extracted with  $CaCl_2$  as compared to filtered stream water. Intuitively, stream water as the equilibrating solution gives the most accurate estimate of what is occurring in the stream environment; however, implementation, repeatability, and comparison of data from this method across regions, timeframes, watersheds, and laboratories could prove difficult.

Haggard et al. (2007) went on to outline issues concerning the drying of sediments for use in P-sorption studies. While studies have witnessed both an increase and decrease in calculated  $EPC_0$  values with use of air-dried sediments, it is clear that drying of sediments will produce different results than using fresh wet sediments and is unadvisable (Baldwin, 1996; Watts, 2000).

The inherent difference of stream sediments and its location in a lotic environment is a factor that is not addressed in standard methods such as Graetz and Nair (2009) for conducting P-sorption experiments. Thus, procedures for sediment P sorption experiments from in-stream locations require a modification to this approach, which was

standardized for soils. Wet sediments should be utilized and equilibrating solution should be comparable for varying streams, labs, and geographic regions.

## **OBJECTIVES**

The current study attempts to determine which equilibrating solution most closely reflects the stream sediment P sorption properties –  $EPC_0$ ,  $P_{max}$ , and binding energy, determined using filtered stream water. Batch P sorption Langmuir isotherms were constructed for sediments from five stream draining agricultural, forest, and urban land areas in the UIRW, using  $0.01 \text{ Mol L}^{-1} \text{ CaCl}_2$ ,  $0.01 \text{ Mol L}^{-1} \text{ KCL}$ , deionized water (DI), or stream water as the supporting solution.

## **MATERIALS AND METHODS**

### **STUDY SITES**

Five stream sites were selected within the UIRW draining urban, agriculture, and forested landscapes. Sites are described in Chapter 3 Materials and Methods.

### **SEDIMENT AND WATER SAMPLING**

Sediment was collected from the five streams in January, 2009. Samples of sediment from 0- to 3-cm depth of stream bed were taken from approximately 10 transects, sieved in-field to  $< 2\text{-mm}$ , and composited. Stream water samples acidified to pH 2 (HCl) were collected from the thalweg and subsequently analyzed for DRP via the ascorbic acid method (APHA, 1998). If samples were not immediately analyzed they were stored at  $4^\circ\text{C}$  and extracted within 24 h. Trace element concentrations of stream water were measured using inductively coupled plasma optical emission spectrometry

(ICP-OES) on a Spectro Genesis Model (Spectro, AMETEK Materials Analysis Division, Kleve, Germany). Sub-samples of sediments were air dried and used for Mehlich-3 extraction (Mehlich, 1984). Particle size analysis was performed for each of the < 2-mm stream sediments to estimate sand (2 – 0.02-mm), silt (0.02 – 0.002-mm), and clay (<0.002-mm) fractions (Arshad et al., 1996).

### **P-SORPTION BATCH EXPERIMENTS**

Sub-samples of sediment were used for determination of gravimetric water content for final dry-weight determination. Duplicates of approximately 1.5 g (dry-weight basis) of wet sediment samples were placed in a 50 mL tube and equilibrated with 30 mL of DI, 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub>, or 0.01 Mol L<sup>-1</sup> KCl containing 0, 2.5, 5, 10, 20, 30, 40, 50 mg P L<sup>-1</sup> (as KH<sub>2</sub>PO<sub>4</sub>). This resulted in a sediment to solution ratio of 1:20. When filtered stream water was used as the equilibrating solution, 29 mL of stream water was added and 1 mL of P solution (i.e., KH<sub>2</sub>PO<sub>4</sub> in DI) was added to give the same final P concentrations as before. By adding 1 mL of P solution to derive each initial P concentration, this procedure diluted stream water by a consistent and minimal amount. The initial DRP concentrations of equilibrating solutions using filtered stream water were corrected for the concentration of DRP in the filtered stream water. All sediment and supporting solutions were shaken end-over-end for 24 h, immediately centrifuged at 4000 rpm for 15 min, and the supernatant filtered (0.45 µm). For all solutions, DRP was determined on a Sans Skalar Wet Chemistry Auto-Analyser (Skalar, Netherlands) via the ascorbic acid method (APHA, 1998).

## LANGMUIR ISOTHERMS

Sorption phenomena of P in soil and sediment can be described by determination techniques which utilize a Langmuir isotherm (Syers et al., 1973). The isotherm is described as an L-curve which results from P's high adsorptive affinity for soil particles (Sposito, 2008). Graetz and Nair, (2009) outline the linearized Langmuir equation as follows:

$$C/S = 1/kP_{\max} + C/P_{\max} \quad \text{Eq. [1]}$$

where S is total amount of P sorbed ( $\text{mg P kg}^{-1}$ ), C is concentration after 24 h equilibration ( $\text{mg P L}^{-1}$ ),  $P_{\max}$  is P sorption maximum,  $\text{mg P kg}^{-1}$ ,  $k$  is a constant related to the binding energy,  $\text{L mg}^{-1} \text{P}$ .

The amount of P sorbed ( $S$ ;  $\text{mg P kg}^{-1}$ ) is the difference between P added and P remaining in solution. Using the Langmuir sorption equation, soil P sorption maximum ( $P_{\max}$ ;  $\text{mg P kg}^{-1}$ ) was calculated as the reciprocal of the slope of the plot  $C/S$  vs.  $C$  and binding energy ( $k$ ) as (slope / intercept) of the same plot (Graetz and Nair, 2009; Pieryznski et al., 1995). The initial linear slope of a graph of P sorbed against P remaining in solution ( $\text{mg L}^{-1}$ ) was used to estimate equilibrium P concentration ( $\text{EPC}_0$ ;  $\text{mg P L}^{-1}$ ) as the solution P concentration at which no net sorption or desorption ( $0 \text{ mg P kg}^{-1}$ ) occurred.

Equilibrium P concentration is particularly important in aquatic systems as it determines the concentration at which water column P and sediment P are at equilibrium.

Thus, knowledge of  $EPC_0$  and stream water DRP can indicate if sediments are acting as sinks or sources of P to the overlying stream water.

## STATISTICAL ANALYSIS

Statistical analysis was performed in SAS. An analysis of covariance (ANCOVA) was performed as follows. A regression line was fit to C/S as a function of solution P based on the linearized Langmuir equation allowing the coefficients to differ by media. Stream site was treated as a random effect and regression coefficients were compared across the four treatment media (Stream, DI, 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub>, and 0.01 Mol L<sup>-1</sup> KCL), using single degree of freedom contrasts. Based on the coefficients from the fitted equations, the values of k and  $P_{max}$  were calculated and approximate standard errors were determined using the delta method.

## RESULTS AND DISCUSSION

### INSTREAM PARAMETERS

Dissolved reactive P at stream sites ranged from 0.017 mg P L<sup>-1</sup> at Mud Creek Tributary to 0.070 mg L<sup>-1</sup> at Moore's Creek (Table 4.1). This is consistent with the trends observed and reported in Chapter 3 and with previous research (0.006 - 0.055 mg P L<sup>-1</sup>) (Haggard et al., 2007). Particle size distribution of collected sediments resulted in a predominance of sand-sized particles (2 – 0.02-mm) across sites ranging from 69 to 94% of the < 2-mm substrate. The silt fraction was the second most abundant size class and ranged from 5 to 26%, with the clay fraction ranging from 1 to 8 % of the < 2-mm substrate. In previous research, the sand dominated sediments extractable P levels have been greater than that of larger sediments (> 2-mm), likely due to the P being less tightly

sorbed (Lottig and Stanley, 2007). Site pH was slightly alkaline at all sites and ranged from 7.3 to 8.3. Within this pH range, calcium phosphates are at their most insoluble (Fig. 4.1; Lindsay, 2001). The calcium concentration of stream water was  $0.001 \text{ Mol L}^{-1}$  for all streams sampled (Table 4.2). Trace element concentrations of K ranged from  $4.3 \times 10^{-5}$  to  $9.1 \times 10^{-5} \text{ Mol L}^{-1}$ , Mg from  $5.6 \times 10^{-5}$  to  $2.2 \times 10^{-4} \text{ Mol L}^{-1}$ , and Mn from not detectable to  $4.9 \times 10^{-7} \text{ Mol L}^{-1}$  (Table 4.2). Mehlich-3 P concentrations of sampled stream sediments ranged from 10.1 to  $40.2 \text{ mg P kg}^{-1}$ .

## **EQUILIBRIUM PHOSPHORUS CONCENTRATION**

Equilibrium P concentrations did not vary statistically across extraction media (Fig. 4.2; Table 4.3). Based on ANCOVA analysis,  $\text{EPC}_0$  concentrations with  $0.01 \text{ Mol L}^{-1} \text{ CaCl}_2$  were numerically lower than values derived with the other background solutions (Table 4.3). The ANCOVA predicted  $\text{EPC}_0$  using  $0.01 \text{ Mol L}^{-1} \text{ CaCl}_2$  ( $0.10 \text{ mg P L}^{-1}$ ) as half of  $\text{EPC}_0$  value using filtered stream water as the equilibrating solution ( $0.019 \text{ mg L}^{-1}$ ). This could be due to higher Ca concentrations in the equilibrating solution ( $0.01 \text{ Mol L}^{-1} \text{ Ca}$ ) compared with stream water ( $0.001 \text{ Mol L}^{-1} \text{ Ca}$ ) and subsequent ionic competition and precipitation of calcium phosphate compounds within the observed stream water pH range (Fig. 4.1).

Stream Ca levels for our 5 study sites ranged from 29 to  $63 \text{ mg Ca L}^{-1}$  or  $\sim 0.001 \text{ Mol L}^{-1} \text{ Ca}$ . Researchers in New Zealand have reported stream water Ca concentrations ranging from 3 to  $21 \text{ mg Ca L}^{-1}$  or  $3 \times 10^{-5}$  to  $0.005 \text{ Mol L}^{-1}$  (Lucci et. al, 2009). Thus, Ca as an equilibrating solution should be used with caution, particularly when stream water pH is  $> 7.0$  (i.e., typical of UIRW) because calcium phosphate precipitation may occur

(Fig. 4.1). Use of  $\text{CaCl}_2$  as an equilibrating solution also creates a logistical problem in that stream Ca concentrations must be determined before extraction can be performed in order to accurately mimic stream water levels. The need for this additional analysis can hinder the timely equilibration of freshly collected sediments (usually required within 24 h of collection), to prevent excessive microbial activity and subsequent anoxic conditions occurring in stored sediment.

Equilibrium P concentrations determined using filtered stream water ranged from 0.012 to 0.032  $\text{mg P L}^{-1}$ , with DI numerically the most similar ranging from 0.015 to 0.032  $\text{mg P L}^{-1}$  (Table 4.3). Using  $\text{CaCl}_2$  and  $\text{KCl}$  as equilibrating solutions gave numerically lower  $\text{EPC}_0$  estimates than either filtered stream water or DI derived  $\text{EPC}_0$  values (Table 4.3). The M3P concentration at Moore's Creek (40.2  $\text{mg P kg}^{-1}$ ) was 2 to 4 times greater than the other sites (10.1 – 18.1  $\text{mg kg}^{-1}$ ). This coupled with a higher stream water DRP at the time of sediment sampling (0.070  $\text{mg P L}^{-1}$ ) likely influences the predicted  $\text{EPC}_0$ , as a larger movement of P from sediment may occur for DI water compared to stream water to reequilibrate (Table 4.1).

The choice of equilibrating solution has important ramifications on  $\text{EPC}_0$  determination, which is used to characterize the functioning of stream sediments as a source or sink for P within streams. For instance, stream water DRP concentrations below  $\text{EPC}_0$  will result in a flux of P from bed sediments to the overlying water column, while higher DRP than  $\text{EPC}_0$  levels will cause a net movement of P from the water column to the sediment, given sediments have not exceeded their P sorption capacity. Thus, conclusions based upon artificially low sediment  $\text{EPC}_0$  values can lead to

misinterpretation of the role of sediments in P dynamics and loading within stream systems.

## **PHOSPHORUS SORPTION MAXIMUM AND BINDING ENERGY**

Estimation of  $P_{\max}$  determined using filtered stream water ranged from 136 to 328 mg P kg<sup>-1</sup>. Equilibration with 0.01 Mol L<sup>-1</sup> KCl gave  $P_{\max}$  values numerically most similar to stream water (126 - 303 mg P kg<sup>-1</sup>; Table 4.3). Deionized water estimates of  $P_{\max}$  were the lowest of the four solutions used for all sites and ranged from 110 to 279 mg P kg<sup>-1</sup>. Use of 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub> gave the highest  $P_{\max}$  values, ranging from 178 to 398 mg P kg<sup>-1</sup>, thus, giving an elevated estimate of the amount of P that can be desorbed by bed sediments compared to what would be expected in the stream environment.

Equilibrating solutions were compared to stream water using the ANCOVA analysis (Table 4.3). The only statistical difference was between DI and 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub>. Phosphorus sorption maximum was not significantly different for the other solutions (Table 4.3). However, the ANCOVA predicted  $P_{\max}$  concentration for 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub> was numerically greater (248 mg P kg<sup>-1</sup>) than stream water (189 mg P kg<sup>-1</sup>). Also, the standard error for DI (8.4 mg P kg<sup>-1</sup>) was lower than the standard error for filtered stream water (12.2 mg P kg<sup>-1</sup>), 0.01 Mol L<sup>-1</sup> KCl (22.3 mg P kg<sup>-1</sup>) and 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub> (11.6 mg P kg<sup>-1</sup>).

Across stream sites, binding energy (k) was relatively constant for stream water equilibration, ranging from 0.22 to 0.27 L kg<sup>-1</sup> (Table 4.3). Equilibrating with the dilute salts 0.01 Mol L<sup>-1</sup> CaCl<sub>2</sub> and 0.01 Mol L<sup>-1</sup> KCl predicted higher k values than either DI or

stream water (0.35 to 0.45 and 0.30 - 0.60 L kg<sup>-1</sup>, respectively). However, *k* was not statistically different across treatments based on ANCOVA analysis.

## CONCLUSIONS

Stream water is the optimal equilibrating solution to determine P sorption and desorption properties of stream sediments. However, use of filtered stream water imposes practical and technical limitations on reproducibility and adaptability to its widespread use in different laboratories and geographical locations. Dilute salts, such as CaCl<sub>2</sub>, which may mimic the ionic strength in stream water, offer an alternative to stream water. However, these impose limitations, especially if multiple streams with varying Ca levels are being evaluated or sampled. Further, a standard Ca concentration of the equilibrating solution is unadvisable as varying stream conditions could lead to excessive amounts of Ca phosphate precipitation. Another limitation is the need to pre-determine in-stream Ca concentrations to establish a similar molar strength of Ca in the equilibrating solution. This analysis would need to be performed within 24 h after sampling to avoid microbial activity and anoxic conditions in the sediment sample occurring, which would change P chemistry.

Equilibrium P concentration is likely the most critical value derived from sorption isotherms. Determination of this parameter shows whether P inputs from various point and nonpoint sources will be stored by stream sediments, or if and when sediments may be a source of P exported. However, no method proved statistically different than stream water for EPC<sub>0</sub> or any of the other calculated isotherm parameters. Thus, a best method cannot be recommended from this study.

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**TABLES**

Table 4.1. Stream water dissolved reactive P (DRP) and sediment chemical and physical properties of five selected streams in the Upper Illinois River Watershed, AR.

Stream	DRP	Sediment					
		Sand	Silt	Clay	pH	M3P	PSR <sub>mod</sub>
	mg P L <sup>-1</sup>	-----%-----				mg P kg <sup>-1</sup>	%
Chamber Springs	0.041	68.6	25.6	5.8	8.2	10.1	3.9
Little Wildcat Creek	0.032	92.0	6.4	1.6	8.0	18.1	4.9
Moore's Creek	0.070	92.9	4.9	2.2	7.3	40.2	7.5
Mud Creek Tributary	0.017	94.1	4.6	1.3	8.1	11.8	2.6
Wildcat Creek	0.030	72.5	20.6	7.0	8.3	11.5	2.3

Table 4.2. Stream water column trace element molar concentrations of five selected streams in the Upper Illinois River Watershed, AR.

	Ca	K	Mg	Mn
Stream	----- Mol L <sup>-1</sup> -----			
Chamber Springs	0.001	4.3 x 10 <sup>-5</sup>	5.6 x 10 <sup>-5</sup>	< DL †
Little Wildcat Creek	0.001	6.9 x 10 <sup>-5</sup>	7.8 x 10 <sup>-5</sup>	< DL
Moore's Creek	0.001	6.9 x 10 <sup>-5</sup>	6.5 x 10 <sup>-5</sup>	1.1 x 10 <sup>-7</sup>
Mud Creek Tributary	0.001	5.0 x 10 <sup>-5</sup>	2.2 x 10 <sup>-4</sup>	2.4 x 10 <sup>-7</sup>
Wildcat Creek	0.001	9.1 x 10 <sup>-5</sup>	1.1 x 10 <sup>-4</sup>	4.9 x 10 <sup>-7</sup>

† < DL is below detection level

Table 4.3. Calculated Langmuir sorption isotherm parameters for five selected streams in the Upper Illinois River Watershed, AR

Stream	Equilibrium P concentration			P sorption maximum			Binding energy						
	Stream Water	DI	0.01M CaCl <sub>2</sub>	0.01M KCl	Stream Water	DI	0.01M CaCl <sub>2</sub>	0.01M KCl	Stream Water	DI	0.01M CaCl <sub>2</sub>	0.01M KCl	
	----- mg P L <sup>-1</sup> -----			----- mg P kg <sup>-1</sup> -----			----- L P kg <sup>-1</sup> -----						
Chamber Springs	0.023	0.024	0.012	0.010	164	139	208	164	0.27	0.30	0.42	0.60	
Little Wildcat Creek	0.032	0.032	0.016	0.017	136	110	178	126	0.23	0.29	0.35	0.46	
Moore's Creek	0.015	0.025	0.010	0.013	255	207	339	208	0.27	0.19	0.39	0.37	
Mud Creek Tributary	0.012	0.015	0.006	0.010	328	279	398	303	0.25	0.25	0.45	0.33	
Wildcat Creek	0.022	0.021	0.010	0.015	210	196	280	219	0.22	0.24	0.36	0.30	
ANCOVA predicted values	0.019a	0.021a	0.010a	0.013a	188ab	159b	247a	186ab	0.27a	0.29a	0.39a	0.41a	

\*estimates followed by the same letter are not statistically different ( $\alpha=0.05$ )

FIGURES

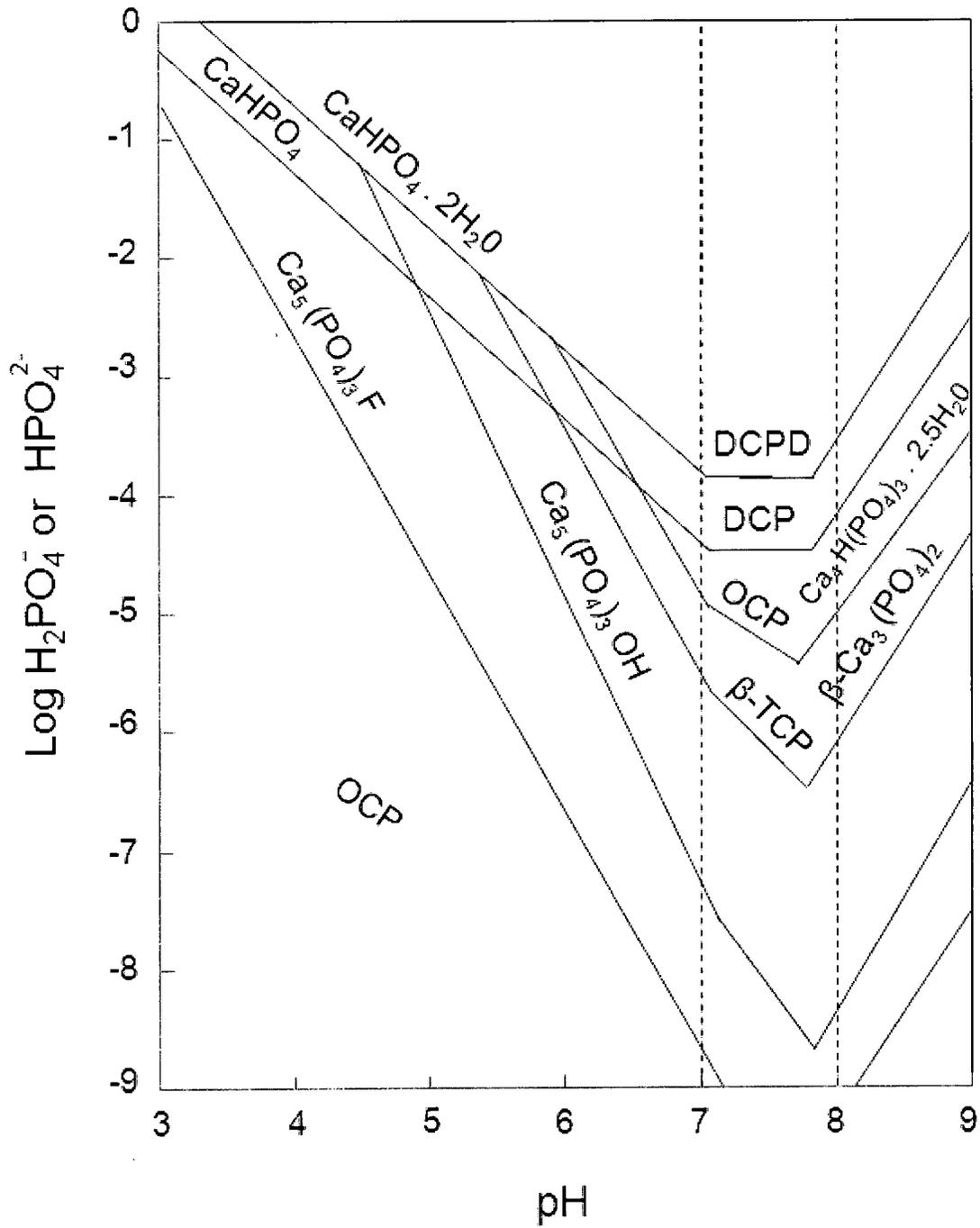


Figure 4.1. Solubility diagram of calcium containing P compounds as related to pH (Lindsay, 2001).

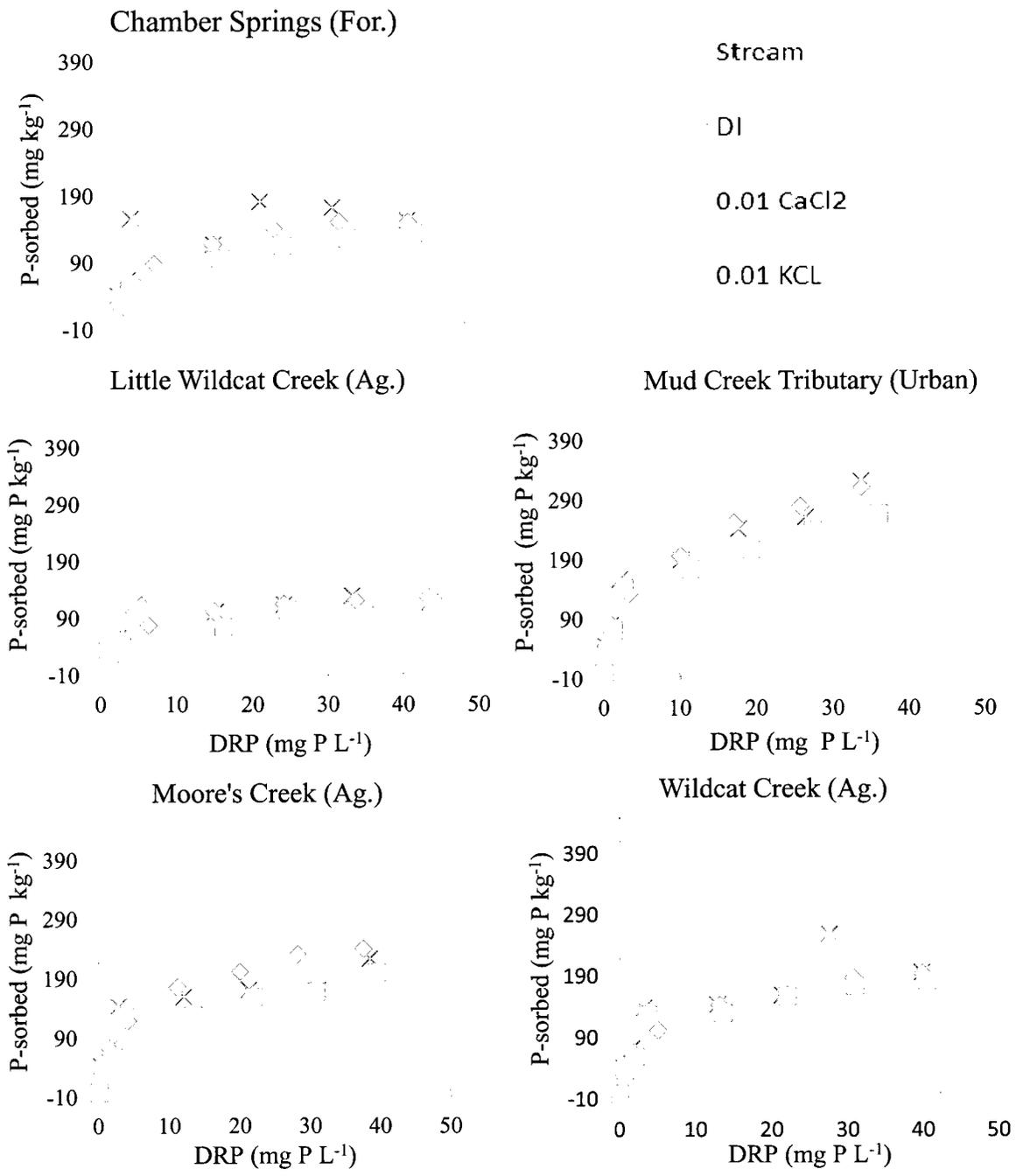


Figure 4.2. P-sorption isotherms for 5 streams in the Upper Illinois River Watershed, AR.

## **CHAPTER 5**

### **PHOSPHORUS DYNAMICS IN A SIMULATED STREAM ENVIRONMENT**

## ABSTRACT

Northwest Arkansas's large population increase in the last decade alongside one of the largest poultry producing regions in the country has led to increased concerns of anthropogenic phosphorus (P) loading to surface waters. Five streams were selected representing urban, agricultural, and forested land uses in the Upper Illinois River Watershed (UIRW). Stream water and < 20-mm sediment (top 0- - 3-cm) were collected from multiple locations within 30 to 70-m reaches. Sediment was immediately transported to and placed in a fluvium and a sub-sample of < 2-mm sediment taken for physical and chemical characterization. The fluvium experiment consisted of three flow phases; (I) initial baseflow ( $< 0.005 \text{ mg P L}^{-1}$ ), (II) uptake-enriched ( $1.8 \text{ mg P L}^{-1}$ ), and (III) re-equilibration ( $< 0.005 \text{ mg P L}^{-1}$ ) flow was circulated over the sediment for 48 h at  $0.001 \text{ m}^3\text{s}^{-1}$  ( $1 \text{ L s}^{-1}$ ). During each phase, flow was monitored and water sampled at regular intervals for determination of dissolved reactive P (DRP). Stream sediments varied in texture (9 - 18% as < 2-mm), Mehlich-3 P (M3P) ( $12 - 40 \text{ mg P kg}^{-1}$ ), and equilibrium P concentration ( $\text{EPC}_0$ ) ( $0.014 - 0.045 \text{ mg P L}^{-1}$ ). In Phase I, DRP reached equilibrium concentrations, which closely mimicked stream DRP at the time of sample collection ( $R^2 = 0.77$ ) and were greatest at Moore's Creek ( $0.080 \text{ mg P L}^{-1}$ ; 56 % agriculture) and lowest at Mud Creek Tributary ( $0.016 \text{ mg P L}^{-1}$ ; 70 % urban). Stream sediments rapidly sorbed P (40% within 1 h) during Phase II. Over the 48-h flow period, 96% (Mud Creek Tributary) to 84% (Chamber Springs) of added P was removed from solution by sorption and biological uptake. Of this bound P, 1 % (Mud Creek Tributary) to 7 % (Chamber Springs; 38 % agriculture) was re-released during phase III. Thus, stream sediments in the UIRW act as transient storage for P during periods of high P inputs, such as from point sources and urban and agricultural nonpoint runoff.

## INTRODUCTION

Both terrestrial plants and algae in aquatic environments need nutrients for growth. Of prime importance are carbon (C), nitrogen (N), and P. The ratio of these nutrients in algae is typically described by the Redfield Ratio, which by weight is approximately 40:7:1 and is used to describe conditions appropriate for optimal growth (Redfield, 1958; Schindler et al., 2008). Phosphorus is usually considered the nutrient of primary concern in freshwater systems, because some blue-green algae can fix N, and C and N can freely exchange between the atmosphere and water (Schindler et al., 2008).

Eutrophication in lakes was initially linked to nutrient loading in the 1960's and P limitation theory was developed around this time (Schindler, 2006). Increased research concerning uptake and release of P within streams dates back to the 1970's when concerns about water quality and understanding of nutrient limitation in freshwaters helped establish the Clean Water Act, which regulates surface waters in the United States (Schindler, 2006; USEPA, 2008). Schindler (1977 and et al., 2008) further discussed P limitation theory based on a 30-year whole-lake research experiment at the Experimental Lakes Area in Canada, from which it was reported that algal growth was regulated by P inputs regardless of N inputs.

While P-limitation theory was being researched, Taylor and Kunishi (1971) undertook one of the initial studies to determine equilibrium P concentrations ( $EPC_0$ ) of sediments in the Manhantango Watershed in Pennsylvania. This research utilized batch P-sorption experiments to determine the characteristics of P transformations in soil and sediments. Numerous studies have utilized batch experiments for describing P uptake and release in stream sediments (Haggard et al., 1999; Haggard et al., 2007; McDowell et al.,

2001; McDowell et al., 2002). Prior studies have alluded to the limitations of this type of experiment and thus, it is recommended that flowing water conditions be replicated when possible (McCallister and Logan, 1978).

A large body of research has been conducted using simulated stream environments to replicate a lotic system. These studies are varied and have determined sediment uptake and release, along with other biotic and abiotic factors in both streams and agricultural drainage ditches (Gainswin et al., 2006; House et al., 1995ab; House and Denison, 2002; McDowell and Sharpley, 2003; Smith and Pappas 2007).

Recent work in Northwest Arkansas streams described sediment water column relationships along with  $EPC_0$  using batch P-sorption experiments (Haggard et al., 2007). However, no known research in this region has specifically looked at P uptake and release in stream sediments using flowing water, which is recommended as the most viable form of analysis for studying in-stream P dynamics.

## **OBJECTIVES**

The objective of this research was to determine P-uptake and release characteristics of sediments from five streams selected to represent drainage areas dominated by agriculture, forest, and urban land, using purpose-built fluvariums. The study consisted of three phases to simulate sediment-water interactions during baseflow (initial Phase I), introduction of P-rich runoff (uptake Phase II), and a return to baseflow (re-release Phase III).

## **MATERIALS AND METHODS**

### **STUDY SITES**

This research focused on the UIRW basin located in Arkansas and the fluvial sediments and streams within. Five sites were selected representing dominantly urban, agricultural, and forested land use. All sites had mixed land use within; Moore's Creek, Wildcat Creek, and Little Wildcat Creek drained areas that were predominately agriculture (> 50%). Agricultural land in the basins was primarily pasture and hay with row crop agriculture virtually non-existent. The watershed draining into Mud Creek Tributary was predominately urban (70%). Chamber Springs was representative of a forested area (61%); however, within this watershed some land adjacent to the stream was in pasture. These sites are described in greater detail in Chapter 3 Methods and Materials.

### **SEDIMENT AND WATER SAMPLING**

Stream sediment and water samples were collected from May, 21 to June 9, 2009. Sediments were collected from the riffle and pools, as established in Chapter 3. At each location, stream water was collected prior to sediments for analysis of samples for dissolved reactive phosphorus (DRP), particulate P (PP), total dissolved P (TDP), and total P (TP). At equal increments, sediment samples were collected using a spade to a depth of 0- to 3-cm and sieved (< 20-mm) to exclude large bed material. Approximately 0.06 m<sup>3</sup> (16 gal) of sediment from each site was collected. Sediment was immediately transported back to the laboratory where it was placed into the fluvium and water flow initiated within an hour of collection. Sites were randomly sampled and troughs run

independently, with a different stream in each trough and each stream replicated. A subsample of the < 2-mm sediment was set aside for determination of particle size (Arshad et al., 1996), Mehlich-3 extractable nutrients (Mehlich, 1984), water extractable P (WEP) (Self-Davis et al., 2009), and P-sorption capacity ( $P_{\max}$ ) (Graetz and Nair, 2009). Prior research has shown that most sediment P sorption and desorption reactivity is associated with fractions < 2-mm (Sharpley et al., 1981; Sharpley, 1985).

## **FLUVARIUM OPERATION**

Research experiments were performed in a purpose-built dual fluvarium (Fig. 5.1; Photo 5.1) described by McDowell and Sharpley (2003). Two troughs were used with dimensions of 10-m long, 20-cm wide, and 20-cm deep with an adjustable slope from 0-15% and a reservoir capacity of 300 L. Within each trough, water could be re-circulated over the sediment from the upslope end via plumbing at rates up to  $20 \text{ L s}^{-1}$ . The reservoirs have back-flow systems attached which siphon off small amounts of water moving through the plumbing and pump it back into the reservoir keeping the reservoir solution continually circulated.

Each fluvarium had approximately 3-cm of sediment placed within and a 1% slope established which corresponded to the mean of sample sites measured from the top of the reach to the bottom. In each of the phases, water was recirculated over the sediment at a rate of  $0.001 \text{ m}^3 \text{ s}^{-1}$  ( $1 \text{ L s}^{-1}$ ), equivalent to the mean estimated flow for the sampled sites during baseflow conditions. This rate was calculated based on the mean surface area of the sampled area of the five streams ( $231 \text{ m}^2$ ) and the surface area of the fluvarium ( $2 \text{ m}^2$ ). The ratio (surface area fluvarium / surface area stream) was calculated

and multiplied by the average measured flow from baseflow conditions ( $0.13 \text{ m}^3 \text{ s}^{-1}$ ) and used as the flow rate for the experiment. An ISCO 6712 automatic sampler took water samples for this phase over 48 h and was filled with ice to minimize temperature increase of samples (ISCO 6712 Autosampler, Teledyne ISCO, Lincoln, NE). Samples were analyzed for DRP and a subset of samples measured for TDP and TP to calculate PP levels present in the fluvarium.

### **PHASE I – “BASEFLOW”**

Reservoirs were filled with 180 L of water ( $P < 0.005 \text{ mg P L}^{-1}$ ), representing baseflow concentrations in the UIRW. Water was recirculated over the sediments in the fluvarium for 48 h, with samples collected at 0, 10, 20, 30, 40, 50 min, and 1, 2, 3, 4, 5, 7, 9, 12, 16, 20, 24, 32, 40, and 48 h for DRP. Particulate P and TP were measured at 0, 5, 24, and 48 h.

### **PHASE II - “P-ENRICHED UPTAKE”**

A stock solution of P-enriched water was created by mixing 1 kg fresh poultry litter (1.22 % P or  $12.2 \text{ g P kg}^{-1}$ ) with 10 L of water. The mixture was filtered (Whatman #1) and stored at  $4^\circ \text{C}$  for use in Phase II of the fluvarium study. For each run, stock solution was added to the reservoir to achieve a fixed DRP concentration of  $\sim 1.8 \text{ mg P L}^{-1}$ . This concentration represents DRP measured in runoff from a 2-ha field in the UIRW one week after litter application at  $1.7 \text{ Mg ha}^{-1}$  (Daniel et al., 2009). The reservoir was circulated to thoroughly mix the stock solution and a sample taken for initial concentration of DRP, PP, and TP. Flow was then initiated at the same rate as Phase I and

water sampled at the same intervals as Phase I. At the end of this phase, sediment samples were taken from upper, mid, and lower locations along the fluvium composited and sieved to < 2-mm for analysis. The initial reservoir DRP concentration varied among runs due to the inherent variability of spiking large volumes of water with a concentrated solution. Thus, the data are presented on a measured concentration and normalized basis. Normalized values are calculated by the equation ( $C_x / C_0$ ) such that  $C_x$  is the concentration at time X divided by  $C_0$ , the initial concentration.

### **PHASE III “RE-EQUILIBRATION”**

Reservoirs were drained, thoroughly cleaned and refilled with 180 L of water ( $P < 0.005 \text{ mg P L}^{-1}$ ) and a water sample taken and analyzed for DRP, PP, and TP. Water was then recirculated for 48 h at  $1 \text{ L s}^{-1}$  as in Phases I and II. Water samples were also collected by automatic sampler and sediment samples as before. Measured DRP concentrations were again normalized ( $M_x / M_{\text{End II}}$ ), where  $M_x$  is the mass of DRP in the water column at time X and  $M_{\text{End II}}$  is the mass in mg P that the sediment bound by the 48 h mark in Phase II. This allows comparison of the P sorbed by the sediment in Phase II that was released back to flowing water.

### **LANGMUIR ISOTHERMS**

At each of the stream locations sampled within the UIRW, a 1-kg sediment subsample was set aside for assessment of P sorption / desorption properties. Sediment equilibrations and isotherms used deionized water based on results from Chapter 4 and were extracted within 24 h of sediment collection. The Langmuir equation is as follows:

$$C/S = 1/kP_{\max} + C/P_{\max} \quad \text{Eq. [1]}$$

where S is total amount of P sorbed ( $\text{mg P kg}^{-1}$ ), C is concentration after 24 h equilibration ( $\text{mg P L}^{-1}$ ),  $P_{\max}$  is P sorption maximum,  $\text{mg P kg}^{-1}$ ,  $k$  is a constant related to the binding energy,  $\text{L mg}^{-1} \text{P}$ .

Centrifuge tubes (50 mL) had 1.5 g dry-weight wet sediment added to the tube and 30 mL of deionized equilibrating solution added at concentrations of 0, 2.5, 5, 10, 20, 30, 40, and 50  $\text{mg P L}^{-1}$  as  $\text{KH}_2\text{PO}_4$  at a sediment to water ratio of 1:20. Sediments were shaken end-over-end for 24 h before filtration through a 0.45  $\mu\text{m}$  filter. The Langmuir equation was used to obtain estimates of the  $\text{EPC}_0$  ( $\text{mg P L}^{-1}$ ), and P sorption maximum ( $P_{\max}$ ;  $\text{mg P kg}^{-1}$ ). The initial slope of a graph of P-sorbed ( $\text{mg P kg}^{-1}$ ) against P remaining in solution ( $\text{mg P L}^{-1}$ ) was used to determine  $\text{EPC}_0$  as the solution P concentration at which no net sorption or desorption occurs. Along with these parameters, binding energy ( $k$ ;  $\text{L mg P}^{-1}$ ) was calculated as  $[\text{slope} / \text{EPC}_0]$ .

## **SEDIMENT AND WATER ANALYSIS**

Wet sediments were stored at 4° C until analyzed. Each sediment had a subsample air dried and oven dried to determine Mehlich-3 (M3) extractable nutrients and moisture content respectively. Water extractable P (WEP) was measured on wet sediments corrected to a dry weight and followed the procedures outlined in the SERA-17 guidelines for extraction of P by water (Self-Davis et al., 2009). A sub-sample of the

sediment was air dried and used for determination of M3 extractable values (Mehlich, 1984).

Microbial biomass P was calculated from wet sediments and reported on a dry-weight basis. The extraction procedure was a modification of Brookes et al. (1982), where 1 mL of chloroform ( $\text{CHCl}_3$ ) was added to 2 g dry-weight fresh wet sediment in a 50-mL test tube, with a control sample prepared without  $\text{CHCl}_3$ . After the addition of the  $\text{CHCl}_3$ , tubes were capped and allowed to fumigate for 2 h; next, samples were uncapped and stood for 18 h. Samples were then extracted with  $0.5 \text{ Mol L}^{-1} \text{ NaHCO}_3$  (pH 8.5) for 16 h on an end-over-end shaker. Samples were digested via an alkaline persulfate autoclave digestion (Hosomi and Sudo, 1986; Lambert and Maher, 1995).

Particle size analysis was determined on a 50 g dry-weight sample of sediment using a hydrometer and was distributed in the following categories (sand: 2 – 0.05-mm, silt: 0.05- 0.002-mm, and clay: < 0.002-mm) (Arshad et al., 1996).

Fluvarium DRP samples were filtered (< 0.45 $\mu\text{m}$ ), acidified to pH 2 (HCl), and stored at 4 °C in the dark along with unfiltered samples. Dissolved reactive P was determined on a Skalar San Plus Wet Chemistry Autoanalyzer (Skalar, Netherlands) using the ascorbic acid method (APHA, 1998). Samples at 0, 12, 24, and 48 h were analyzed for TDP and TP after alkaline persulfate autoclave digestion of filtered and unfiltered samples, respectively (Hosomi and Sudo, 1986; Lambert and Maher, 1995). Particulate P was calculated as the difference between TP and TDP.

## STATISTICAL ANALYSIS

Phase II (enriched uptake) was fit to a standard power function in Sigma Plot;  $C=C_0 + \alpha t^\beta$  where  $C$  is concentration ( $\text{mg P L}^{-1}$ ),  $C_0$  is the initial concentration ( $\text{mg P L}^{-1}$ ),  $t$  is time since onset of flow,  $\alpha$  is the rate constant and  $\beta$  is a constant. Phase III (re-equilibration) was also fit to a power function in Sigma Plot;  $C=\alpha t^\beta$  with variables the same as in Phase II. Linear Regression analysis was performed in Sigma Plot.

## RESULTS AND DISCUSSION

### STREAM SEDIMENT PROPERTIES

Particle-size distribution of the sediments ranged from 81 to 94% sand, 4 to 13 % silt, and 3 to 6% clay (Table 5.1). Thus, all sediments had only a small proportion of clay-sized particles, which are the most chemically reactive. At the time of sampling, pH ranged from 7.1 to 8.0. Stream DRP concentrations ranged from  $0.016 \text{ mg P L}^{-1}$  at Mud Creek Tributary to  $0.080 \text{ mg P L}^{-1}$  at Moore's Creek (Table 5.1). This is consistent with Haggard et al. (2007) who found DRP ranged from  $0.003$  to  $0.072 \text{ mg P L}^{-1}$  in Ozark streams. Total P concentrations ranged from  $0.020$  to  $0.138 \text{ mg P L}^{-1}$  with PP levels very low to negligible. No significant relationships were found between particle size and measured sediment P properties; prior studies have suggested mineralogy is often more important for P sorption estimates than particle size (Stone and Murdoch, 1989).

Mehlich-3 P was variable across sites ranging from  $11.9 \text{ mg P kg}^{-1}$  at Little Wildcat Creek to  $40.0 \text{ mg P kg}^{-1}$  at Moore's Creek (Table 5.1). A calculated  $\text{PSR}_{\text{mod}}$  parameter as described by Haggard et al. (2007) was also calculated and ranged from 2.5

to 8.0%, relatively consistent as previous values which ranged from 2.7 to 12.6%. This parameter was compared to P saturation ratio (PSR) calculated from M3 divided by  $P_{\max}$ , as described by Kleinman and Sharpley (2002) and adapted from Breeuswma and Silva (1992). A strong correlation was present between the two methods ( $r = 0.91$ ) conveying the influence of trace metals and M3P content on determining the maximum amount of P a sediment can bind (Fig. 5.2). Sediment WEP ranged from 0.028 mg P L<sup>-1</sup> at Mud Creek to 0.098 mg P L<sup>-1</sup> at Moore's Creek (Table 5.1). Initial microbial P ranged from 1.98 to 3.76 mg P kg<sup>-1</sup> and was from 6 to 20% of M3P (Table 5.2). However, no consistent trends in microbial P as related to land use or other sediment properties was observed with the limited data available for this highly dynamic P form.

Trace elements were variable across sediments, M3Ca ranged from a low of 661 mg Ca kg<sup>-1</sup> at Little Wildcat Creek to 3084 mg Ca kg<sup>-1</sup> at Wildcat Creek (Table 5.3). Mehlich-3 Fe ranged from 93.5 mg Fe kg<sup>-1</sup> in Little Wildcat Creek to 352.6 mg Fe kg<sup>-1</sup> in Moore's Creek, and M3Zn ranged from 5.1 mg Zn kg<sup>-1</sup> at Chamber Springs to 8.9 mg Zn kg<sup>-1</sup> at Wildcat Creek.

Baseflow DRP at the time of sediment sampling was related to sediment M3P ( $r = 0.93$ ) (Fig. 5.3). Our relationship is much stronger than previously reported values from Haggard et al. (2007) ( $r = 0.50$ ) and is driven by Moore's Creek which had much greater M3P concentrations than other sites, skewing the results. Along with this,  $PSR_{\text{mod}}$  was strongly correlated ( $r = 0.90$ ) to stream DRP concentrations (Fig. 5.4). While our results had a stronger correlation than previous research, similar relationships ( $r = 0.71$ ) in Ozark streams were reported by Haggard et al. (2007). Along with this,  $PSR_{\text{mod}}$  was inversely related to binding energy ( $r = 0.66$ ), and thus, as  $PSR_{\text{mod}}$  increases and saturation is

increased, P is unable to bind as tightly to the sediment (Fig. 5.5). Our research indicated that under low or baseflow conditions, stream DRP concentrations are a function of M3P and are accurately estimated by  $PSR_{mod}$ .

## **P-SORPTION ISOTHERMS**

Isotherms are presented for 3 sites representing agricultural, forested, and urban land uses (Fig. 5.6). Langmuir isotherms were highly significant for all sites ( $R^2 > 0.96$ ; Table 5.4). Little Wildcat Creek sediment had the highest  $EPC_0$  concentration (0.045 mg P L<sup>-1</sup>) and Mud Creek Tributary the lowest (0.014 mg P L<sup>-1</sup>; Table 5.4). This suggests that stream sediment in Little Wildcat Creek could support higher stream flow DRP than Mud Creek Tributary. In fact, slightly higher stream DRP concentrations were measured in Little Wildcat Creek (0.021 mg P L<sup>-1</sup>) than Mud Creek Tributary (0.016 mg P L<sup>-1</sup>) at the time of sediment collection (Table 5.1). Other data also suggests that sediments in Mud Creek Tributary ( $EPC_0 = 0.014$  mg P L<sup>-1</sup>) could sorb P added to the stream more readily than Little Wildcat Creek (0.045 mg P L<sup>-1</sup>) (Table 5.4).

Previous research in the Ozark's Eucha-Spavinaw Basin, directly north of the UIRW, reported  $EPC_0$  values ranging from 0.017 to 3.33 mg P L<sup>-1</sup> (Popova et al., 2006). Other work in Ozark streams reported  $EPC_0$  ranging from < 0.001 mg P L<sup>-1</sup> to 0.298 mg P L<sup>-1</sup> (Haggard et al., 2007). McDowell et al. (2002) found ranges in  $EPC_0$  from 0.001 to 0.0240 mg P L<sup>-1</sup> for sites in Vermont. Therefore, compared to previous work,  $EPC_0$  concentrations of sampled sites were within the typical range. Extremely high values, such as 3.3 mg P L<sup>-1</sup> reported by Popova et al. (2006) are uncommon, because the site

discussed was directly downstream from a WWTP and had likely become P saturated, limiting the sediments ability to buffer incoming P.

During baseflow, sediments may act as a long-term source of P when stream DRP falls below sediment  $EPC_0$  values. Of the sampled sites, two acted as sources during baseflow with  $DRP < EPC_0$  and included Chamber Springs ( $0.039 < 0.041 \text{ mg L}^{-1}$ , respectively) and Little Wildcat Creek ( $0.021 < 0.045 \text{ mg L}^{-1}$ , respectively  $0.039 < 0.041 \text{ mg L}^{-1}$ , respectively), while three acted as sinks for P from the water column  $DRP > EPC_0$ ; Moore's Creek ( $0.080 > 0.036 \text{ mg L}^{-1}$ , respectively), Mud Creek Tributary ( $0.016 > 0.014 \text{ mg L}^{-1}$ , respectively), and Wildcat Creek ( $0.035 > 0.028 \text{ mg L}^{-1}$ , respectively) (Tables 5.1 and 5.4). Also, binding energy ( $k$ ) ranged from  $0.130 \text{ L mg P}^{-1}$  at Moore's Creek to  $0.220 \text{ L mg P}^{-1}$  at Mud Creek Tributary.

P sorption maxima ranged from 136 to  $323 \text{ mg P kg}^{-1}$  across sites (Table 5.4). Mud Creek Tributary sediments had the greatest capacity to store P in sediment as indicated by the highest  $P_{\text{max}}$  ( $323 \text{ mg P kg}^{-1}$ ), whereas Little Wildcat sediments had the lowest capacity to sorb P ( $136 \text{ mg P kg}^{-1}$ ). Further, it was observed that  $EPC_0$  was inversely related to  $P_{\text{max}}$ , in that stream sediments which have a high  $EPC_0$  are unable to store P to as great a degree as those with a lower  $EPC_0$  (Fig. 5.7). Similar to our  $P_{\text{max}}$  for UIRW sediments, McDowell and Sharpley (2003) measured  $P_{\text{max}}$  ranging from 281 to  $556 \text{ mg P kg}^{-1}$ , along a 500-m reach of a stream draining an agricultural watershed in south-central PA.

## FLUVARIUM

### *PHASE I*

During the 48 h flow period, sediment bound P was rapidly desorbed into flowing water at the initiation of flow, largely due to the disturbed nature of the samples and subsequent suspension and resettling (Fig. 5.8). Within 10 h, sediments had begun to equilibrate with flowing water and by 24 h, all sites except Moore's Creek sediments were essentially at  $EPC_0$  with flowing water. Moore's Creek sediments continued to release P, even after 24 h of flow, likely due to this stream site having the highest initial DRP level of those sampled (Table 5.1; Table 5.5). Desorption of P from these sediments during Phase I resulted in water column DRP levels closely related to initial stream concentrations ( $R^2 = 0.77$  ; Fig. 5.9). This significant and nearly 1:1 relationship between steady-state fluvarium and stream DRP concentrations clearly indicated the experimental fluvarium systems closely mimicked in-stream conditions. Final DRP concentrations, averaged for both replicates, ranged from 0.014 to 0.071 mg P L<sup>-1</sup>, while final TP concentrations ranged from 0.032 to 0.113 mg P L<sup>-1</sup> (Table 5.5). During this initial phase, DRP averaged 54% of TP (ranging from 28 to 76%; Table 5.5).

### *PHASE II*

Similar to other studies utilizing a simulated stream environment, P fractions were removed from the water column over time (House et al., 1995ab; McDowell and Sharpley, 2003). These studies fit the resulting data to various kinetic equations; however, our uptake data was best modeled with a standard power equation  $C=C_0 + at^\beta$ .

Initial spiking of flume water was set at  $1.8 \text{ mg P L}^{-1}$  to represent the input of P-enriched runoff from fields that had recently received poultry litter (Daniel et al., 2009). However, due to the large dilutions needed in spiking, actual initial DRP concentrations varied from  $1.63$  to  $1.81 \text{ mg P L}^{-1}$ , TP from  $2.07$  to  $2.27 \text{ mg P L}^{-1}$ , and total mass of DRP added from  $293$  to  $327 \text{ mg}$  (Table 5.6). Within the first hour of flow being initiated, DRP concentrations decreased to half of the initial value (Fig. 5.10). The rate of decrease was most rapid for sediment from Mud Creek tributary and least for Chamber Springs, as shown in Figure 5.10 and represented by the rate function “ $\alpha$ ” of the highly significant power equation  $C=C_0 + \alpha t^\beta$  (Table 5.7). By the end of the 48 h flow, DRP concentrations had decreased to  $0.064$  to  $0.268 \text{ mg P L}^{-1}$  (Table 5.5).

As initial starting DRP concentration varied from  $1.63$  to  $1.81 \text{ mg L}^{-1}$ , concentrations during the 48 h Phase II were normalized to starting concentrations. Normalization allows comparison of P uptake properties among sediments. Normalized DRP concentrations show an approximate 40% uptake by sediment within the 1<sup>st</sup> 24 h (Fig. 5.11). Over the 48 h flow, 96% (Mud Creek) to 85% (Wildcat Creek) of the added P was removed from solution by sorption and biological uptake. This decrease equates to 252 to 315 mg of DRP bound by sediments during this phase (Table 5.8). Across sites, a power function accurately described percent DRP uptake ( $R^2 = 0.99$ ; Table 5.7). Rate of uptake was most rapid for sediment from Mud Creek Tributary ( $\alpha = 69.5$ ) and slowest at Wildcat Creek ( $\alpha = 53.9$ ; Table 5.7).

While 85 to 96% of added P was removed by stream sediment during the 48 h Phase II equilibration, this was not reflected in any consistent change in stream sediment properties from initial collection values at the end of this phase (Table 5.8). For example,

no relationship was found between P uptake and M3P,  $PSR_{mod}$  (Table 5.9), microbial P (Table 5.2), or Mehlich-3 extractable Ca, Fe, Mg, Mn or Zn (Table 5.10).

### ***PHASE III***

At the end of Phase II, fluvium water was replaced with water of low DRP concentration to evaluate the amount of P sorbed during Phase II that could be desorbed to flowing water. This phase was best fit by a power function and three representative streams are presented showing the change in DRP concentration across the 48 h flow event. All streams except Mud Creek Tributary were well fit by the power function ( $R^2 > 0.76$ ), where the function was applicable (Table 5.11). Mud Creek Tributary witnessed a greater flux and subsequent decrease of P in the water column compared to other sites. This same pattern was also present in Zn concentrations within the water column. Re-release was normalized, to the amount sorbed in Phase II, and was described by a power function ( $R^2 > 0.76$ ) for all sites except Mud Creek Tributary, where it was not statistically significant (Table 5.11).

Sediments desorbed varying amounts of bound-P back into the water column during Phase III, with the greatest flux within the first 10 h of flow and DRP levels stabilizing around this time with the exception of Mud Creek Tributary (Fig. 5.12). Final concentrations for DRP ranged from 0.022 to 0.098 mg P L<sup>-1</sup> and for TP from 0.071 to 0.115 mg P L<sup>-1</sup> (Table 5.12). Normalizing the data to the amount of P bound in Phase II shows that only 1.2 to 7.0 % of sediment bound P was re-released during the 48 h flow, which again occurred mainly within the first 10 h of flow (Table 5.13; Fig. 5.13). Thus, the urban sample site (Mud Creek Tributary) bound the greatest amount of P and retained

the lowest DRP level with the forested site (Chamber Springs) binding the least and having a greater DRP (Table 5.12). No consistent changes occurred in M3P measured at the end of Phases II and III (Table 5.9). Similarly, there was no consistent change in  $PSR_{mod}$  or Mehlich-3 extractable elements in sediment at the ends of Phases II and III (Table 5.9).

Trace elements varied across sites, for example M3Ca levels decreased at some sites and increased at others and ranged from 613 to 3181 mg Ca kg<sup>-1</sup> (Table 5.10). Mehlich-3 Fe remained the same or decreased across all sites with final concentrations ranging from 85 to 312 mg Fe kg<sup>-1</sup>. As no loss of nutrients occurred between phase II and III, this again is possibly related to the binding of P in insoluble Fe-phosphates, which were not extracted via the Mehlich-3 extraction. Small changes in M3Mg levels were apparent ranging from a loss of 18 mg Mg kg<sup>-1</sup> to a gain of 3 mg Mg kg<sup>-1</sup>. Mehlich-3 Mn decreased across sites except Moore's Creek with final concentrations ranging from 89 to 200 mg Mn kg<sup>-1</sup>. Finally, M3Zn decreased from Phase II at all sites except Moore's Creek implying that Zn may have influenced P sorption to sediment (Table 5.10). Microbial-P increased at all sites except Moore's Creek (Table 5.3).

## CONCLUSIONS

Regulation of water column P during baseflow conditions is strongly influenced by sediments. Routine soil analysis (M3) for both P and other associated elements can be used as an indicator of the sediments ability to maintain baseflow DRP.

Based on the fluvium experiment, stream sediments in the UIRW can rapidly bind incoming P and act as transient storage for P during periods of high P inputs, such as

from point sources and urban and agricultural nonpoint runoff. Stream sediments with lower  $EPC_0$  concentrations are more likely to act as sinks for P entering a stream. The extent to which this occurs is reflected by sediment  $P_{max}$  and  $EPC_0$ . The corollary is that stream sediments with high  $EPC_0$  and low  $P_{max}$  values will have a lower ability to act as transient storage sites for P during periods of high P inputs.

Management of P sources and loss to streams will be critical in watersheds where sediments have a low capacity to retain P, as in-stream P-buffering is less. In these situations, DRP levels are less likely to be reduced during rapid P-fluxes by in-stream sediment processes. In contrast, streams with low  $EPC_0$  values and high  $P_{max}$  are likely to have a greater effect on DRP levels during high P-fluxes and less likely to act as sources of P during baseflow. For instance, sediment from streams selected for this research removed 85 to 96% of added P. However, these sediments are not infinite sinks for P and, thus, P-based land management within these watersheds is still critical to mitigate a situation in which the sediment uptake capacity has been surpassed. Also, once bound or stored by sediment, P can be slowly released back to stream flow, providing a legacy of past land management.

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Table 5.1. Initial physical and chemical sediment and stream water column properties of five selected streams in the Upper Illinois River Watershed, AR.

Stream †	Stream sediment										Stream water		
	Sand	Silt	Clay	pH	WEP	M3P	PSR <sub>mod</sub>	PSR	DRP	TP			
	----- % -----				mg P L <sup>-1</sup>	mg P kg <sup>-1</sup>	----- % -----					----- % -----	
Chamber Springs (For.)	81.5	12.3	6.2	7.1	0.054	14.7	4.9	10.7	0.039	0.045			
Little Wildcat Creek (Ag.)	92.5	4.8	2.7	7.4	0.053	11.9	4.7	9.1	0.021	0.138			
Moore's Creek (Ag.)	93.4	3.7	2.9	7.4	0.099	40.0	8.0	18.8	0.080	0.128			
Mud Creek Tributary (Urban)	90.6	5.0	4.4	7.9	0.028	12.4	2.5	3.8	0.016	0.020			
Wildcat Creek (Ag.)	81.1	13.2	5.7	8.0	0.068	24.3	6.0	11.8	0.035	0.040			

† Land use is dominated by forest – For., agriculture – Ag., and urban.

Table 5.2. Microbial-P levels in sediments from initial samples and end of Phases II and III of five selected streams in the Upper Illinois River Watershed, AR.

Stream		Microbial P	Microbial P / M3P
		mg P kg <sup>-1</sup>	%
Chamber Springs	Initial	1.98	14
	Phase II	3.18	14
	Phase III	3.68	24
Little Wildcat Creek	Initial	2.02	17
	Phase II	2.12	14
	Phase III	2.54	16
Moore's Creek	Initial	2.54	6
	Phase II	8.34	22
	Phase III	2.40	6
Mud Creek Tributary	Initial	2.54	21
	Phase II	1.64	15
	Phase III	2.92	26
Wildcat Creek	Initial	3.76	16
	Phase II	3.88	20
	Phase III	4.54	27

Table 5.3. Initial Mehlich-3 (M3) extractable trace element concentrations of sediments from five selected streams in the Upper Illinois River Watershed, AR.

<b>Stream</b>	<b>Ca</b>	<b>Cu</b>	<b>Fe</b>	<b>Mg</b>	<b>Mn</b>	<b>Zn</b>
	----- mg kg <sup>-1</sup> -----					
Chamber Springs	1078	9.4	174.0	33.2	92.7	5.1
Little Wildcat Creek	661	5.6	93.5	27.2	135.3	6.0
Moore's Creek	703.	5.9	352.6	35.3	113.2	6.6
Mud Creek Tributary	1965	4.9	181.3	67.4	249.2	7.3
Wildcat Creek	3084	12.8	163.0	44.1	163.3	8.9

Table 5.4. Mean Langmuir P-sorption isotherm parameters of sediments extracted with DI water from five selected streams in the Upper Illinois River Watershed, AR.

<b>Stream</b>	<b>R<sup>2</sup></b>	<b>DRP</b>	<b>EPC<sub>0</sub></b>	<b>P<sub>max</sub></b>	<b>Binding Energy</b>
		mg P L <sup>-1</sup>	mg P L <sup>-1</sup>	mg P kg <sup>-1</sup>	L mg P <sup>-1</sup>
Chamber Springs	0.96	0.039	0.041	149	0.186
Little Wildcat Creek	0.96	0.021	0.045	136	0.176
Moore's Creek	0.97	0.080	0.036	215	0.130
Mud Creek Tributary	0.97	0.016	0.014	323	0.220
Wildcat Creek	0.97	0.035	0.028	210	0.181

Table 5.5. Ending water column dissolved reactive P (DRP), total P (TP), and percentage DRP as TP concentrations of Phases I, II, and III of five selected streams in the Upper Illinois River Watershed, AR.

Stream	Phase	DRP			TP			Percent TP as DRP
		Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean	
Chamber Springs	I	0.035	0.029	0.032	0.126	0.099	0.113	28
	II	0.244	0.213	0.229	0.344	0.265	0.305	75
	III	0.098	0.097	0.098	0.111	0.114	0.113	87
Little Wildcat Creek	I	0.020	0.037	0.029	0.051	0.057	0.054	54
	II	0.114	0.121	0.118	0.155	0.166	0.161	73
	III	0.041	0.079	0.060	0.051	0.089	0.070	86
Mud Creek Tributary	I	0.011	0.016	0.014	0.042	0.022	0.032	44
	II	0.096	0.032	0.064	0.138	0.059	0.099	65
	III	0.028	0.015	0.022	0.045	0.025	0.035	63
Moore's Creek	I	0.059	0.082	0.071	0.091	0.117	0.104	68
	II	0.215	0.195	0.205	0.287	0.240	0.264	78
	III	0.082	0.099	0.091	0.117	0.113	0.115	79
Wildcat Creek	I	0.042	0.031	0.037	0.056	0.042	0.049	76
	II	0.355	0.180	0.268	0.441	0.237	0.339	79
	III	0.120	0.057	0.089	0.136	0.068	0.102	87

Table 5.6. Initial concentration of dissolved reactive P (DRP) and total P (TP) within fluvarium reservoir at initiation of Phases I, II, and III for five selected streams in the Upper Illinois River Watershed, AR.

Stream	DRP			TP			DRP added		
	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean
	----- mg P L <sup>-1</sup> -----						----- mg P -----		
Chamber Springs	1.75	1.51	1.63	2.20	1.91	2.06	315.3	271.3	293.3
Little Wildcat Creek	1.93	1.64	1.78	2.19	1.92	2.06	346.6	295.7	321.1
Moore's Creek	1.70	1.70	1.70	2.16	1.97	2.07	306.1	305.6	305.8
Mud Creek Tributary	1.89	1.74	1.81	2.46	2.08	2.27	340.8	312.4	326.6
Wildcat Creek	1.98	1.60	1.79	2.30	1.83	2.07	356.3	287.3	321.8

Table 5.7. Calculated parameters of power function for actual and normalized dissolved reactive P (DRP) concentrations from Phase II for five selected streams in the Upper Illinois River Watershed, AR.

Stream	R <sup>2</sup>	C <sub>0</sub>	α	β
<i>Actual DRP concentration</i>				
Chamber Springs	0.99	1.63	-0.93	0.11
Little Wildcat Creek	0.99	1.79	-1.19	0.10
Moore's Creek	0.99	1.70	-1.00	0.10
Mud Creek Tributary	0.98	1.83	-1.26	0.10
Wildcat Creek	0.99	1.79	-0.96	0.12
<i>Normalized DRP concentration</i>				
Chamber Springs	0.99	100.0	-56.8	0.11
Little Wildcat Creek	0.99	100.6	-66.7	0.10
Moore's Creek	0.99	99.7	-59.1	0.10
Mud Creek Tributary	0.99	100.8	-69.5	0.10
Wildcat Creek	0.99	100.0	-53.9	0.12

Table 5.8. Mass of dissolved reactive P (DRP) removed by sediment and percent remaining as DRP in solution at the end of Phase II for five selected streams in the Upper Illinois River Watershed, AR.

Stream	DRP mass uptake			Solution DRP		
	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean
	----- mg P -----			----- % -----		
Chamber Springs	271	233	252	13.9	14.1	14.0
Little Wildcat Creek	326	274	300	5.9	7.4	6.7
Moore's Creek	267	271	269	12.6	11.5	12.1
Mud Creek Tributary	324	307	315	5.0	1.9	3.5
Wildcat Creek	292	255	274	17.9	11.3	14.6

Table 5.9. Sediment chemical parameters across Phases I, II, and III for five selected streams in the Upper Illinois River Watershed, AR.

Phase	pH			M3P			PSR <sub>mod</sub>			WEP		
	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean
Chamber Springs				----- mg P kg <sup>-1</sup> -----			----- % -----			----- mg P L <sup>-1</sup> -----		
I	6.8	7.4	7.1	16.3	13.0	14.6	5.0	4.8	4.9	0.047	0.061	0.054
II	7.1	7.3	7.2	24.9	20.1	22.5	6.3	6.2	6.3	0.098	0.101	0.100
III	7.3	7.9	7.6	15.5	15.8	15.7	4.8	6.7	5.8	0.043	0.088	0.065
Little Wildcat Creek												
I	7.4	7.4	7.4	12.4	11.4	11.9	4.7	4.6	4.7	0.055	0.051	0.053
II	7.3	7.4	7.4	15.9	14.2	15.1	5.9	6.1	6.0	0.078	0.128	0.103
III	7.4	8.0	7.7	17.5	14.2	15.9	6.3	6.5	6.4	0.072	0.104	0.088
Moore's Creek												
I	7.4	7.4	7.4	41.5	38.4	39.9	8.2	7.7	8.0	0.095	0.102	0.099
II	7.1	7.3	7.2	35.5	40.9	38.2	8.0	8.1	8.1	0.146	0.129	0.138
III	7.6	7.3	7.5	38.8	38.3	38.6	8.2	8.2	8.2	0.139	0.138	0.139
Mud Creek Tributary												
I	7.7	8.1	7.9	13.2	11.6	12.4	2.6	2.3	2.5	0.032	0.023	0.028
II	7.8	7.9	7.9	11.2	10.9	11.1	2.9	2.6	2.8	0.044	0.032	0.038
III	8.0	8.0	8.0	12.4	10.2	11.3	3.2	2.7	2.6	0.045	0.035	0.040
Wildcat Creek												
I	7.8	8.2	8.0	25.9	22.6	24.2	5.8	6.1	6.0	0.061	0.075	0.068
II	7.8	8.1	8.0	17.6	21.3	19.5	5.6	6.4	6.0	0.085	0.088	0.087
III	8.1	8.0	8.1	12.5	21.4	17.0	5.0	6.5	5.8	0.092	0.072	0.082

Table 5.10. Mean Mehlich-3 (M3) extractable trace element concentrations across Phases I, II, and III for five selected streams in the Upper Illinois River Watershed, AR.

Stream	Phase	Ca	Fe	Mg	Mn	Zn
		----- mg P kg <sup>-1</sup> -----				
Chamber Springs	I	1078	174	33	83	5.2
	II	1389	194	49	118	16.5
	III	800	157	31	89	4.5
Little Wildcat Creek	I	661	94	27	136	6.0
	II	642	88	31	134	6.9
	III	678	86	32	131	6.4
Mud Creek Tributary	I	1965	181	67	249	7.3
	II	1614	120	67	214	5.5
	III	1532	120	64	200	5.3
Moore's Creek	I	703	536	35	113	6.6
	II	596	328	31	115	5.1
	III	613	312	34	122	5.5
Wildcat Creek	I	3084	201	40	163	8.9
	II	3159	145	41	139	6.0
	III	3181	123	43	122	5.4

Table 5.11. Average power function parameters for Phase III (re-equilibration) for five selected streams in the Upper Illinois River Watershed, AR.

<b>Stream</b>	<b>R<sup>2</sup></b>	<b><math>\alpha</math></b>	<b><math>\beta</math></b>
<i>Actual DRP concentration</i>			
Chamber Springs	0.87	0.07	0.10
Little Wildcat Creek	0.75	0.05	0.09
Moore's Creek	0.83	0.07	0.14
Mud Creek Tributary	NS	NS	NS
Wildcat Creek	0.81	0.07	0.13
<i>Normalized DRP Mass</i>			
Chamber Springs	0.86	5.0	0.10
Little Wildcat Creek	0.76	3.2	0.09
Moore's Creek	0.83	4.4	0.14
Mud Creek Tributary	NS	NS	NS
Wildcat Creek	0.80	4.5	0.13

Table 5.12. Water column dissolved reactive P (DRP) and total P (TP) levels at the end of Phase III for five selected streams in the Upper Illinois River Watershed, AR.

Stream	Solution DRP			Solution TP		
	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean
	----- mg P L <sup>-1</sup> -----					
Chamber Springs	0.098	0.097	0.098	0.111	0.114	0.113
Little Wildcat Creek	0.041	0.079	0.060	0.051	0.090	0.071
Moore's Creek	0.082	0.099	0.091	0.117	0.113	0.115
Mud Creek Tributary	0.028	0.015	0.022	0.045	0.025	0.035
Wildcat Creek	0.120	0.057	0.089	0.136	0.068	0.102

Table 5.13. Water column dissolved reactive P (DRP) mass and % release from sediment from Phase III for five selected streams in the Upper Illinois River Watershed, AR.

Stream	Solution DRP			DRP Release		
	Rep 1	Rep 2	Mean	Rep 1	Rep 2	Mean
	----- mg P -----			----- % -----		
Chamber Springs	17.7	17.4	17.6	6.5	7.5	7.0
Little Wildcat Creek	7.4	14.3	10.9	2.3	5.2	3.8
Moore's Creek	14.8	17.8	16.3	5.5	6.6	6.1
Mud Creek Tributary	5.1	2.8	4.0	1.6	0.9	1.2
Wildcat Creek	21.7	10.2	16.0	7.4	4.0	5.7

**FIGURES**

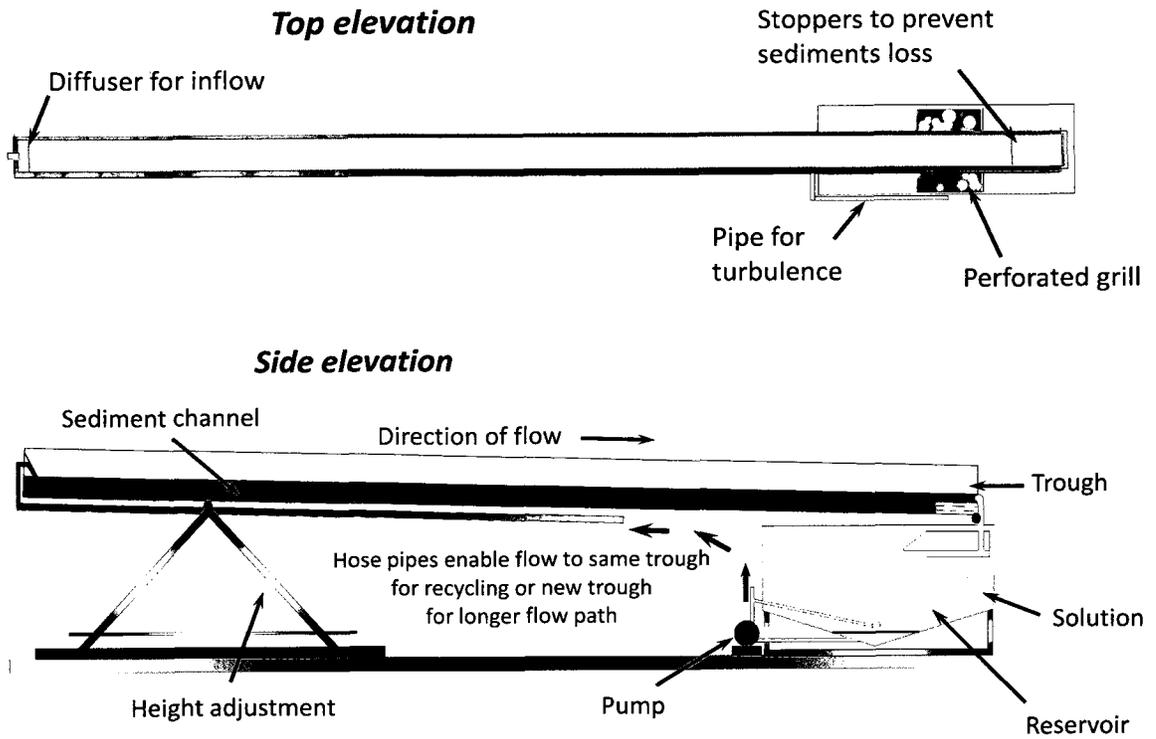


Figure 5.1. Schematic of experimental stream simulation channel -purpose built dual fluvarium.

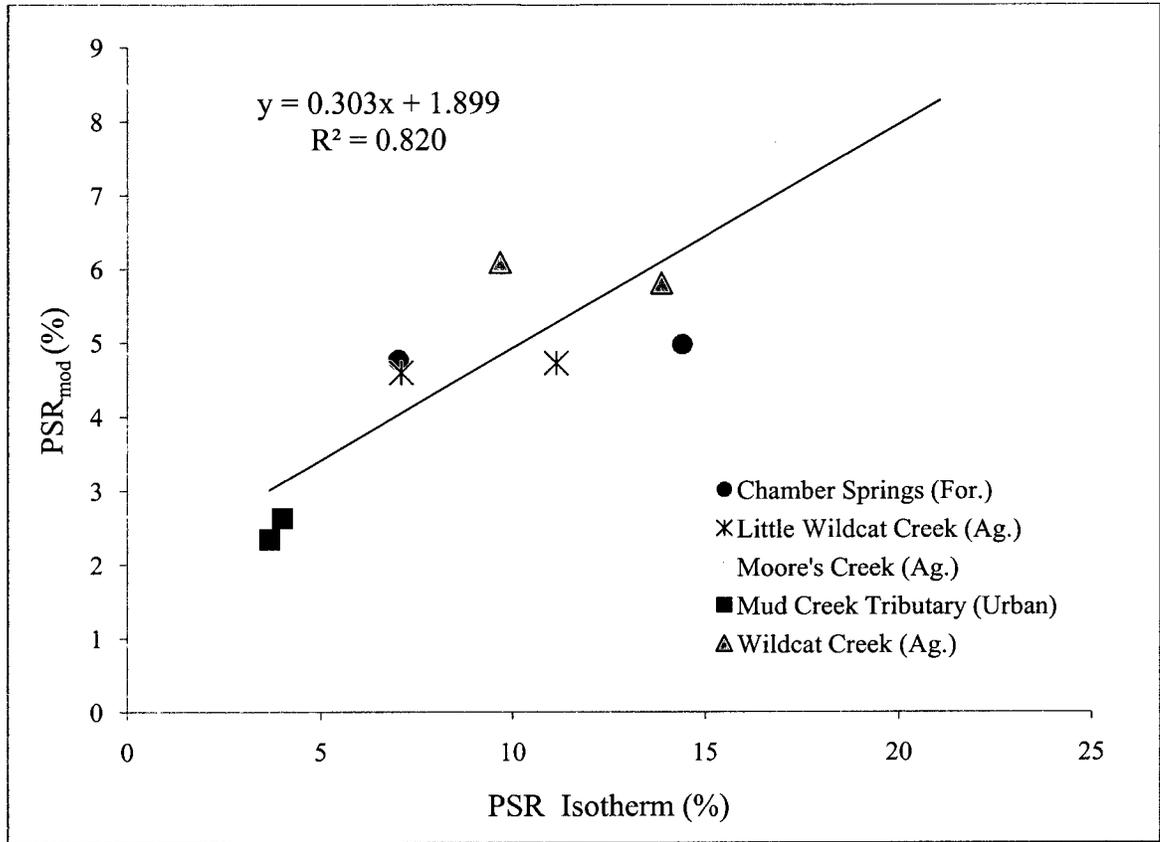


Figure 5.2. Relationship between modified P saturation ratio (PSR<sub>mod</sub>) and P saturation ratio (PSR) as calculated from Lanmuir Isotherms for five streams in the Upper Illinois River Watershed, AR.

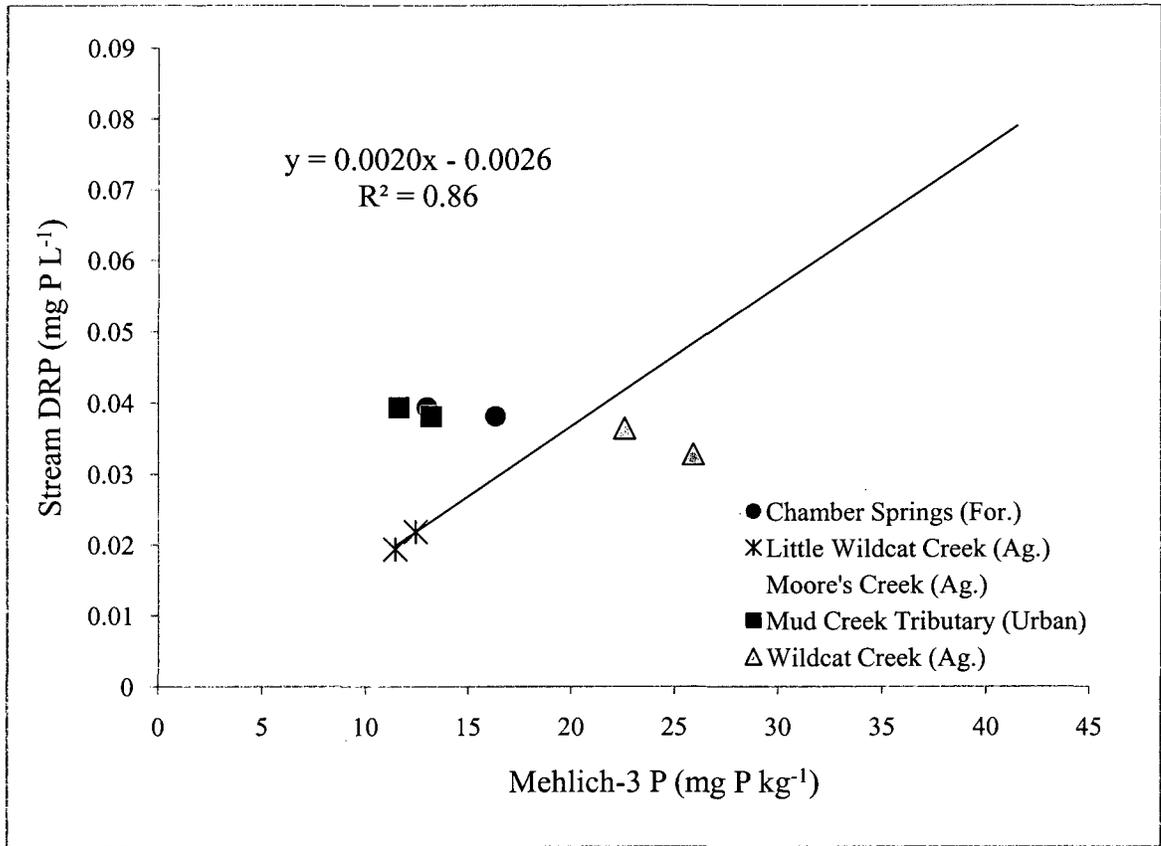


Figure 5.3. Relationship between Mehlich-3 P (M3P) as related to water column dissolved reactive P concentration (DRP) at initial time of collection for five streams in the Upper Illinois River Watershed, AR.

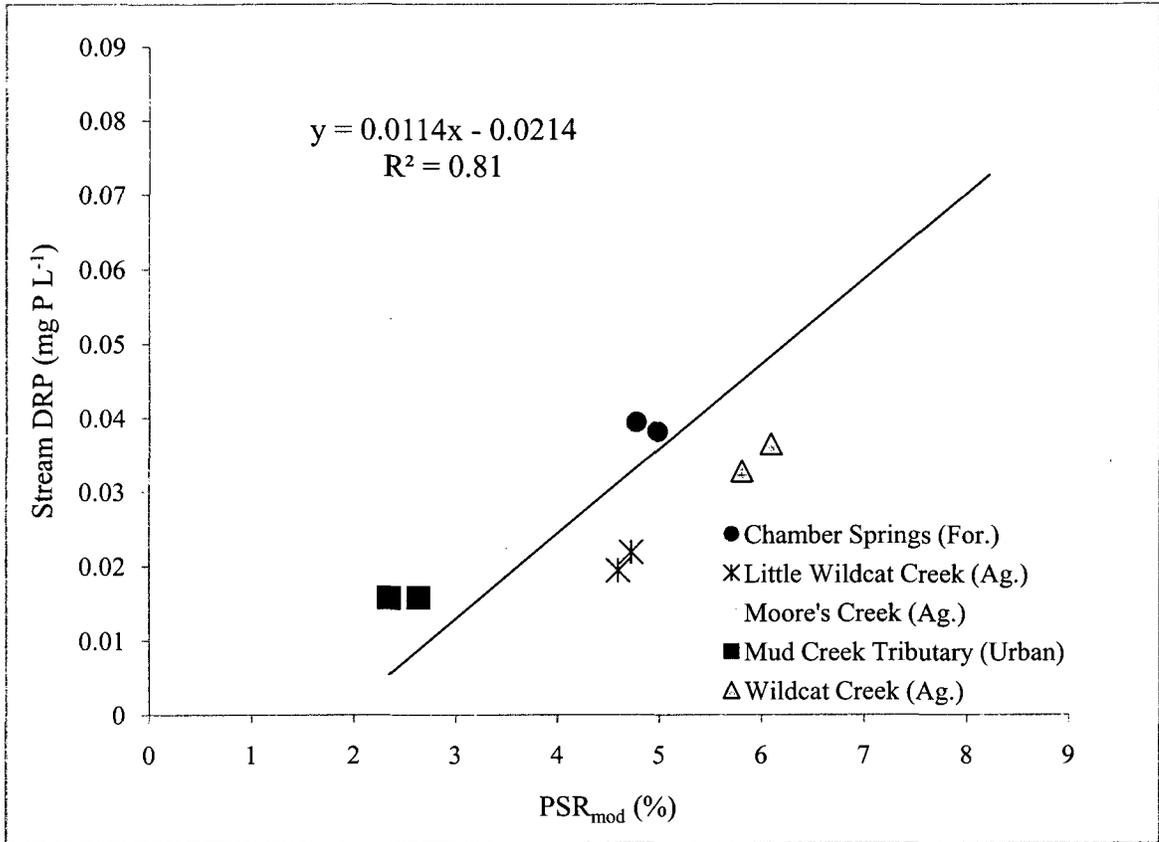


Figure 5.4. Relationship between modified P saturation ratio (PSR<sub>mod</sub>) to water column dissolved reactive P concentration (DRP) at initial time of collection for five streams in the Upper Illinois River Watershed, AR.

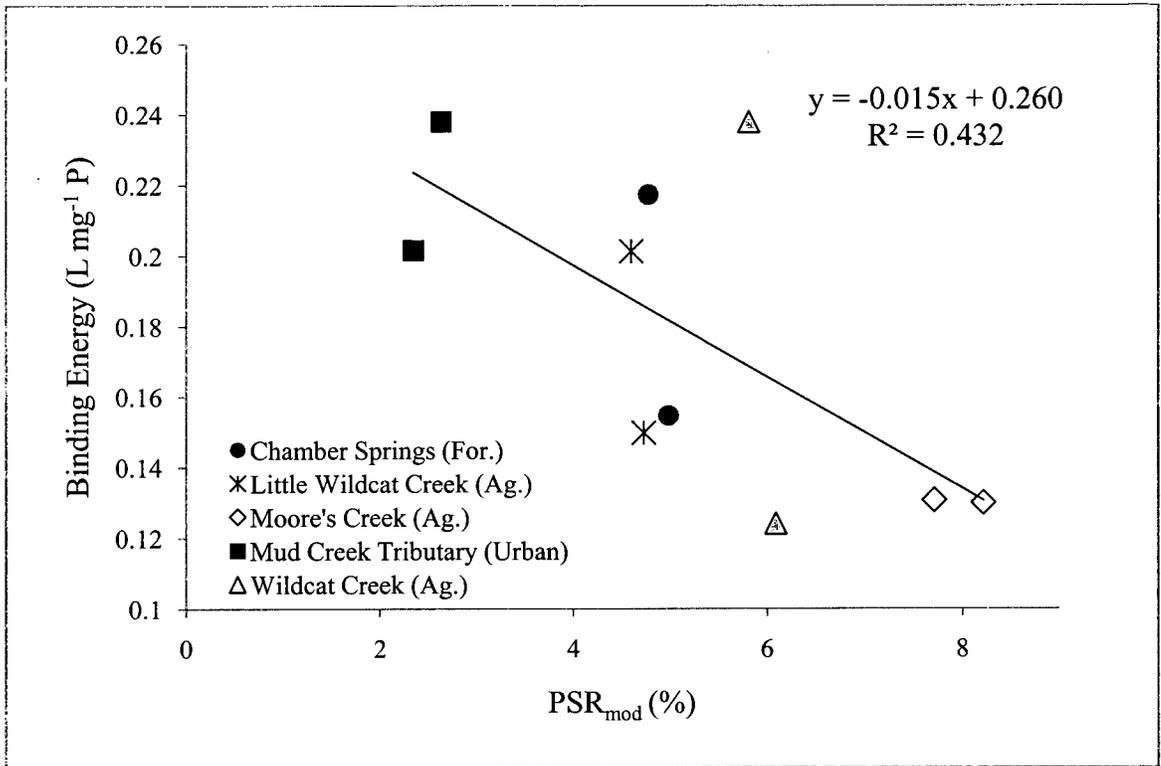


Figure 5.5. Relationship between binding energy (k) as calculated from the Langmuir isotherm to modified P saturation ratio PSR<sub>mod</sub> for five streams in the Upper Illinois River Watershed, AR

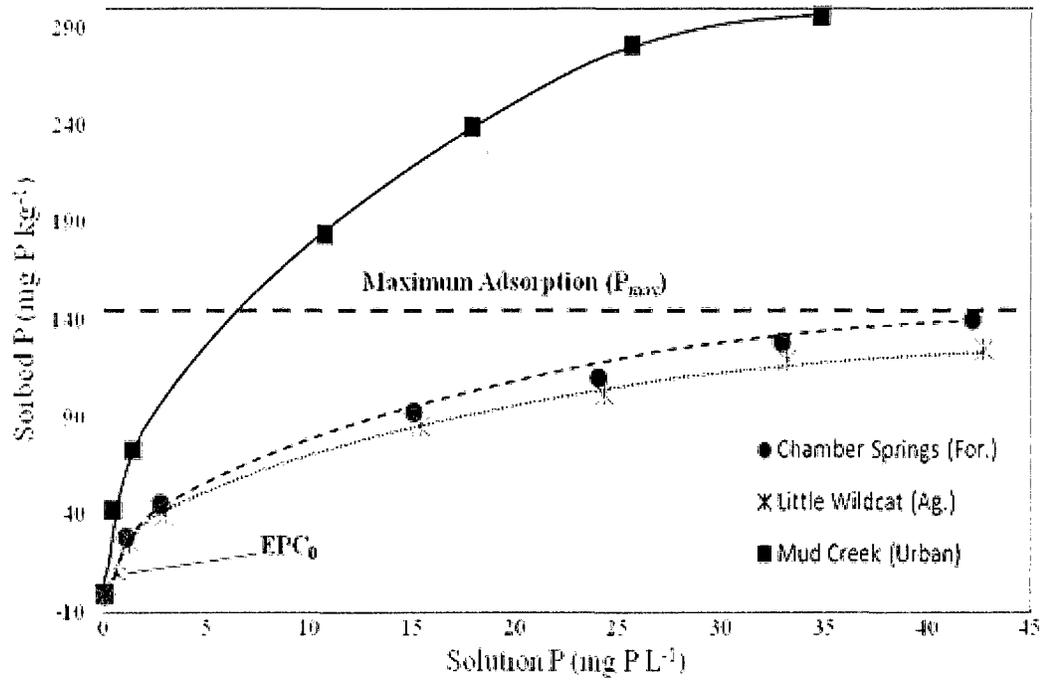


Figure 5.6. Langmuir isotherms representing urban, agricultural, and forest land uses for thee stream in the Upper Illinois River Watershed, AR.

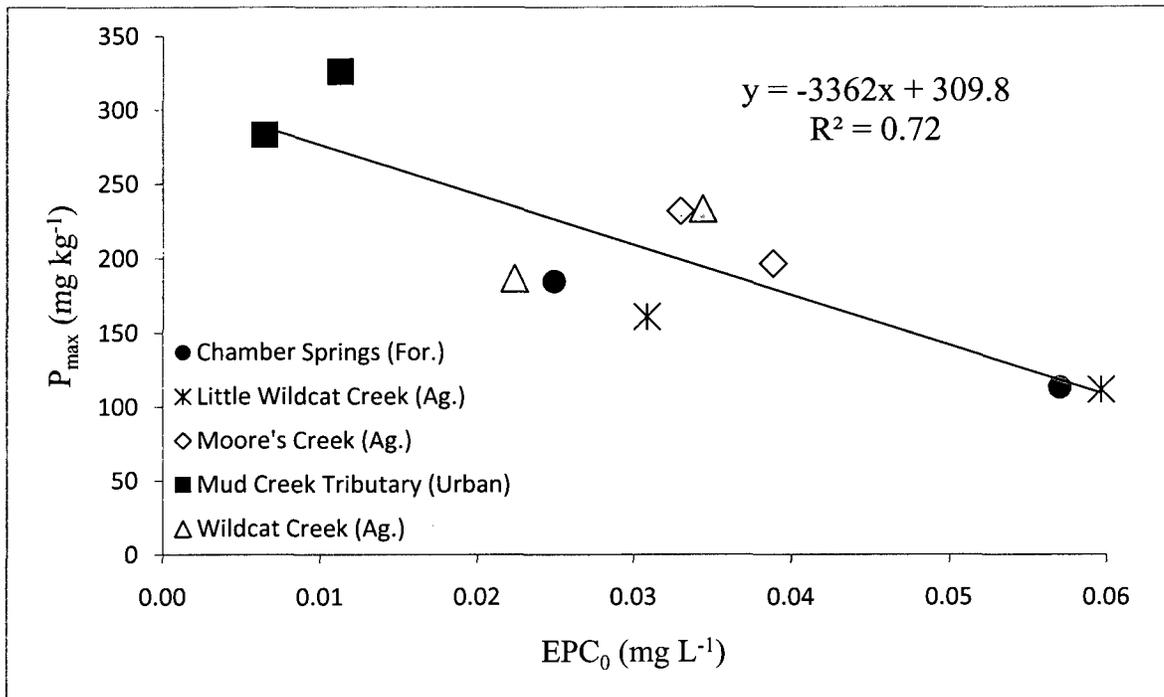


Figure 5.7. Relationship between equilibrium P concentration ( $EPC_0$ ) and maximum P adsorption ( $P_{max}$ ) as calculated from Langmuir isotherms for five streams in the Upper Illinois River Watershed, AR

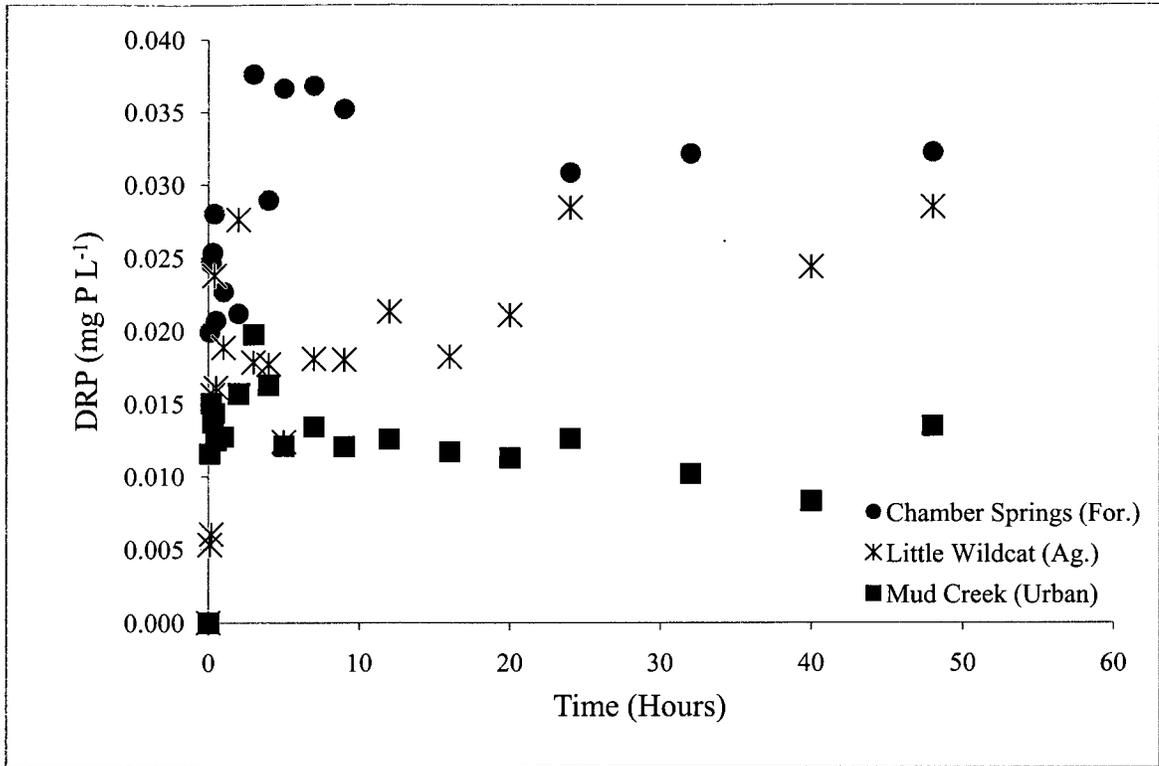


Figure 5.8. Phase I dissolved reactive P (DRP) concentrations over a 48 h flow event for agricultural, forest, and urban streams in the Upper Illinois River Watershed, AR.

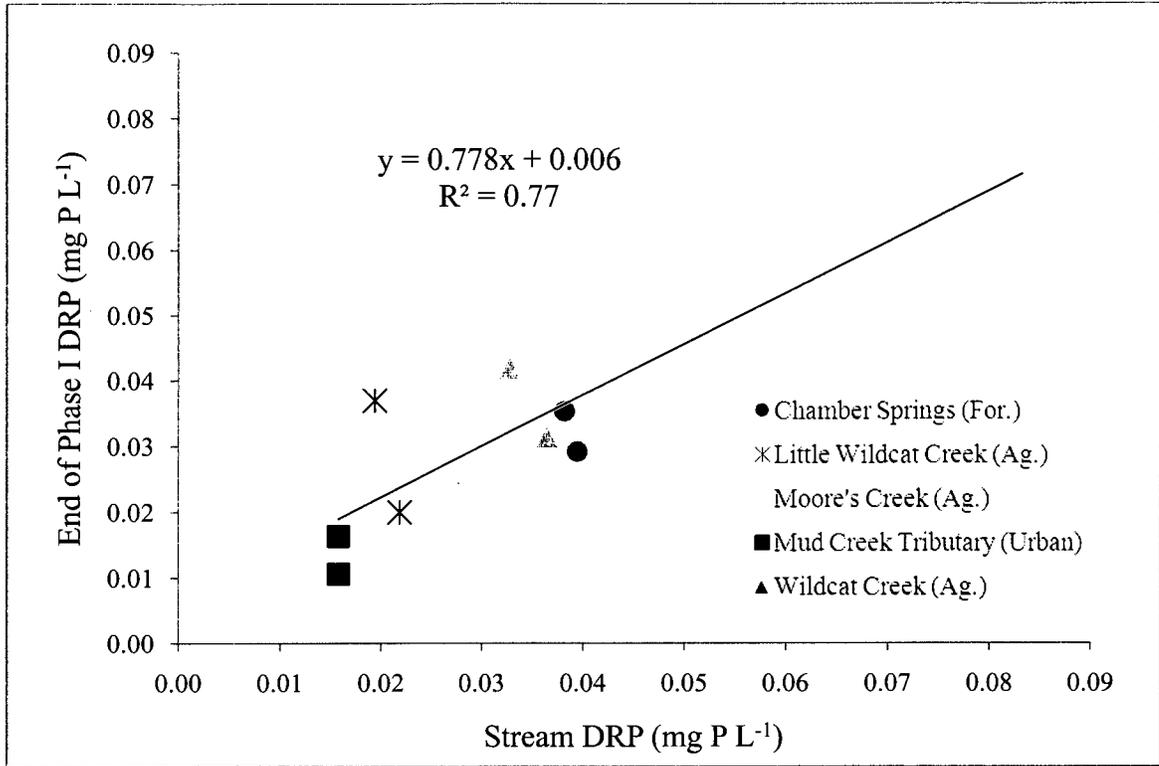


Figure 5.9. Relationship between end of Phase I dissolved reactive P concentration (DRP) to initial in-stream DRP levels

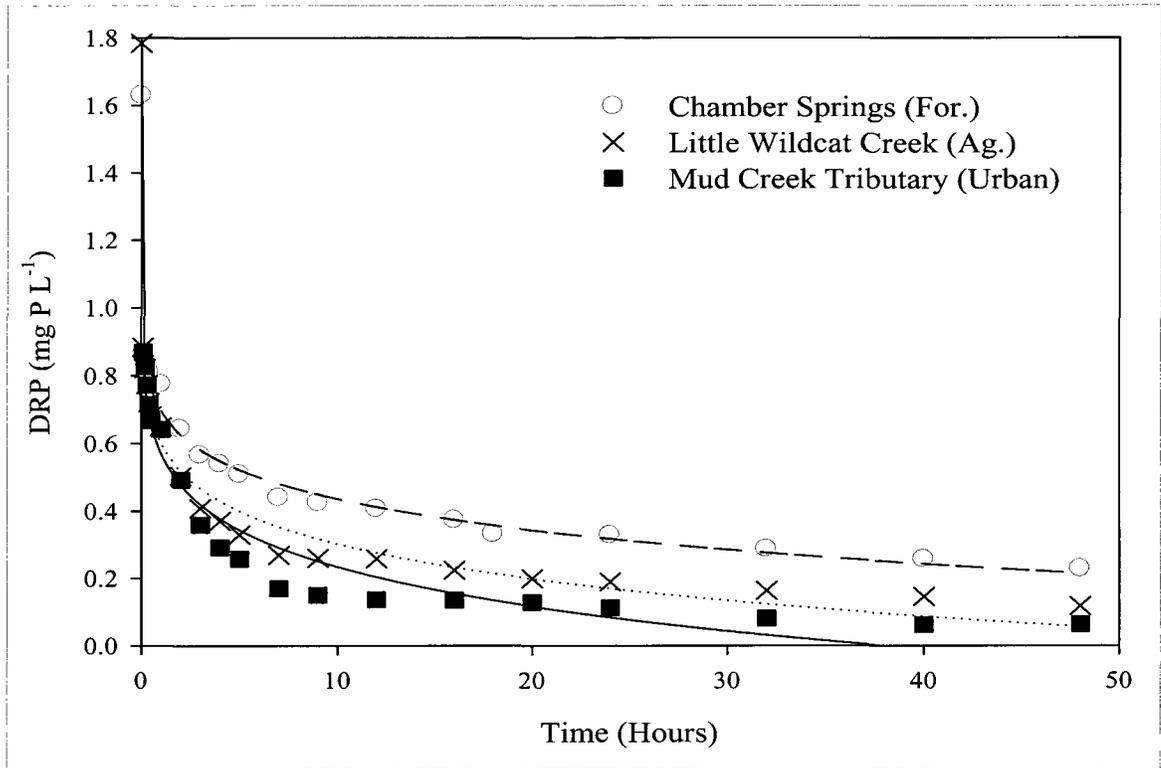


Figure 5.10. Phase II (poultry litter addition) dissolved reactive P concentration (DRP) decrease and sediment uptake over a 48 h flow event for agricultural, forest, and urban streams in the Upper Illinois River Watershed, AR.

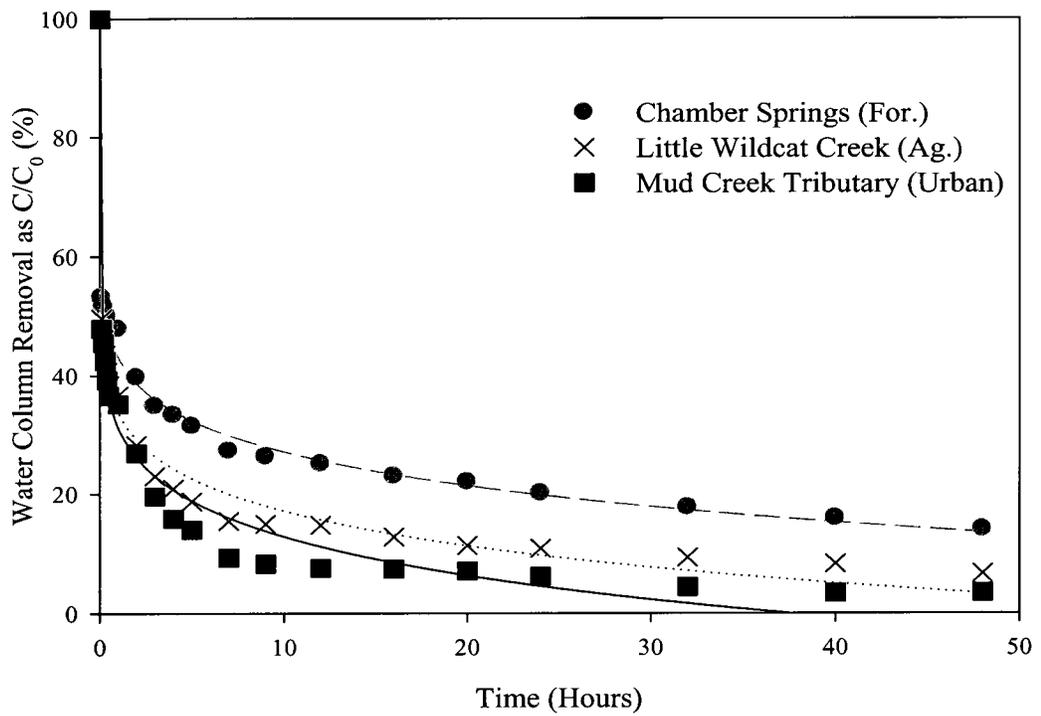


Figure 5.11. Phase II (poultry litter addition) normalized P decrease and sediment uptake over a 48 h flow event for agricultural, forest, and urban streams in the Upper Illinois River Watershed, AR.

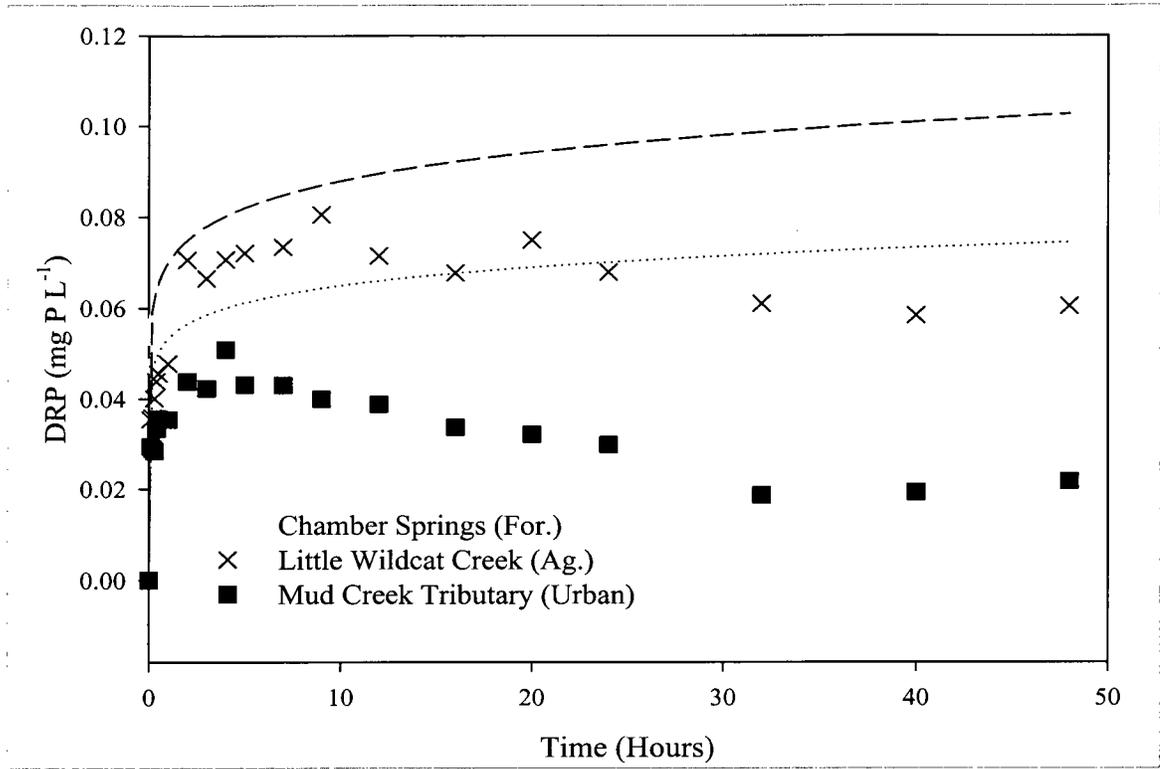


Figure 5.12. Phase III P release from sediment as measured by dissolved reactive P concentration (DRP) of water column for agricultural, forest, and urban streams in the Upper Illinois River Watershed, AR.

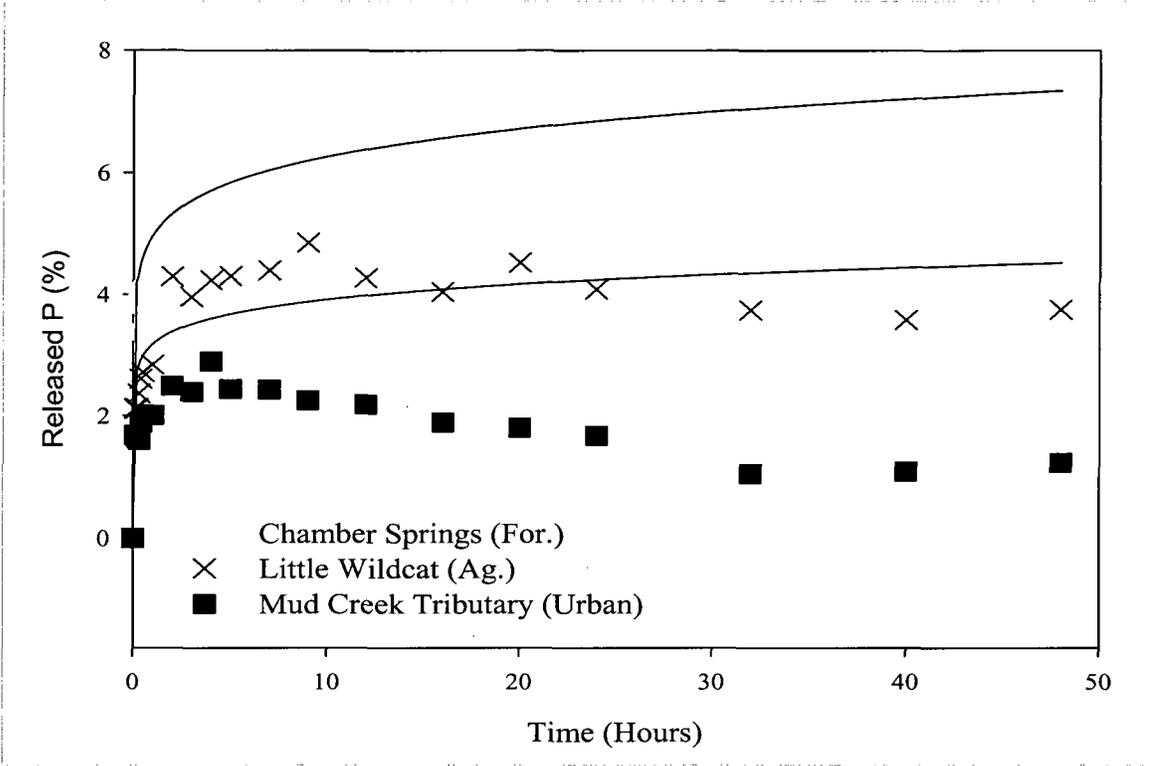


Figure 5.13. Phase III P release from sediment as measured by normalized P concentration of water column for agricultural, forest, and urban streams in the Upper Illinois River Watershed, AR.

## PHOTOS

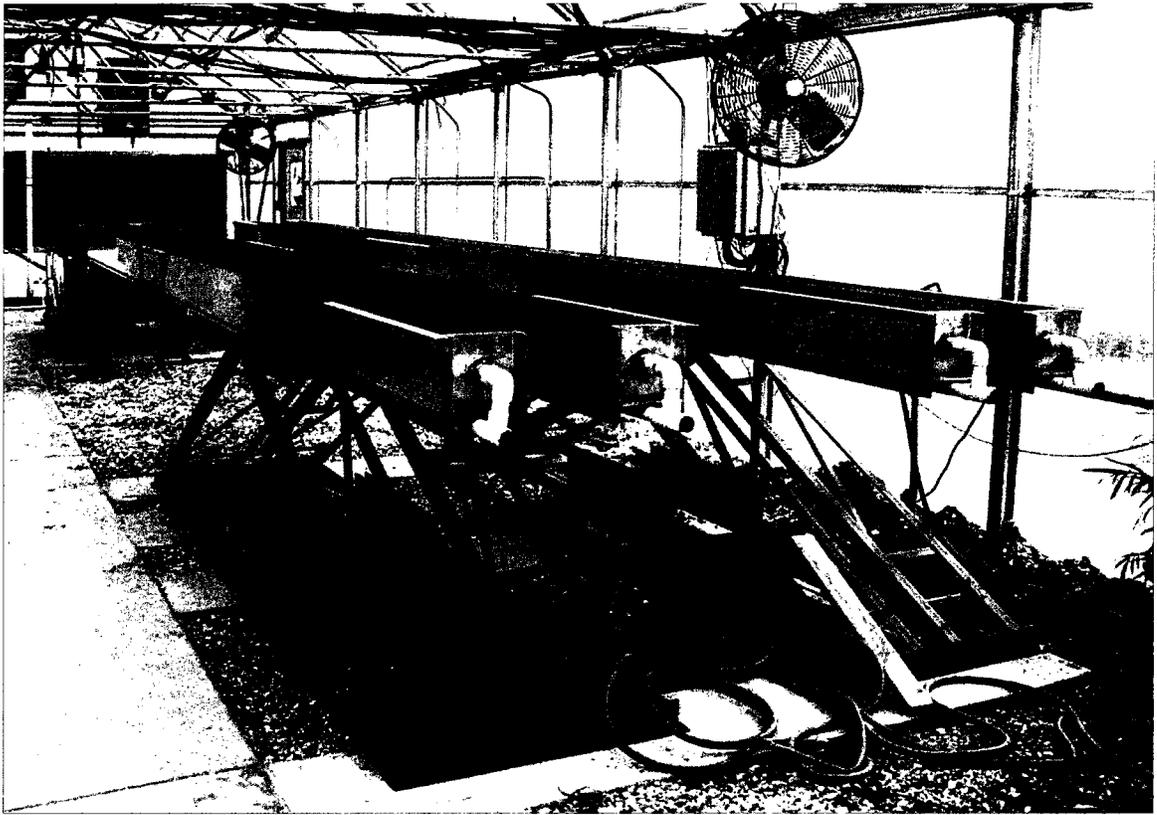


Photo 5.1. Stream simulation channel (fluvarium)

**CHAPTER 6**  
**OVERALL CONCLUSIONS**

## GENERAL CONCLUSIONS

Sediments in the Upper Illinois River Watershed (UIRW) are crucial in agricultural, forested, and urbanized streams, as they effectively act as transient storage mechanism through abiotic and biotic processes. Within streams, sediment size classification identifies constituents associated with the predominant mechanisms of chemically dominated phosphorus (P) uptake associated with fine (< 2-mm) and biologically driven biofilm production primarily confined to larger-sized sediment. Thus, further research on the interrelated biological and chemical controls that determine P processing in the fluvial system as a whole is necessary to have a full understanding of the controlling mechanisms of P transport within the UIRW. Use of batch P sorption experiments is an effective means of estimating sorption / desorption characteristics associated with sediment water column interactions. Utilization of this technique requires the researcher to be cognizant of important factors for adapting a soil technique to submerged sediments. Primarily, rapid processing of wet sediments to avoid microbial changes and subsequent anoxia, and awareness of Ca levels in stream water to avoid excessive levels in spiking solution, which could lead to precipitation, especially as pH becomes alkaline. Sediments within the UIRW act as transient storage locations for P transported from the landscape during rapid influxes of P such as occur during high rainfall events. In contrast, during baseflow sediments act as a slow release mechanism, where bound P is released to the water column, which is well correlated by routine soil analysis parameters (Mehlich-3). Modified P saturation ratio ( $PSR_{mod}$ ) calculated from Mehlich-3 extractable elements, was correlated to P saturation ratio as estimated by batch P sorption experiments. Determination of this ratio is a faster and equally effective

alternative for estimating the relationship between sediment bound P as related to base flow dissolved reactive P concentrations (DRP). Little relationship was apparent based on the physical (size fractions), chemical (Mehlich-3 extractable elements), and P sorption and desorption properties of sediments based on land use land classification. This is likely due to the limited sample size (five streams) and thus, for statistical trends to become apparent a larger number of sites need to be included. Finally, changes in nutrient management regarding land application of P from poultry litter and implementation of best management practices along with subsequent reduction in both field application and runoff P levels may not be well correlated to stream water column P levels. This potential lack of water quality improvement is in part due to a legacy effect of both soil (and subsequent runoff) and sediment P levels regulating during storm and baseflow respectively.



## Change Point Analysis of Phosphorus Trends in the Illinois River (Oklahoma) Demonstrates the Effects of Watershed Management

J. Thad Scott,\* Brian E. Haggard, Andrew N. Sharpley, and J. Joshua Romeis

Detecting water quality improvements following watershed management changes is complicated by flow-dependent concentrations and nonlinear or threshold responses that are difficult to detect with traditional statistical techniques. In this study, we evaluated the long-term trends (1997–2009) in total P (TP) concentrations in the Illinois River of Oklahoma, and some of its major tributaries, using flow-adjusted TP concentrations and regression tree analysis to identify specific calendar dates in which change points in P trends may have occurred. Phosphorus concentrations at all locations were strongly correlated with stream flow. Flow-adjusted TP concentrations increased at all study locations in the late 1990s, but this trend was related to a change in monitoring practices where storm flow samples were specifically targeted after 1998. Flow-adjusted TP concentrations decreased in the two Illinois River sites after 2003. This change coincided with a significant decrease in effluent TP concentrations originating with one of the largest municipal wastewater treatment facilities in the basin. Conversely, flow-adjusted TP concentrations in one tributary increased, but this stream received treated effluent from a wastewater facility where effluent TP did not decrease significantly over the study period. Results of this study demonstrate how long-term trends in stream TP concentrations are difficult to quantify without consistent long-term monitoring strategies and how flow adjustment is likely mandatory for examining these trends. Furthermore, the study demonstrates how detecting changes in long-term water quality data sets requires statistical methods capable of identifying change point and nonlinear responses.

THE ILLINOIS RIVER WATERSHED in the Ozark Highlands of northwest Arkansas and northeast Oklahoma has become widely known, following the 2005 filing of the lawsuit by the Oklahoma attorney general against several poultry companies based in northwest Arkansas. The lawsuit focused on several elements, including P, which is fed to poultry in diets as feed plus mineral phosphates. Excess P not assimilated by birds is accumulated in poultry litter generated in each house and then often land applied. Poultry litter has many beneficial nutrients and trace elements that increase forage growth (Lucero et al., 1995; Mitchell and Tu, 2005). Land application of poultry litter is now guided by soil P indices within each state (DeLaune et al., 2006; Sharpley et al., 2003). However, historical application rates were based on nitrogen content, which resulted in over application of P with regard to plant requirements (Maguire et al., 2009; Sims et al., 2000).

The application of P above forage needs has been shown to increase the pool of soil test P (STP) in upper soil layers (Kingery et al., 1994; Sharpley, 1999; Sharpley et al., 1994). Soils with elevated levels of stored P (as STP) are prone to greater P loss in runoff waters (Pote et al., 1999; Schroeder et al., 2004; Sharpley et al., 2007; Vadas et al., 2005) and the amount of water extractable P (WEP) in land-applied P sources (be it poultry litters, other animal manures, biosolids, or mineral fertilizer) also controls P concentrations and transport in runoff waters (Haggard et al., 2005b; Kleinman et al., 2002; Tasistro et al., 2004; Vadas et al., 2004). Watershed management requires sound balance, using poultry litter to increase forage yields, while managing application rates to limit potential water quality degradation.

At larger scales, P concentrations in streams vary with catchment land use characteristics (Buck and Townsend, 2004; Omernik et al., 1981; Tufford et al., 1998), where concentrations generally decrease in streams with increasing percentage of forest in its watershed, including the Ozark Highlands (Haggard et al., 2007). Thus, the amount of pastureland use in a watershed influences stream P concentrations during base flow and storm flow. But, agricultural landscapes and STP stores (i.e., WEP and STP)

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**Abbreviations:** APIP, Arkansas phosphorus index for pastures; LOESS, locally weighted regression; STP, soil test P; TP, total phosphorus; WEP, water extractable phosphorus; WWTP, wastewater treatment plant.

do not represent the only P sources to streams. Stream P enrichment can also be derived from other anthropogenic sources, such as treated wastewater effluent, septic systems, runoff from fertilized lawns and impervious surfaces, and erosion from construction sites. In fact, northwest Arkansas has experienced rapid human population growth over the last two decades (i.e., urban land use increased from 6% in 1992 to 13% in 2006), increasing regional P imports and exports through food items and other human-oriented sources. Historically (1997–2000), the major wastewater treatment plant (WWTP) effluent discharge accounted for ~40% of the P transported in the Illinois River from Arkansas to Oklahoma (Haggard, 2010). Elevated P concentrations in water samples collected during base-flow conditions could be traced over 45-river km upstream to one municipal wastewater discharge in the headwaters (Haggard, 2010). Effluent discharges not only influence water column P concentrations but also the amount of P stored within the bed material of the fluvial channel (Ekka et al., 2006), representing a legacy P source that can be released from the sediments when effluent P concentrations are low (Haggard et al., 2005a).

Like many locations nationwide, land management and wastewater treatment changes within the Illinois River Watershed have occurred over the last decade, which have decreased the amount of P entering streams. However, a documented response in stream P concentrations has not been reported in the scientific literature at sites within Oklahoma. Identifying trends with traditional techniques such as linear regression and Kendall–Tau statistics may be problematic because P concentrations are flow-dependent and long-term trends may be nonlinear or threshold-type (change point) responses.

The objective of this study was to evaluate long-term trends in P concentrations in the Illinois River, its tributaries, and in the major wastewater effluents in the watershed. We used data from USGS for in-stream P concentrations and self-reporting data from wastewater treatment plants for the analyses. Phosphorus concentrations in the Illinois River and its tributaries are usually flow dependent (Green and Haggard, 2001; Vieux and Moreda, 2003), with greater P concentrations occurring during greater flow. Therefore, we used a flow-adjusted estimate of in-stream P concentration to evaluate the temporal trends over a 12-yr period from January 1997 to January 2009. We used regression tree analysis (see description below; also see De'ath and Fabricius, 2000) and locally weighted regression (LOESS) to identify changes in flow-adjusted P concentrations over time. Regression tree was used to identify specific change points in the flow-adjusted P concentrations that could be linked to calendar dates (Qian et al., 2003). Conversely, LOESS regressions were used to identify longer periods of directional change in P concentrations. This allowed us to compare the timing of any changes in river P concentrations to the timing of management changes in the watershed.

## Materials and Methods

### Site Selection and Data Availability

The Illinois River Watershed comprises ~4200 km<sup>2</sup> in eastern Oklahoma and western Arkansas (Fig. 1) and includes

the Lake Tenkiller Ferry (hereafter, Lake Tenkiller), which was constructed between 1947 and 1952 for the purposes of flood control and hydroelectric power. The headwaters of the Illinois River and its major tributaries (i.e., Baron Fork and Flint Creek) originate in the Ozark Highlands and Boston Mountains of northwest Arkansas. A high-density urban area exists in the headwaters, primarily within the city limits of Fayetteville, Springdale, and Rogers, AR. The Illinois River drainage area from Lake Tenkiller upstream has a land use distribution of 43, 42, and 5% in forest, pasture, and urban, respectively (Andrews et al., 2009), whereas its distribution solely on the Arkansas side is about 36, 50, and 13% (National Land Cover Database, 2006).

The stream monitoring sites selected for this study were the Illinois River near Watts, OK (USGS Station Number 07195500); the Illinois River near Tahlequah, OK (USGS Station Number 07196500); Flint Creek near Kansas, OK (USGS Station Number 07196000), and the Baron Fork near Eldon, OK (USGS Station Number 07197000). These sites were selected because the water quality monitoring program was similar across all sites and the program generally consisted of water sampled every month during the calendar year in 1997 and 1998. Sampling was changed to every other month during base-flow conditions, plus six supplemental storm-event samples starting from 1999 through January 2009. The water samples were collected by USGS personnel using the equal-width-increment technique (Edwards and Glysson, 1999) and then analyzed for total P (TP) concentrations (USGS Parameter Code 00666) at the USGS National Water Quality Laboratory in Denver, CO (<http://nwql.usgs.gov>). The time period chosen for this study was 1997 through 2009, representing 12 complete calendar years' worth of data at these selected sites. Data on TP concentrations in treated wastewater for a similar time period were obtained from the major (discharge permits >3500 m<sup>3</sup> d<sup>-1</sup>) WWTPs within the basin.

### Trend Analyses

Simple trend analysis of in-stream TP concentrations was completed using three steps (see White et al., 2004). Briefly, the steps include: (i) daily mean discharge and TP concentrations were log transformed to account for typical log-normal distribution of water quality data and minimize the effects of outliers within the data (Hirsch et al., 1991; Lettenmaier et al., 1991); (ii) log-transformed TP concentrations were adjusted against log-transformed daily mean discharge using the LOESS two-dimensional smoothing technique (Richards and Baker, 2002; Hirsch et al., 1991); and (iii) flow-adjusted TP concentrations (derived from residuals of the LOESS regression of discharge versus concentration) were analyzed for temporal trends using regression tree analysis and LOESS.

Trend analyses were also conducted on raw stream TP concentrations using LOESS regressions only. Trend analyses on raw TP concentrations in treated wastewater effluent were conducted with regression tree analysis. Details of the flow adjustments to TP concentrations and temporal trend analyses using regression tree analysis and LOESS are provided in the following sections.

The relationship between log-transformed stream discharge and log-transformed TP concentrations were quantified using

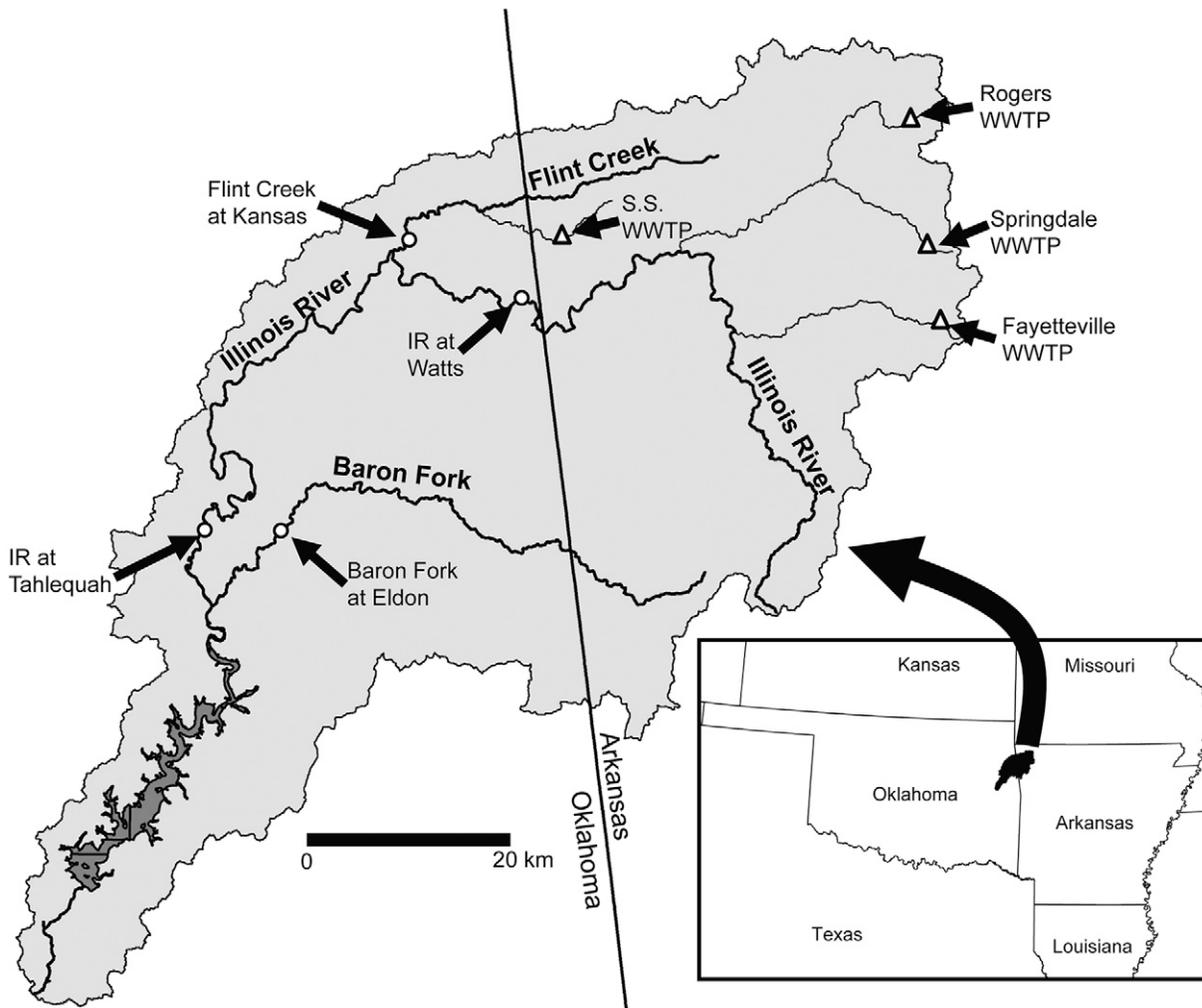


Fig. 1. The Illinois River Basin of northwest Arkansas and northeast Oklahoma. Triangles represent the location of municipal wastewater effluent discharges in the basin that are permitted to exceed  $3500 \text{ m}^3 \text{ d}^{-1}$ . "S.S. WWTP" represents the Siloam Springs wastewater treatment plant. Circles represent USGS monitoring locations on the Illinois River and its major tributaries.

LOESS two-dimensional smoothing in SigmaPlot, with a sampling proportion of 0.5 and a first order polynomial function (Systat Software, Inc., San Jose, CA). Bekele and McFarland (2004) observed that a sampling proportion of 0.5 was adequate to reduce variability in concentrations with stream discharge. The LOESS smoothing uses locally weighted regression algorithms and overcomes limitations often associated with parametric techniques that are more sensitive to outliers in the data (Lettenmaier et al., 1991). The residuals from this LOESS smoothing of log-transformed discharge and concentration represent the flow-adjusted concentrations.

Nonlinear temporal trends in flow-adjusted TP concentrations were evaluated using LOESS as previously described. We also used regression tree analysis (De'ath and Fabricius, 2000) to identify change points (Qian et al., 2003) in the flow-adjusted TP concentrations at approximate calendar dates. Regression tree analysis is an empirical modeling technique useful for identifying change points and hierarchical relationships in environmental data. The method uses recursive partitioning to separate data into increasingly homogeneous subsets through deviance reduction. Data are divided into all possible subsets based on change points in the predictor variable and the change point yielding the greatest deviance reduction is

chosen to split the data. This process is repeated in the data subsets, invoking a tree-like structure (multiple change points in increasingly homogeneous data subsets).

We used the MVPART library in R software (<http://www.r-project.org>) for regression tree analyses. The procedure in the R software is similar in concept and coding to the procedure developed using the RPART library in S-Plus (personal communication, R. King, Baylor University). Sampling date was the only predictor variable used in the analysis, with flow-adjusted TP concentration as the dependent variable. We allowed multiple splits in the data to identify multiple change points, if applicable, for each stream sampling site or WWTP effluent over the 12-yr period. In constructing models, we required a minimum of 20 observations be included in deriving any single change point and that at least 10 observations should occur on either side of the change point providing the best model fit. Cross validation of each model was conducted by deriving 10 similarly sized data sets from the original data by randomly removing observations. Models were recalculated for each data set. The number of change points in each model was determined using the minimum cross-validated error rule (De'ath and Fabricius, 2000), which identifies the maximum number of possible splits where the relative cross-validated

error was minimized. Models are presented as change points in scatterplots between date and flow-adjusted TP concentrations.

## Results

Long-term monitoring data revealed that median TP concentrations were least in the Baron Fork (35°55'16" N, 94°50'18" W) (0.04 mg L<sup>-1</sup>) and greatest in either Flint Creek (36°11'11" N, 94°42'24" W) (0.18 mg L<sup>-1</sup>) or the Illinois River at Watts, OK (36°07'48" N, 94°34'19" W) (0.19 mg L<sup>-1</sup>, Table 1). Raw TP concentrations, which were not flow adjusted, were highly variable among dates within a site but were generally greatest during the period from 1999 to 2003 at Baron Fork and in the Illinois River at Watts and Tahlequah (35°55'22" N, 94°55'24" W) (Fig. 2A, 2C, and 2D). Unadjusted TP concentrations in Flint Creek increased through the entire period of record (Fig. 2B), although this trend was not statistically significant in linear regression analysis ( $R^2 = 0.02$ ;  $P = 0.144$ ).

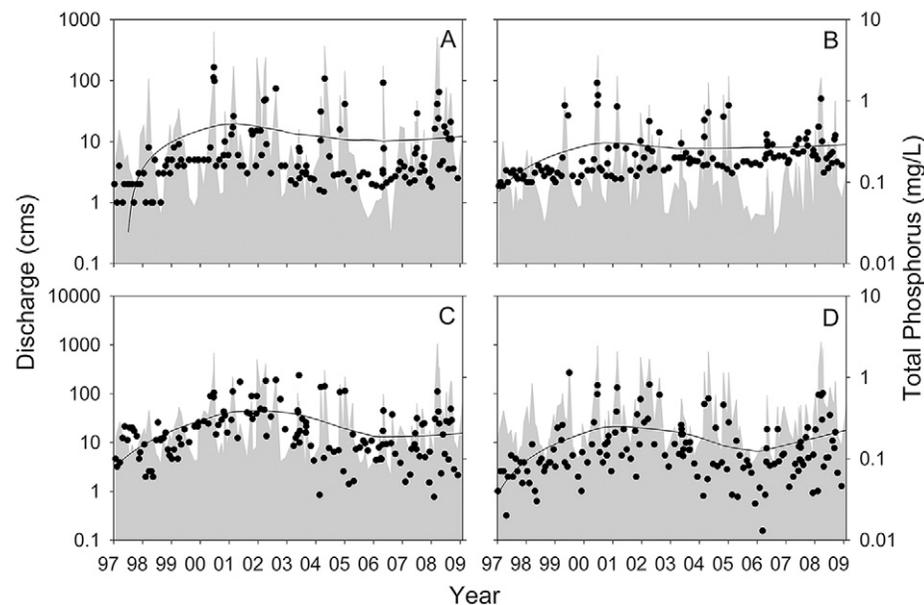
Phosphorus concentrations were generally less during base flow and greater during storm events (Fig. 3). The maximum TP concentrations observed during storm events ranged from slightly more than 1 mg L<sup>-1</sup> at the Illinois River to ~1.6 mg L<sup>-1</sup> at Baron Fork and Flint Creek. The LOESS regressions showed that TP concentrations either did not change (Baron Fork [Fig. 3A] and Illinois River at Tahlequah [Fig. 3D]), or slightly decreased (Flint Creek [Fig. 3B] and Illinois River at Watts [Fig. 3C]) as discharge varied over a range of base-flow conditions (<10 cm s<sup>-1</sup>). However, TP concentrations increased exponentially with streamflow at all sites when discharge exceeded 10 cm s<sup>-1</sup>, i.e., storm-event conditions (Fig. 3).

Regression tree analysis and LOESS regressions revealed that flow-adjusted TP concentrations (i.e., residual values from LOESS regressions of discharge versus TP concentration) changed significantly over the 12-yr study. Regression tree analysis showed that flow-adjusted TP concentrations in the Baron Fork were greater after May 1998 (Fig. 4A). However, LOESS models showed that flow-adjusted TP concentrations in Baron Fork decreased slightly from 2001 to 2004 and remained relatively constant thereafter (Fig. 4A). In Flint Creek, regression tree analysis identified a change point in March 1999, after which TP concentrations were generally greater (Fig. 4B). Similarly, LOESS regression demonstrated a positive linear increase in flow-adjusted TP concentrations in Flint Creek from 1997 to 2007, with a slight decrease occurring after 2008 (Fig. 4B). The increasing trend in flow-adjusted TP concentration in Flint Creek from 1997 to 2007 was confirmed to be statistically significant using linear regression ( $R^2 = 0.24$ ,  $P < 0.001$ ). In the Illinois River, regression tree analysis demonstrated that flow-adjusted TP concentrations increased after either May 1999 or May 1998, at the monitoring locations at Watts, OK, and Tahlequah, OK, respectively, but decreased after the fall of 2003 at both locations (Fig. 4C and 4D). The LOESS trends suggested that flow-adjusted TP concentrations remained on a decreasing trajectory in the Illinois River at Watts (Fig. 4C) but were relatively constant after fall 2003 at the Illinois River at Tahlequah (Fig. 4D).

Total P concentrations in WWTP effluents were highly variable across plants in the watershed (Fig. 5). There was no trend in effluent TP concentrations for the Fayetteville WWTP.

**Table 1. Descriptive statistics of flow conditions and total P concentrations in the Baron Fork Creek, Flint Creek, Illinois River at Watts, OK, and Illinois River at Tahlequah, OK. Statistics represent the period from January 1997 through January 2009.**

Site	Discharge				Total P			
	Min.	Max.	Median	Mean	Min.	Max.	Median	Mean
	m <sup>3</sup> s <sup>-1</sup>				mg L <sup>-1</sup>			
Baron Fork	0.28	630	6.8	36	0.01	1.65	0.04	0.12
Flint Creek	0.28	254	2.3	14	0.09	1.66	0.18	0.26
Illinois River at Watts	2.0	1050	14	59	0.03	1.06	0.19	0.25
Illinois River at Tahlequah	2.6	1100	24	87	0.01	1.14	0.11	0.17



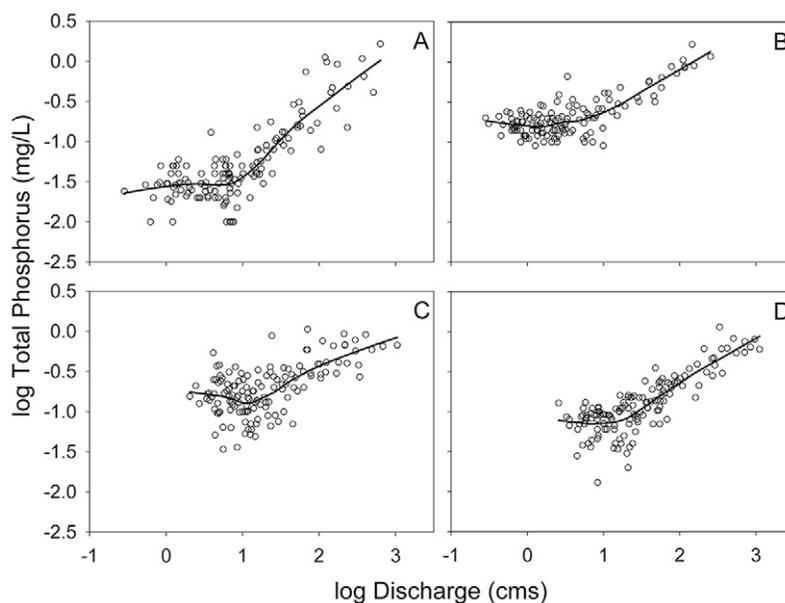
**Fig. 2. Discharge (gray area) and total P concentrations (points) over the 12-yr study period at: (A) Baron Fork, near Eldon, OK; (B) Flint Creek, near Kansas, OK; (C) Illinois River at Watts, OK; and (D) Illinois River at Tahlequah, OK. Solid line represents the locally weighted regression fit to the total P data.**

Effluent TP concentrations for the Springdale WWTP were greater before October 2002 (Fig. 5A). For the Rogers WWTP, effluent TP concentrations were greater before May 2000. Effluent TP in the Siloam Springs WWTP did not change drastically over the study period but demonstrated a minor decrease after October 2007.

Change point dates identified by regression tree analysis that reflected a decrease in Illinois River TP concentrations followed change point dates for decreases in effluent TP concentrations in two major WWTPs (Table 2). In particular, the Springdale WWTP decreased its geometric mean effluent TP concentration by  $>6 \text{ mg L}^{-1}$  during this time. A  $1.5\text{-mg L}^{-1}$  reduction in effluent TP (geometric mean) occurred at the Rogers WWTP. Geometric mean TP concentrations decreased by  $0.18 \text{ mg L}^{-1}$  after October 2003 in the Illinois River at Watts and by  $0.05 \text{ mg L}^{-1}$  after November 2003 in the Illinois River at Tahlequah (Table 2).

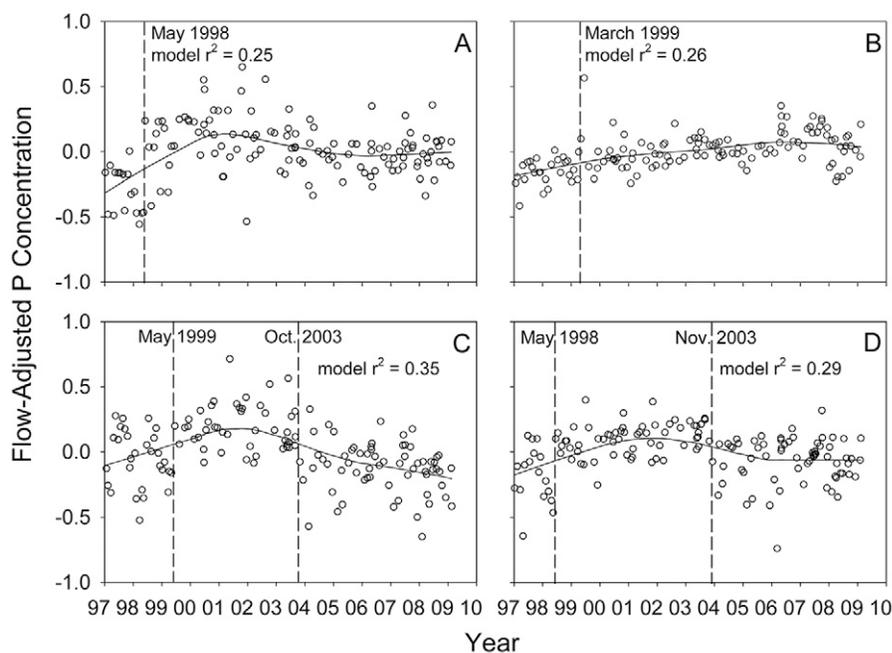
## Discussion

Total P concentrations in the Illinois River and its tributaries are one aspect of an ongoing lawsuit between the state of Oklahoma and several poultry integrators operating in the Arkansas portion of the Illinois River Watershed. The data presented in this study, generated by USGS, represent the best, publicly available information on P concentrations in these streams within the Oklahoma portion of the Illinois River Watershed. Our analysis of these data suggested that flow-adjusted TP concentrations at the two locations in the Illinois River in Oklahoma have decreased since 2003 (Fig. 4C, D; Table 2). Furthermore, flow-adjusted TP concentrations at one of these locations (Illinois River, near Watts, OK) were continuing on a decreasing trajectory through the end of the study period (Fig. 4C). Rebich and Domcheck (2007) and Andrews et al. (2009) found that TP concentrations in the Illinois River and its tributaries were increasing from the late 1990s to the early 2000s. The addition of more recent data, however, shows this pattern has reversed since 2003. The timing of water quality improvements shown here is supported by the qualitative change point observed by Haggard (2010) for the Illinois River further upstream in Arkansas. However, the use of regression tree in our analysis provided a quantitative framework for identifying specific calendar dates at which change points were apparent, making it possible to link changes in flow-adjusted TP trends with changes in watershed management or monitoring activities (Table 2).

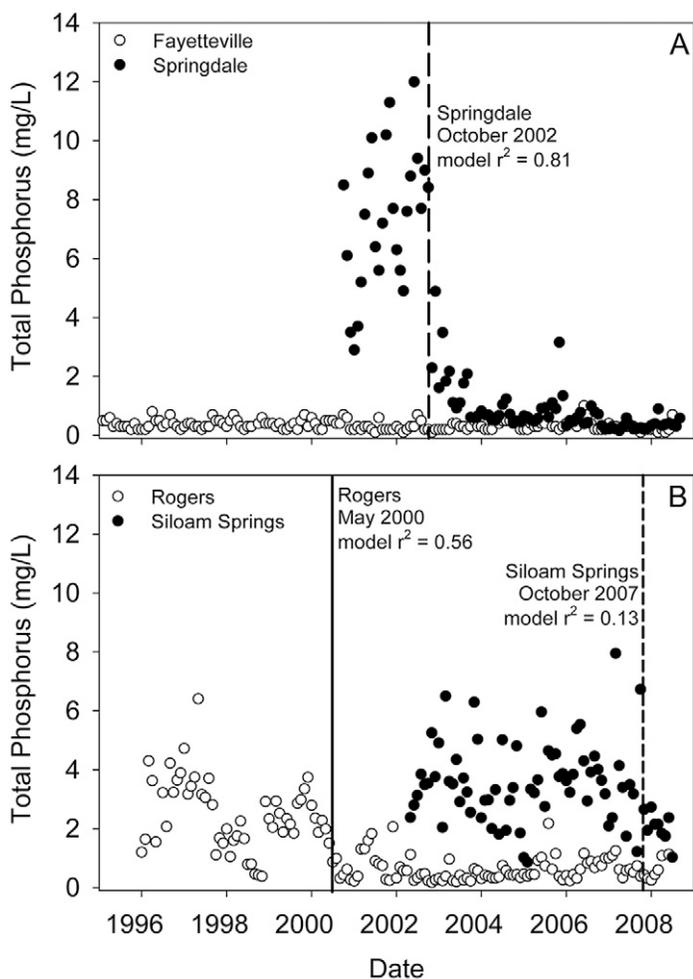


**Fig. 3.** Relationship and locally weighted regression between logarithmic discharge and logarithmic total P concentrations over the 12-yr study period at: (A) Baron Fork, near Eldon, OK; (B) Flint Creek, near Kansas, OK; (C) Illinois River at Watts, OK; and (D) Illinois River at Tahlequah, OK. Logarithmic transformations were all  $\log_{10}$ .

The first change point observed in this study occurred between May 1998 and March 1999 at all four sampling locations (Fig. 4), which predated watershed management changes that occurred from 2002 to 2004. This suggests that water quality may have continued to degrade in response to agricultural and effluent P inputs over this time. However, it is unlikely that the rate of change observed in flow-adjusted TP between 1997 and 2000 was controlled only by watershed P inputs. Rather, this time period coincided with a change in methodology of sample collection by USGS. After 1998, USGS specifically



**Fig. 4.** Residual values from the discharge total P locally weighted regression (LOESS) plotted through time for: (A) Baron Fork, near Eldon, OK; (B) Flint Creek, near Kansas, OK; (C) Illinois River at Watts, OK; and (D) Illinois River at Tahlequah, OK. The LOESS residuals are used as a proxy for flow-adjusted total P concentrations.



**Fig. 5.** Total P concentrations for the four major treatment facilities in the Illinois River Basin where permitted discharge is  $>3500 \text{ m}^3 \text{ d}^{-1}$ : (A) Fayetteville and Springdale, where the vertical dashed line represents the change point for Springdale identified by regression tree analysis, and (B) Rogers and Siloam Springs, where the vertical solid line represents the change point identified for Rogers and the vertical dashed line represents the change point identified for Siloam Springs by regression tree analysis. All measurements were approximately monthly from 1995 to 2008 (where data were available).

targeted storm event samples in one-half (six of 12) of their annual sampling events in the Illinois River Watershed (Pickup et al., 2003). Thus, the increase in flow-adjusted TP concentration after this change was probably caused by an increase in the number of intentional storm flows sampled, which had greater TP concentrations than base flow (Fig. 3).

The second change point observed in our study occurred between October and November 2003 but only at the Illinois River sampling locations (Fig. 4C, 4D). This change point corresponds to the qualitative change point identified by Haggard (2010) for the Illinois River in Arkansas and closely followed a significant decrease in effluent TP concentrations in the Springdale and Rogers WWTP discharges (Fig. 5; Table 2). Ekka et al. (2006) showed that reducing the Springdale effluent TP concentrations dramatically reduced TP concentrations in its receiving stream, both in the water column and streambed sediments. These WWTPs undertook a voluntary improvement in waste treatment and processing, which decreased

effluent and stream TP concentrations, as well as reduced flow-adjusted TP loads in the Illinois River in Arkansas (Haggard, 2010). The  $>1$ -yr lag time between the effluent P change point in the Springdale WWTP (Fig. 5A) and the in-stream P change point in the Illinois River sites (Fig. 4C, 4D) is likely related to legacy effects, such as the depletion of P from P-rich stream sediments and other sources of in-stream transient P storage (Meals et al., 2010; Sharpley et al., 2009b).

Improvements in WWTPs that decreased effluent TP concentrations were not the only change occurring in the watershed during 2003. Poultry litter management also transitioned from N- to P-based applications, following adoption of the Arkansas P Index for Pastures (APIP; DeLaune et al., 2004). Use of APIP could have decreased poultry litter applications from those typically used before its implementation. For example, adopting P-based application rates in the adjacent Eucha–Spavinaw Watershed reduced the amount of poultry litter applied from  $\sim 1000$  to  $500 \text{ kg ha}^{-1}$  (Sharpley et al., 2009a); however, the Eucha–Spavinaw P Index was more restrictive than APIP, due to a court-mandated STP threshold of  $300 \text{ mg kg}^{-1}$ , above which no litter could be applied irrespective of site risk (DeLaune et al., 2006). The APIP has since been revised and the changes to its P source and transport components will likely result in further reductions in poultry litter application rates (Sharpley et al., 2010a, 2010b). In 2004, Arkansas and Oklahoma also established a poultry litter transport program, which provided a mechanism to export excess poultry litter out of the Illinois River Watershed to fields deficient in STP (i.e., less than agronomic optimal levels) in eastern Arkansas and western Oklahoma. Nutrient management planning records show that  $>70\%$  of the litter produced in the adjacent Eucha–Spavinaw Watershed has been exported out of the watershed each year since the program was established in 2004 (Sharpley et al., 2009a).

It is difficult to ascertain whether the observed trends in flow-adjusted TP concentrations in the Illinois River were due to changes in effluent alone or also to changes in agricultural management practices. However, the general trends at the Baron Fork site provide some evidence that changes in agricultural landscape management reduced TP concentrations. Flow-adjusted TP concentrations in the Baron Fork were slightly elevated from 1998 to 2003 (Fig. 4A), which coincided with the greatest TP concentrations observed at the Illinois River sites (Fig. 4C, 4D). However, the Baron Fork is not influenced by an effluent discharge  $>3500 \text{ m}^3 \text{ d}^{-1}$  that implemented voluntary P management (Fig. 1). Therefore, any reduction in flow-adjusted TP concentrations in the Baron Fork was likely associated with changing agricultural management. The decrease in flow-adjusted P concentrations in the Baron Fork was minimal compared with that observed in the Illinois River and no trend in TP in the Baron Fork was apparent after 2004.

Long-term P trends in Flint Creek also support the premise that effluent TP concentrations strongly influence flow-adjusted stream TP concentrations. The LOESS regression of the flow-adjusted TP concentrations revealed a monotonic increase throughout the study period, which was confirmed by linear regression analysis ( $R^2 = 0.24$ ,  $P < 0.001$ ). Flint Creek

**Table 2. Change points (CPs) in effluent and stream total P concentrations over the study period.**

Site	CP date	Total P geometric mean		Possible cause
		Before CP	After CP	
		mg L <sup>-1</sup>		
Springdale WWTP†	Oct. 2002	7.0	0.62	Improved P removal in WWTP
Rogers WWTP	May 2000	2.2	0.54	Improved P removal in WWTP
Siloam Springs WWTP	Oct. 2007	3.3	1.9	Improved P removal in WWTP
Baron Fork	May 1998	0.019	0.061	No storm flow samples before Jan. 1999
Flint Creek	Mar. 1999	0.12	0.24	No storm flow samples before Jan. 1999
IR at Watts‡	May 1999	0.14	0.33	No storm flow samples before Jan. 1999
IR at Watts	Oct. 2003	0.33	0.15	Effluent P reductions
IR at Tahlequah§	May 1998	0.06	0.16	No storm flow samples before Jan. 1999
IR at Tahlequah	Nov. 2003	0.16	0.11	Effluent P reductions

† WWTP, wastewater treatment plant.

‡ Illinois River at Watts, OK.

§ Illinois River at Tahlequah, OK.

receives discharge from the Siloam Springs WWTP (Fig. 1), where effluent TP concentrations were greatest among all dischargers in the latter part of the study period (Fig. 5). However, the Siloam Springs WWTP began lowering effluent TP in late 2007, which was identified by change point analysis (Fig. 5B; Table 2). Although not identified by change point analysis, a slight decrease in TP in Flint Creek was apparent from the LOESS trend after 2007. All WWTPs in northwest Arkansas that discharge into the headwater streams of the Illinois River Watershed have or will have an effluent TP limit of 1 mg L<sup>-1</sup> in future permits. Our study indicates that this can reduce, and should continue to reduce, the flow-adjusted TP concentrations in the Illinois River near the Arkansas–Oklahoma border and in Flint Creek.

The trajectory of change in P in the Illinois River at Watts was decreasing through the end of our study period. However, the long-term P trend in the Illinois River at Tahlequah, which is ~75-river km downstream of the Watts location (Fig. 1), did not appear to be changing much after the “step-down” decrease observed in 2003. This is probably because Flint Creek enters the Illinois River between these two monitoring locations and the long-term P trend in Flint Creek indicated an increasing flow-adjusted TP concentration. Future studies are warranted that will track the trends in TP concentrations at all three locations (Illinois River at Watts and Tahlequah, and Flint Creek) to determine if effluent-controlled TP decreases in Flint Creek result in further P decreases in the Illinois River at Tahlequah. It will also be important to quantify when P concentrations in the Illinois River at Watts begin to stabilize and what base flow P concentration is related to this stabilization.

## Conclusions

This study presents a practical application of regression tree analysis for identifying change points in water quality data at specific calendar dates. Our results indicate that effluent TP in headwaters can invoke a major control on in-stream, flow-adjusted TP concentrations at locations that may be 100-river km or more downstream. Future reductions in effluent TP and continued improvements in agricultural management in the Illinois River Basin should only further decrease stream TP concentrations. Our results also suggest that the increase in

flow-adjusted TP concentrations observed after the late 1990s in the Illinois River was probably associated with a change in monitoring methodologies, where storm flow samples were actively pursued beginning in 1999. Therefore, monitoring methods can have a profound effect on the evaluation of long-term trends. Stream and river monitoring programs should adopt and sustain monitoring strategies that are consistent over many years to assess long-term trends.

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## NUTRIENT CONCENTRATIONS AND YIELDS IN UNDEVELOPED STREAM BASINS OF THE UNITED STATES<sup>1</sup>

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**ABSTRACT:** Data from 85 sites across the United States were used to estimate concentrations and yields of selected nutrients in streams draining relatively undeveloped basins. Flow-weighted concentrations during 1990-1995 were generally low with median basin concentrations of 0.020, 0.087, 0.26, 0.010, and 0.022 milligrams per liter (mg/L) for ammonia as N, nitrate as N, total nitrogen, orthophosphate as P, and total phosphorus, respectively. The flow-weighted concentration of nitrate exceeded 0.6 mg/L in only three basins. Total nitrogen exceeded 1 mg/L in only four basins, and total phosphorus exceeded 0.1 mg/L in only four basins. The median annual basin yield of ammonia as N, nitrate as N, total nitrogen, orthophosphate as P, and total phosphorus was 8.1, 26, 86, 2.8, and 8.5 kilograms per square kilometer, respectively. Concentrations and yields of nitrate tended to be highest in northeastern and mid-Atlantic coastal states and correlated well with areas of high atmospheric nitrogen deposition. Concentrations and yields of total nitrogen were highest in the southeastern part of the nation and in parts of the upper Midwest. In the northeast, nitrate was generally the predominant form of nitrogen, and in the southeast and parts of the upper Midwest, organic nitrogen was the dominant form. Concentrations of total phosphorus were generally highest in the Rocky Mountain and Central Plain states.

(KEY TERMS: nitrogen; phosphorus; undeveloped watersheds; concentrations; loads; atmospheric deposition.)

### INTRODUCTION

Population growth and industrial activities in the United States (U.S.) during the 20th century have affected, and will continue to affect the quality of the nations' water resources. Although natural processes and anthropogenic activities affect water quality in streams, past water-quality studies primarily have been designed to evaluate the anthropogenic affects. To fully evaluate the extent of anthropogenic activities, however, it is also important to describe water quality in streams draining relatively undeveloped

environments and to understand the factors that control it. Natural variations in water quality occur among different regions of the nation because of differences in geology, vegetation, and climate, yet standards typically do not account for these differences. For example, some of the most pristine streams in parts of the southeastern U.S. have dissolved oxygen concentrations that are substandard according to national water-quality criteria (Omernik and Griffith, 1991). Attempting to meet criteria in parts of the nation where they may not be attainable is technically and economically unrealistic. Thus, an understanding of regional patterns in natural water quality provides for a more valid baseline for setting objective, attainable water-quality goals and ultimately will provide a more rigorous tool for separating natural and anthropogenic factors affecting water quality in streams across the nation.

The chemistry of natural waters varies both spatially and temporally and is controlled by factors such as atmospheric deposition, biological activity in soils, and chemical weathering of soils and bedrock (Likens *et al.*, 1977). Approaches used to describe regional water-quality characteristics in natural environments include physiographic provinces (Biesecker and Leifeste, 1975), hydrologic drainage basins (Smith, 1969), and ecoregions (Omernik and Gallant, 1986; Hughes and Larsen, 1988; Larsen *et al.*, 1988). Although these frameworks are useful for describing natural spatial variations that occur in different regions of the nation, water quality in natural environments may also be influenced by anthropogenic factors that cross basin and regional boundaries. For example, atmospheric deposition introduces sulfur, nitrogen, base cations, and acidity to relatively

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undeveloped basins in the northeastern U.S. (Likens *et al.*, 1996), which in turn may influence the weathering rate and buffering capacity of underlying soils and bedrock (Murdoch *et al.*, 1998; Clow and Mast, 1999; Lawrence and Huntington, 1999). Stoddard (1994) and Williams *et al.* (1996) suggest that the biologic demand for nitrogen has been exceeded by atmospheric inputs in a number of forested basins in the eastern U.S. and in the Rocky Mountains of Colorado. Atmospheric deposition of nitrogen can account for nearly all the downstream nitrogen load in some Midwestern and Northeastern streams (Smith *et al.*, 1987; Puckett, 1995). Other studies in the northeast have documented the relation between air temperature and nitrogen mineralization and suggest that climate change may be influencing nitrification rates in undeveloped basins where excess nitrogen is accumulating (Murdoch *et al.*, 1998).

The purpose of this paper is to evaluate concentrations and yields of selected nutrients (nitrogen and phosphorus species) in streams draining relatively undeveloped basins across the nation and to identify broad regional and national patterns. No attempt was made to describe concentrations and yields in relation to a defined regional or national framework, such as physiographic province, hydrologic drainage basin, or ecoregion. Nutrient data collected as part of three U.S. Geological Survey (USGS) programs were used for this assessment. To ensure data comparability, differences in selected physical and nutrient characteristics between the basins in each program were assessed. Nutrients were selected for this study because of their long-standing role not only as constituents of concern for aquatic health in streams and coastal areas of the nation, but also in ground water. Nitrogen and phosphorus are known to be primary factors that can initiate the excessive growth of algae and macrophytes in freshwater systems. Under the guidelines of the Clean Water Action Plan, the U. S. Environmental Protection Agency (USEPA) is developing regional nutrient criteria for surface-water bodies across the nation. Findings from this assessment will provide baseline data as part of that effort.

## METHODS

Nutrient data collected from 85 streams draining relatively undeveloped basins from across the U.S. were used for this assessment. Basins were selected from three programs of the USGS; the Hydrologic Benchmark Network (HBN), the National Water-Quality Assessment (NAWQA), and the Research Program. Drainage basins of size useful to characterize regional patterns in natural conditions are difficult to

find or are not being monitored in many parts of the nation. In order to fill these gaps, some of the basins used for this assessment may be slightly affected by residential development, selective logging, grazing, and other agricultural disturbances. Even with the inclusion of these minimally affected basins, some areas of the nation are poorly represented in this assessment. This is especially apparent in the "Corn Belt" region of the upper Midwest and in the Southern Plains states of Kansas, Oklahoma, and Texas (Figure 1).

The HBN program was initiated in 1958 to track water-quality trends in streams draining basins free from anthropogenic influence and to study cause and effect relationships between various physiographic, meteorologic, and hydrologic variables (Cobb and Biesecker, 1971). The HBN network is primarily comprised of relatively undeveloped basins encompassing a wide variety of natural environments from across the nation (Clark *et al.*, 1999; Mast and Turk, 1999a,b). To ensure minimal anthropogenic effects, many of the HBN basins are in wilderness areas, national and state parks, national forests, and in areas set aside for scientific study. For this assessment, 43 basins from the HBN network were used, with individual basins ranging in area from about 6.1 to about 2,500 km<sup>2</sup>.

The USGS NAWQA program (initiated in 1990), was designed to identify and describe major factors that affect observed water-quality conditions over large spatial and temporal scales (Hirsch *et al.*, 1988). Thus, streams sampled as part of the NAWQA represent water-quality conditions influenced by a wide range of landuse and water-use conditions. Of the 200 stream sites sampled as part of the NAWQA during 1992-1995, 22 drain relatively undeveloped basins. These latter sites were included in this assessment (Figure 1). The range in area of NAWQA basins included in this study is similar to the range in area of the HBN basins, 18 to about 2,700 km<sup>2</sup>.

The 20 USGS research basins used in this assessment were selected from the Water, Energy, and Biogeochemical Budgets (WEBB) program (USGS, 1999a), the Long Term Ecological Research (LTER) program, and other USGS research (O. Bricker, D. Burns, P. Murdoch, and K. Rice, USGS, written commun., 1999). The research basins included in this assessment are predominantly located in the Appalachian and Rocky Mountains (Figure 1). The periods of data collection for the research basins varied, but all research data used for this assessment were collected during water years 1982-1997 (October 1 to September 30). The primary focus of study in the research basins used in this assessment is the effects of atmospheric deposition on biogeochemical cycling within small, undisturbed watersheds. The research

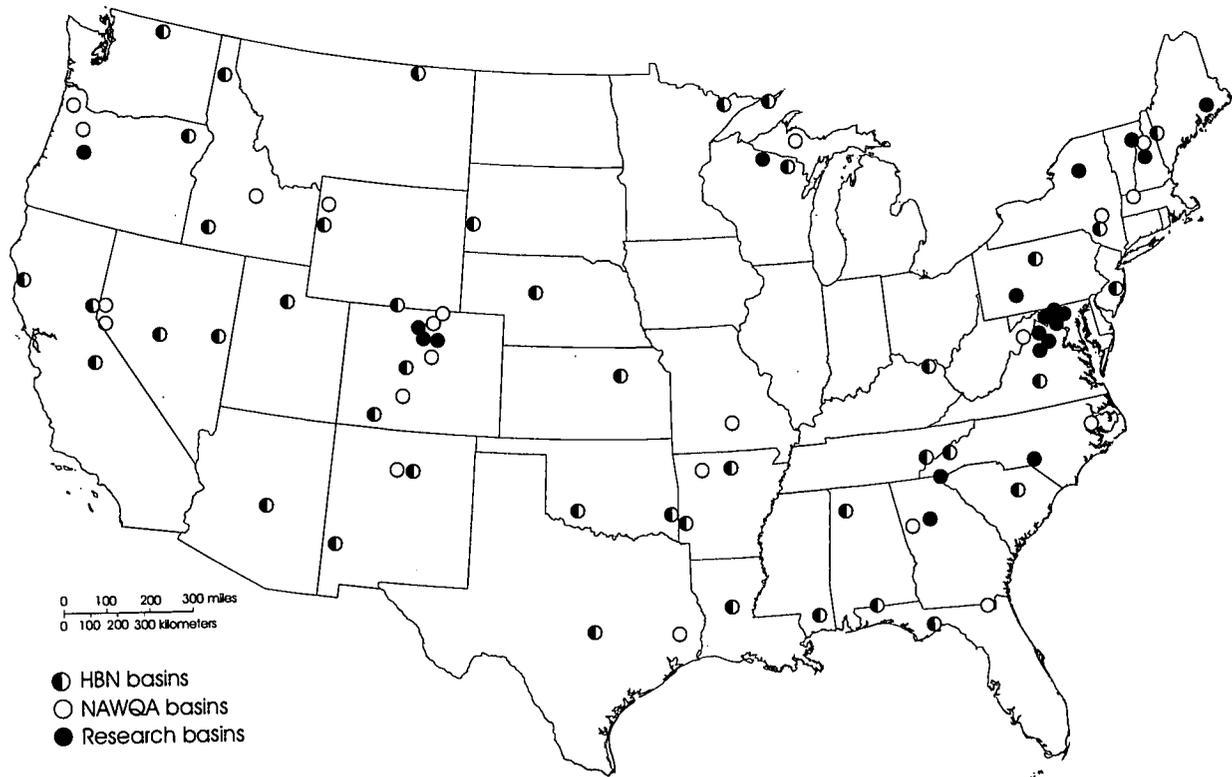


Figure 1. Location of Hydrologic Benchmark Network (HBN), National Water-Quality Assessment (NAWQA) and Research Sites Used for Assessment of Nutrient Concentrations and Yields in Relatively Undeveloped Stream Basins of the United States.

basins used in this assessment range in size from 0.1 to about 22 km<sup>2</sup> and are about 1-2 orders of magnitude smaller than the NAWQA and HBN basins.

Samples from most basins were collected on a weekly to bimonthly schedule. Research basins typically had the highest sampling frequency while HBN basins typically had the lowest. Samples from all of the basins were analyzed for nutrient concentrations at either the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado or USGS research laboratories. Analyses of samples collected at NAWQA and HBN basins included:

- dissolved nitrate plus nitrite as nitrogen (nitrate),
- dissolved ammonia plus ammonium as nitrogen (ammonia),
- dissolved orthophosphate as phosphorus (orthophosphate), and
- total phosphorus.

In addition, concentrations of total nitrogen were computed as the sum of nitrate and total Kjeldahl nitrogen (ammonia plus organic nitrogen). For the research basins, only nitrate data were used in this assessment.

Nutrient concentrations generally vary in relation to streamflow. For example, in some areas of the country, concentrations of nitrate and total phosphorus are greatest during high streamflow and are generally smaller during low streamflow (Murdoch and Stoddard, 1992; Mueller *et al.*, 1995). This variability creates some difficulties for data analysis:

- summary statistics, such as mean concentration, used to characterize a basin might be biased because of variations in sampling frequency during the period of data collection, and
- comparisons among basins might be biased because of different sampling frequencies and total numbers of samples collected at different basins.

These data issues were overcome by estimating a concentration value for each day of a common period of record and computing a flow-weighted concentration based on the daily estimates. There is a long history of statistical models that have been used to make such estimates. The model selected for this analysis is based on the rating-curve method (Cohn *et al.*, 1989, 1992; Crawford, 1991). This method uses multiple regression to estimate constituent transport (load or

mass discharge) in relation to streamflow and time. Separate regression models were calibrated for each constituent in each basin. The dependent variable in each case was the natural logarithm of the daily constituent load, computed as the product of the sample concentration and the mean streamflow on the day of sampling. The explanatory (independent) variables for each model were selected from a set of potential predictor variables:

- natural logarithm of mean streamflow for the day of sample collection,
- logarithm of streamflow, squared,
- time, in decimal years,
- sine of time, and
- cosine of time.

Because nutrient concentrations included censored values [values less than the method detection limit (mdl)], model coefficients were estimated by the maximum-likelihood method (Dempster *et al.*, 1977; Wolynetz, 1979). In the absence of censored values, the maximum-likelihood method is equivalent to ordinary least-squares regression.

For each nutrient species in each basin, models were calibrated using the natural logarithm of streamflow plus all possible combinations of other variables. For NAWQA basins, the calibration period was 1992-1995; for HBN and research basins the calibration period was 1976-1997 or whatever data were available within the time period. The best model for each species-basin combination was selected based on the Akaike Information Criteria (Akaike, 1981; Judge *et al.*, 1985).

Estimates of logarithms of daily constituent load were computed using the selected model and daily mean streamflow for a period of several water years. Estimates were converted to load values (in kilograms). Bias introduced by this conversion was corrected using the Bradu-Mundlak method (Bradu and Mundlak, 1970; Cohn *et al.*, 1989; Crawford, 1991). For NAWQA basins, loads were estimated for water years 1994-1995. For HBN and research basins, loads were estimated for water years 1990-1995, although in some basins data were not collected for the entire period and estimates reflect only a subset of those years. Although some annual variability in nutrient concentrations and yields occurred in these basins, the annual variability was relatively small as compared to the annual variability in nutrient concentrations and yields in more intensively developed basins sampled by the NAWQA during 1992-1995. The small amount of annual variability in relatively undeveloped basins is probably the result of small, but consistent inputs of nutrients. For this reason, it was deemed that although not all of the basins in this

assessment had a complete data record during water years 1990-1995, a comparison of basins with slightly different periods of analysis during 1990-1995 was appropriate.

Annual loads, in kilograms (kg), were estimated as the sum of the daily loads for each year. Annual yields represent the load per unit area of drainage basin and were estimated as the annual load divided by the contributing basin area, in kilograms per square kilometer ( $\text{kg}/\text{km}^2$ ). Flow-weighted concentration, in milligrams per liter (mg/L), was estimated as the total load over the entire estimation period divided by the total stream discharge during the estimation period.

For some of the nutrient species in some basins, concentrations were less than the mdl in almost all of the samples. In these cases, it was not possible to calibrate a regression model; however, this affected only 34 of the 361 combinations of nutrient species and basins. Flow-weighted concentrations for these nutrients in these basins were estimated as less than the mdl; loads and yields for these basins were estimated using a concentration of one-half the mdl.

In addition, the USGS NWQL recently raised the mdl for total phosphorus analysis to 0.05 mg/L and indicated that for data analyzed since 1991, 0.03 mg/L is a more appropriate mdl (USGS NWQL, written comm., 1998). Thus, the total phosphorus numbers in this paper reported as less than 0.03 mg/L should be considered as estimated values and used only on a qualitative basis.

## RESULTS AND DISCUSSION

Flow-weighted concentrations of nutrients in the relatively undeveloped basins varied across the nation, but, in most basins, they were generally low. The median flow-weighted concentrations for all basins were 0.020 mg/L, ammonia as N; 0.087 mg/L, nitrate as N; 0.26 mg/L, total nitrogen; 0.010, orthophosphate as P; and 0.022 mg/L, total phosphorus (Table 1). Median flow-weighted nutrient concentrations in the relatively undeveloped basins ranged from three times less for ammonia to 13 times less for nitrate as compared to concentrations in samples collected from a variety of land use settings across the nation by the NAWQA program during 1992-1995 (USGS, 1999b).

### Nitrate

Flow-weighted concentrations of nitrate in relatively undeveloped basins tended to be highest in the

Nutrient Concentrations and Yields in Undeveloped Stream Basins of the United States

TABLE 1. Statistical Summary of Flow-Weighted Nutrient Concentrations and Mean Annual Nutrient Yields for Relatively Undeveloped Stream Basins in the United States. Values are based on available data for water years 1990-1995. Basin locations are shown in Figure 1. (Note: For Research basins, only data for nitrate concentrations and yields were available.)

Basins	Number of Basins	Minimum	Percentile			Maximum
			25th	50th (median)	75th	
<b>Flow-Weighted Concentration (in milligrams per liter)</b>						
Dissolved Ammonia, as N						
All	65	<0.01	0.016	0.020	0.026	0.10
HBN	43	<0.01	0.015	0.019	0.026	0.058
NAWQA	22	0.010	0.020	0.020	0.030	0.10
Dissolved Nitrate+Nitrite, as N						
All	82	<0.01	0.040	0.087	0.21	0.77
HBN	41	0.020	0.036	0.075	0.14	0.49
NAWQA	21	0.010	0.050	0.080	0.17	0.77
Research	20	<0.01	0.020	0.15	0.40	0.73
Total Nitrogen						
All	63	0.10	0.20	0.26	0.50	2.6
HBN	41	0.10	0.19	0.24	0.52	1.1
NAWQA	22	0.20	0.20	0.32	0.49	2.6
Dissolved Orthophosphate, as P						
All	65	<0.01	<0.01	0.010	0.011	0.13
HBN	43	<0.01	<0.01	<0.01	0.010	0.13
NAWQA	22	<0.01	<0.01	0.010	0.014	0.074
Total Phosphorus						
All	63	<0.01	0.014	0.022	0.037	0.20
HBN	41	<0.01	0.014	0.020	0.030	0.20
NAWQA	22	0.010	0.013	0.037	0.052	0.12
<b>Mean Annual Yield (in kilograms per square kilometer)</b>						
Dissolved Ammonia, as N						
All	65	<1.0	4.4	8.1	12	33
HBN	43	<1.0	4.6	8.1	12	33
NAWQA	22	<1.0	4.1	7.8	13	33
Dissolved Nitrate+Nitrite, as N						
All	82	<1.0	11	26	87	580
HBN	41	1.0	11	23	39	380
NAWQA	21	<1.0	10	27	79	580
Research	20	<1.0	13	110	290	510
Total Nitrogen						
All	63	<1.0	45	86	220	840
HBN	41	2.1	50	94	170	560
NAWQA	22	<1.0	30	62	280	840
Dissolved Orthophosphate, as P						
All	65	<1.0	1.6	2.8	4.8	23
HBN	43	<1.0	1.6	3.1	4.7	10
NAWQA	22	<1.0	1.2	2.7	5.4	23
Total Phosphorus						
All	63	<1.0	4.8	8.5	12	82
HBN	41	<1.0	4.7	7.5	11	28
NAWQA	22	<1.0	5.1	11	25	82

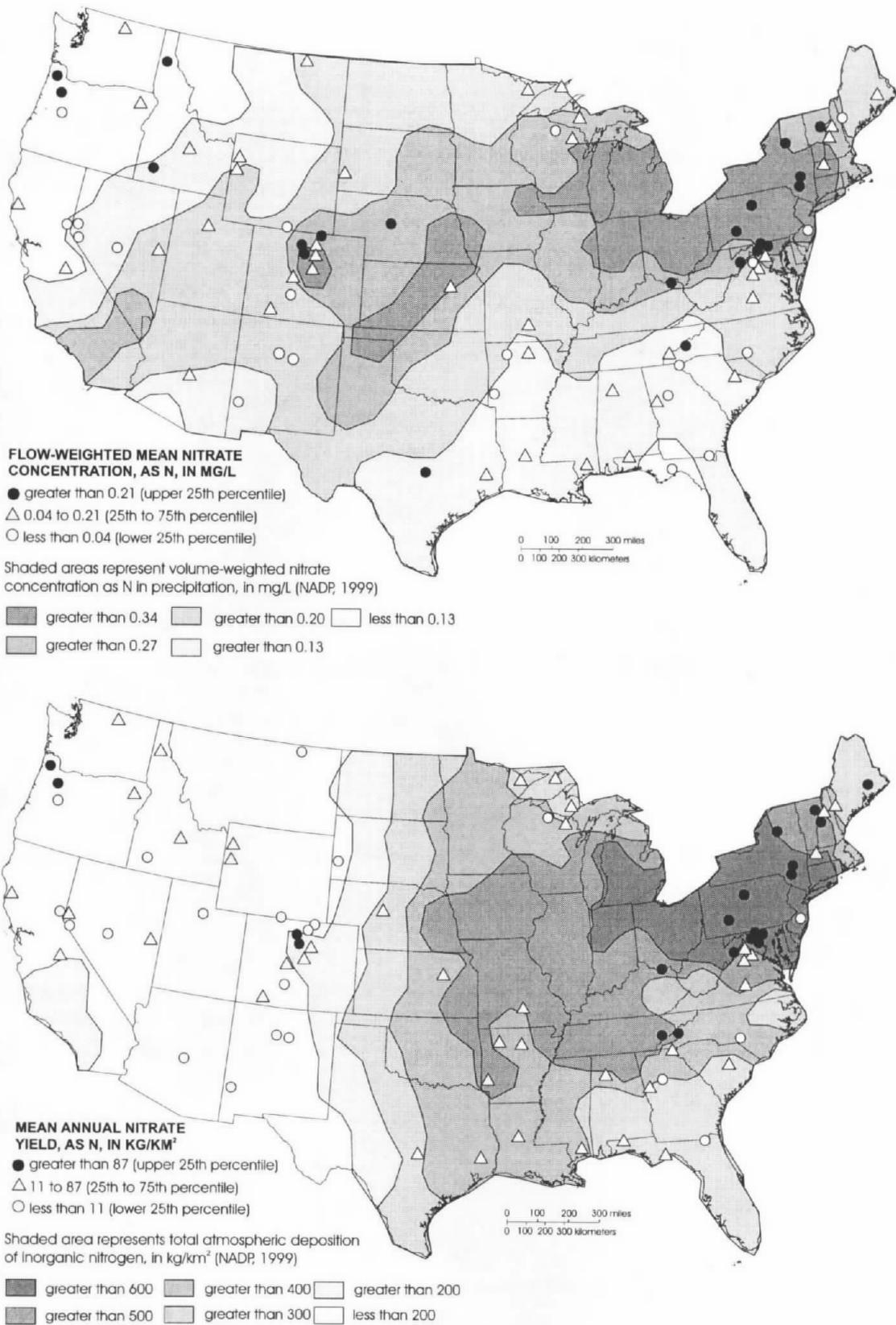


Figure 2. Flow-Weighted Concentrations and Mean Annual Yields of Nitrate in Relatively Undeveloped HBN, NAWQA, and Research Basins and Their Relation to Atmospheric Deposition of Nitrogen. Basin concentration and annual yield values are based on available data for water years 1990-1995. Atmospheric deposition data are from 1994.

northeastern part of the U.S. (Figure 2). Twelve of 21 basins with flow-weighted nitrate concentrations exceeding 0.21 mg/L (the 75th percentile value for all basins; Table 1) were located in the northeastern or mid-Atlantic coastal states. However, only three of the relatively undisturbed basins had a flow-weighted nitrate concentration that exceeded 0.6 mg/L. The highest flow-weighted nitrate concentration of 0.77 mg/L was found in the South Fork of the Potomac River in northeastern West Virginia. The southeastern and southwestern parts of the nation, in general, tended to have the lowest flow-weighted nitrate concentrations (Figure 2). The median flow-weighted concentration of nitrate for all basins, 0.087 mg/L, was exceeded in only one of the 12 basins located in Arizona, California, Nevada, New Mexico, and Utah.

For basins in the northeastern part of the nation, and in Colorado's Rocky Mountains, the above-average concentrations of nitrate were coincident with areas of elevated nitrate concentrations in atmospheric deposition. Precipitation-chemistry data collected in 1994 as part of the interagency National Atmospheric Deposition Program (NADP) indicate that volume-weighted concentrations of nitrate in wet deposition exceeded 0.27 mg/L over the Rocky Mountains in Northern Colorado, a large part of the central plains, and most of the northeastern U.S. (NADP, 1999) (Figure 2). Some areas of Ohio, Pennsylvania, and New York received wet deposition with nitrate concentrations exceeding 0.40 mg/L. The lowest concentrations of nitrate in precipitation were in the western and southeastern parts of the U.S. (NADP, 1999) where the concentration generally ranged from 0.02-0.27 mg/L. Although some annual variability may occur, NADP data indicate that concentrations and total deposition of nitrogen from wet deposition remained relatively consistent over most of the nation from 1983-1994 (Lynch *et al.*, 1996).

The spatial pattern of annual nitrate yields from undeveloped basins across the nation was similar to the pattern of flow-weighted nitrate concentrations (Figure 2). Annual nitrate yields correlated well with wet deposition of total inorganic nitrogen (nitrate plus ammonia as N) from the atmosphere (Figure 2). Annual deposition of inorganic nitrogen over the entire eastern U.S. during 1994 exceeded 300 kg/km<sup>2</sup>, and in most of the northeastern U.S. exceeded 500 kg/km<sup>2</sup> (NADP, 1999). For 11 basins in Maryland, New York, Ohio, Pennsylvania, and West Virginia (the area of largest atmospheric deposition of inorganic nitrogen) the annual basin yield of nitrate averaged about 250 kg/km<sup>2</sup>. In contrast, the average annual basin yield of nitrate from 12 basins in Arizona, California, Nevada, New Mexico, and Utah (the area of smallest inorganic nitrogen deposition) was only 8.3 kg/km<sup>2</sup>. For nearly all basins, annual deposition of

inorganic nitrogen exceeded annual nitrate yield indicating that some nitrogen is retained within basins. However, in two Oregon basins annual nitrate yield averaged almost 400 kg/km<sup>2</sup>, or more than two times the amount of inorganic nitrogen introduced by wet deposition. Because these two predominantly forested basins are essentially free of anthropogenic effects, excess nitrate yield is probably derived from localized atmospheric inputs or higher rates of organic decomposition within the basin relative to vegetative growth.

Because the HBN, NAWQA, and Research Programs contain basins with dramatically different physical characteristics, comparisons were made to examine the differences in nitrate concentrations and yields between programs. A statistical comparison between programs for drainage basin area, mean streamflow, mean annual runoff, nitrate concentrations, and nitrate yields is shown in Figure 3. Although some significant differences ( $p < 0.05$ ) between programs were apparent for drainage basin area, mean streamflow, and mean annual runoff, differences in flow-weighted nitrate concentrations were not statistically significant ( $p > 0.05$ ). However, annual nitrate yield from research basins was significantly larger than yields from HBN ( $p = 0.002$ ) and NAWQA ( $p = 0.049$ ) basins. These differences in nitrate yield are primarily attributable to higher annual runoff from research basins. There was no statistically significant difference in annual nitrate yield between NAWQA and HBN basins (Figure 3).

#### *Total Nitrogen*

Only 4 of 63, or 6 percent, of the relatively undeveloped basins had a flow-weighted total nitrogen concentration exceeding 1 mg/L. By comparison, 83 percent of 97 NAWQA basins sampled during 1990-1995 in areas dominated by agricultural and urban residential land had a flow-weighted concentration of total nitrogen exceeding 1.0 mg/L (USGS, 1999b). Flow-weighted concentrations and mean annual yields of total nitrogen tended to be largest in basins in the eastern half of the U.S., particularly in southeastern basins and four north-central basins in Michigan, Minnesota, and Wisconsin (Figure 4). In basins in the northeastern U.S., nitrate generally comprised about 70-80 percent of the total nitrogen concentration and annual yield, and in the southeastern and four north-central basins, nitrate generally comprised less than 25 percent of the total nitrogen concentration and annual yield. Organic forms of nitrogen accounted for most of the total nitrogen concentration and annual yield in the southeastern and four north-central basins. Southeastern and north-central basins

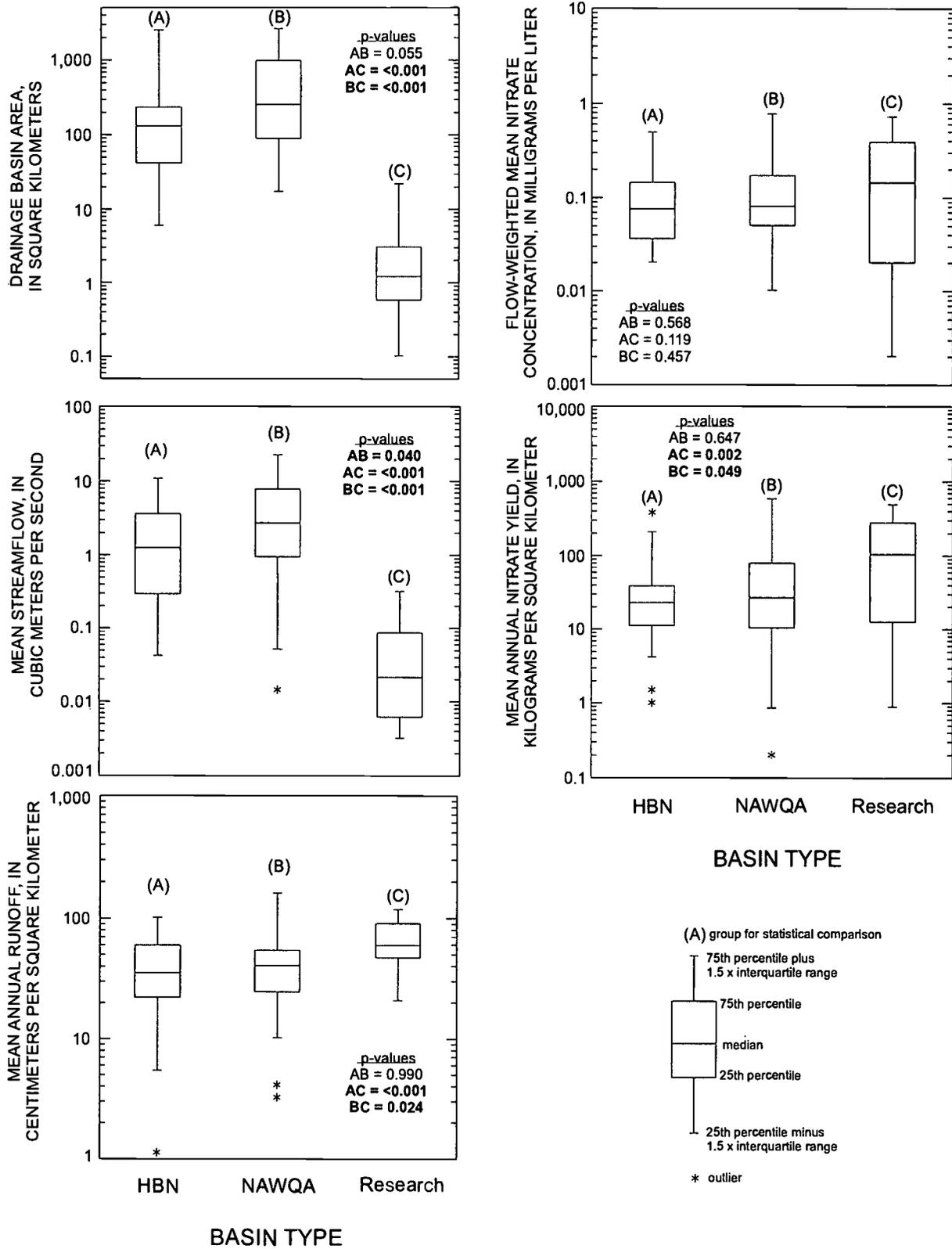


Figure 3. Physical and Hydrologic Characteristics and Flow-Weighted Nitrate Concentrations and Mean Annual Yield in HBN, NAWQA, and Research Basins. Values are based on available data for water years 1990-1995. P-values of less than 0.05 (bolded) indicate a significant difference between basin type using a Wilcoxon signed-rank test at a 95 percent confidence level.

Nutrient Concentrations and Yields in Undeveloped Stream Basins of the United States

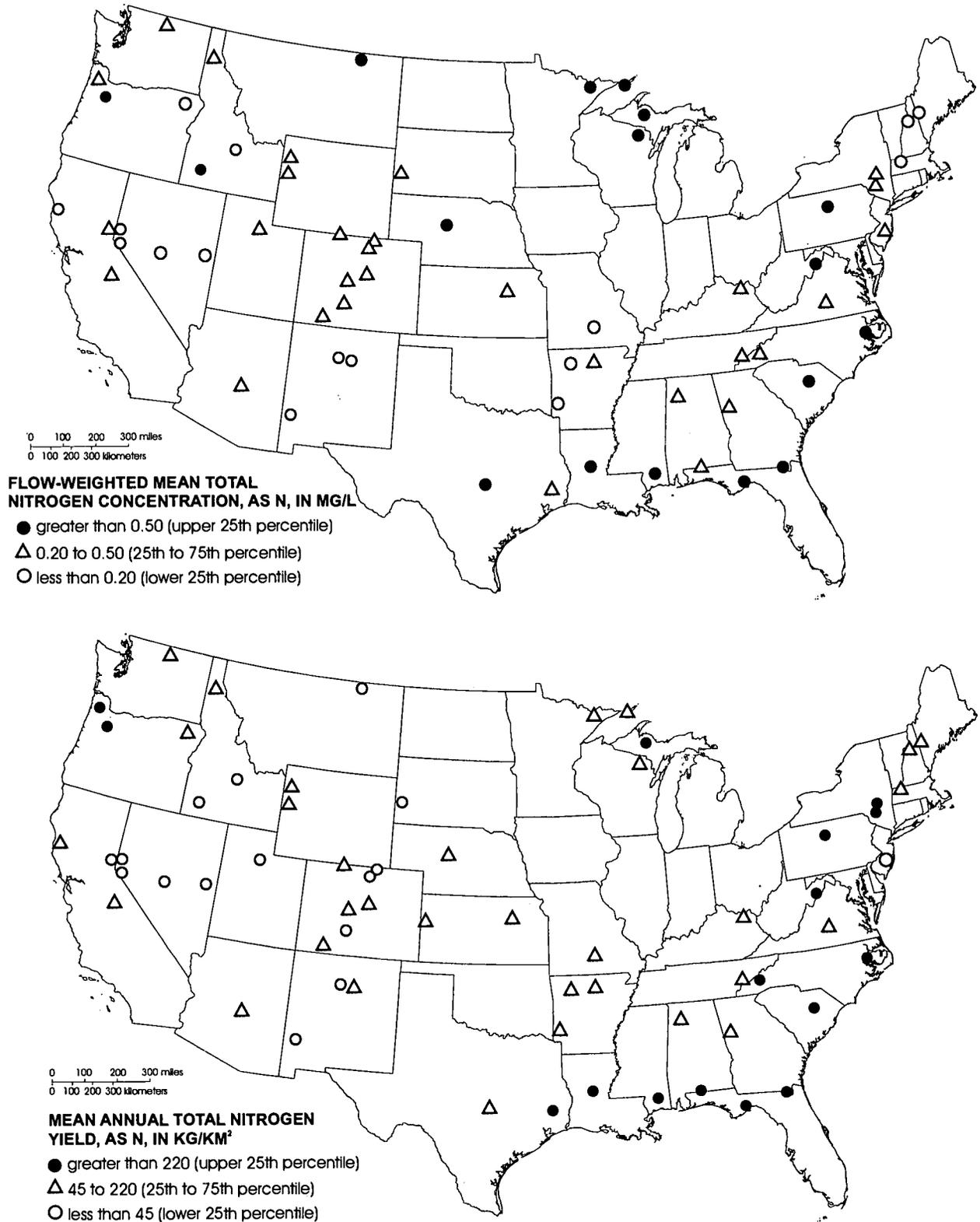


Figure 4. Flow-Weighted Concentrations and Mean Annual Yields of Total Nitrogen in Relatively Undeveloped HBN and NAWQA BASINS of the United States. Values are based on available data for water years 1990-1995.

also had some of the highest ammonia concentrations of all the relatively undeveloped basins in the nation. Higher concentrations of ammonia in north-central basins probably result from high rates of atmospheric ammonia deposition over large parts of the upper midwest (NADP, 1999). Of the basins for which both total nitrogen and ammonia data were available, Van Swamp in eastern North Carolina had the highest flow-weighted concentration and mean annual yield of total nitrogen (2.6 mg/L and 840 kg/km<sup>2</sup>, respectively) and ammonia (0.10 mg/L and 33 kg/km<sup>2</sup>, respectively).

### Total Phosphorus

The median flow-weighted concentration of total phosphorus in the relatively undeveloped basins was 0.022 mg/L, about five times less than the concentration threshold, 0.1 mg/L, generally recommended for prevention of nuisance aquatic growth in streams (USEPA, 1986). Of 63 basins analyzed nationwide for total phosphorus only four, or 6 percent, had a flow-weighted concentration of total phosphorus exceeding 0.1 mg/L. By comparison, 70 percent of 97 NAWQA basins sampled during 1992-1995 in areas dominated by agricultural and urban residential land had a flow-weighted concentration of total phosphorus exceeding 0.1 mg/L (USGS, 1999b). Flow-weighted concentrations of total phosphorus were generally highest in the Rocky Mountain and Central Plain states and parts of the southeast (Figure 5). Flow-weighted concentrations of total phosphorus exceeding 0.10 mg/L occurred in basins of the Dismal River in central Nebraska (0.20 mg/L), Rock Creek in northern Montana (0.20 mg/L), Big Jacks Creek in southwestern Idaho (0.15 mg/L), and Saguache Creek in southern Colorado (0.12 mg/L). In these four basins, orthophosphate, on average, accounted for about 65 percent of the total phosphorus concentration and yield. In contrast, in basins in the southeastern U.S., orthophosphate generally accounted for less than 35 percent of the total phosphorus concentration and yield, with organic and particulate forms accounting for the rest. Larger flow-weighted concentrations of total phosphorus in some of the western basins may result from mineral weathering of phosphorus enriched sediments. For instance, the Dismal River, Rock Creek, and Big Jacks Creek basins are underlain by either marine shale or mafic volcanic rocks (Clark *et al.*, 1999) that are typically enriched in phosphorus. Land use factors such as rangeland grazing of cattle may also contribute to higher phosphorus concentrations in some western basins (Clark *et al.*, 1999). Some of the lowest flow-weighted concentrations of total phosphorus were found in the northeastern part of the

U.S. (Figure 5). Of the seven basins located in Maine, Massachusetts, New Hampshire, New Jersey, New York, and Pennsylvania, six had flow-weighted concentrations of total phosphorus less than 0.01 mg/L, the mdl for total phosphorus analysis. Annual basin yields of total phosphorus ranged from less than 1 kg/km<sup>2</sup> from a number of basins to 82 kg/km<sup>2</sup> from Gales Creek in Western Oregon. Gales Creek also had the highest mean annual yield of orthophosphate (23 kg/km<sup>2</sup>). As with total nitrogen, basins in the southeastern part of the U.S. had above-average concentrations of organic forms of phosphorus and some of the highest mean annual yields of total phosphorus (Figure 5). The large fraction of organic forms of nitrogen and phosphorus in southeastern basins probably results from higher rates of organic decomposition as compared to western basins. The difference in flow-weighted total phosphorus concentrations and mean annual yields between NAWQA and HBN basins was not statistically significant.

## CONCLUSIONS

The U.S. Environmental Protection Agency has recognized natural variability of nutrient levels throughout the nation and is developing nutrient criteria for protection of surface-water bodies based on regional background conditions. This study provides a description of background conditions for nutrients in a number of relatively undeveloped basins of the U.S. These results can be used to determine achievable baseline conditions for nutrients in basins with similar geographic and hydrologic conditions and to evaluate human effects on water quality in more intensively developed basins. To permit a nationally consistent analysis, only data collected by the USGS were used for this study.

Data from 1990-1995 indicate that background concentrations and yields of nitrate are controlled more by anthropogenic inputs from the atmosphere rather than natural factors. Concentrations and yields of nitrate were highest in the northeastern and mid-Atlantic coastal states and correlated well with wet deposition of nitrate and total inorganic nitrogen from the atmosphere. In contrast, background concentrations and yields of total nitrogen and total phosphorus seem to be controlled by natural factors such as the rates of organic decomposition and mineral weathering. Concentrations and yields of total nitrogen were highest in the southeastern part of the nation and in parts of the upper Midwest. Concentrations and yields of total phosphorus were highest in the western and southeastern U.S.

Nutrient Concentrations and Yields in Undeveloped Stream Basins of the United States

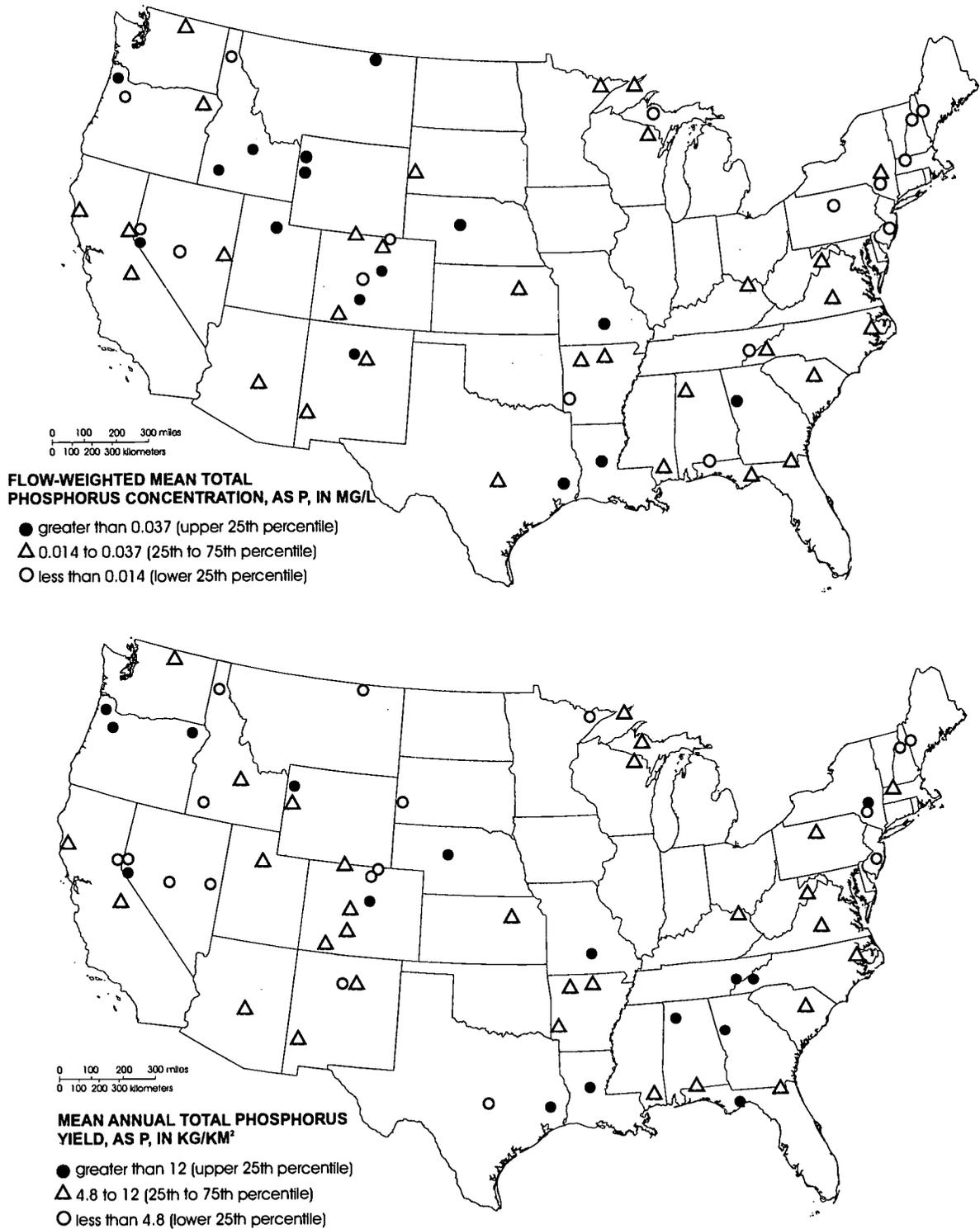


Figure 5. Flow-Weighted Concentrations and Mean Annual Yields of Total Phosphorus in Relatively Undeveloped HBN and NAWQA Basins of the United States. Values are based on available data for water years 1990-1995.

Although some national and regional patterns for nutrients were identified in this study, the number of basins was inadequate to define nutrient conditions in any type of established regional framework such as ecoregions or physiographic provinces. Filling in

monitoring gaps, such as the upper Midwest and south-central U.S. may provide necessary data to define regions of similar baseline water-quality conditions. A regional delineation in natural concentrations of nutrients in surface water would be a valuable tool

for agencies at the local, regional, and national scale to adopt attainable water-quality goals and management strategies.

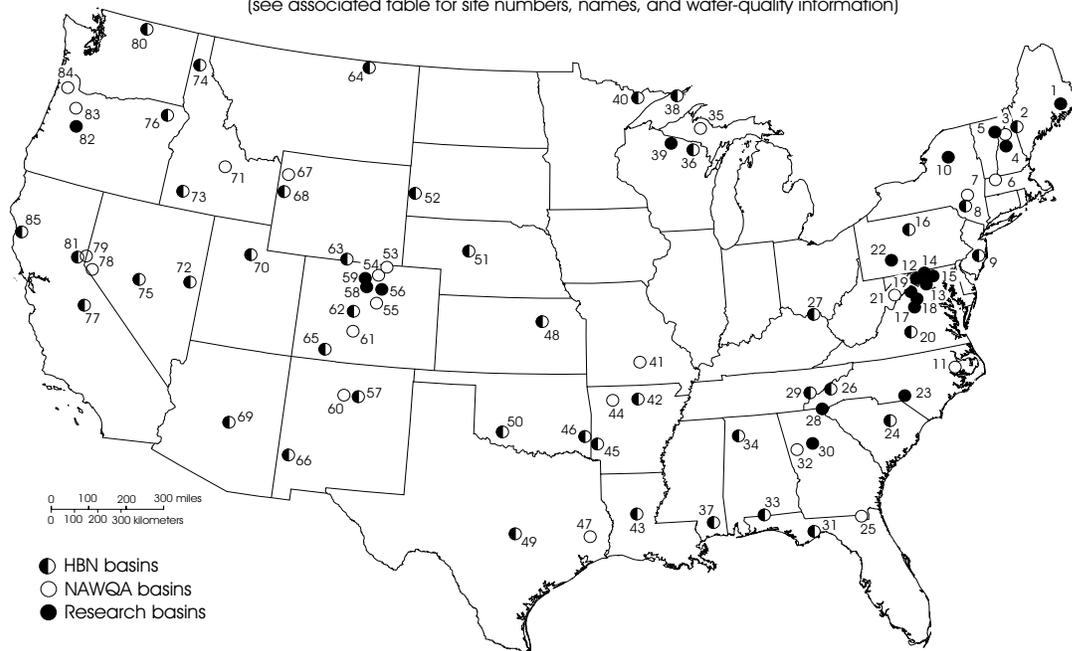
#### ACKNOWLEDGMENTS

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Locations and site numbers of relatively undisturbed watersheds used for analysis of flow-weighted nutrient concentrations and mean annual yields. (see associated table for site numbers, names, and water-quality information)



Data supporting the JAWRA article "Nutrient concentrations and yields in undeveloped stream basins of the United States," by Clark and others, 2000 [in press]. Specific methods of computations are noted in that article. HBN, hydrologic benchmark network; ---, station ID not listed for research stations; Blank fields, insufficient data to compute mean-annual concentration of constituent; <, less than the method reporting limit (MRL) or for total phosphorus, the new (October 1, 1998) long-term method detection limit (LT-MDL). Because mean flow-weighted concentrations are estimates from the mean annual discharge and the mean annual load, some constituents may have calculated concentrations less than the MRL or LT-MDL. A value flagged with "e" indicates a lower level of confidence in the reported concentration.

Map number	Station Name	Station ID	Station type	Mean Annual Runoff (cm)	Mean Annual Flow-Weighted Concentration (milligrams per liter)				
					NH4-N	NO3+NO2-N	Total N	PO4-P	Total P
1	East Bear Brook, ME	---	research	92.7		0.135			
2	Wild River, ME	01054200	HBN	83.5	0.015e	0.029e	0.12e	0.007e	<0.030
3	Ammonoosuc R., NH	01137500	nawqa	61.4	0.020	0.130	<0.20	<0.010	<0.030
4	Hubbard Brook, NH	---	research	102		0.155			
5	Sleepers R., VT	---	research	62.1		0.235			
6	Green R., CT	01170100	nawqa	54.2	0.020	0.130	<0.20	<0.010	<0.030
7	Esopus Creek, NY	01362200	nawqa	67.4	0.020	0.250	0.35	0.010	0.037e
8	Biscuit Brook, NY	01434025	HBN, research	83.9	0.024	0.456	0.46	0.003e	<0.030
9	MacDonalds Branch, NJ	01466500	HBN	21.5	0.023	0.025e	0.19e	0.006e	<0.030
10	Woods Lake,	---	research	91.5		0.554			
11	Van Swamp, NC	02084557	nawqa	32.6	0.100		2.57	0.018	0.032e
12	Bear Branch, MD	---	research	57.7		0.464			
13	Fishing Creek Trib., MD	---	research	48.2		0.179			
14	Hunting Creek, MD	---	research	49.6		0.726			
15	Hauver Branch, MD	---	research	58.4		0.560			
16	Young Womans Creek, PA	01545600	HBN	60.1	0.017e	0.335	0.50	0.005e	<0.030
17	Old Rag Mountain, VA	---	research	28.2		0.100			
18	Mill Run, VA	---	research	44.8		0.050			
19	Shelter Run, VA	---	research	56.1		0.019e			

Data supporting the JAWRA article "Nutrient concentrations and yields in undeveloped stream basins of the United States," by Clark and others, 2000 [in press]. Specific methods of computations are noted in that article. HBN, hydrologic benchmark network; ---, station ID not listed for research stations; Blank fields, insufficient data to compute mean-annual concentration of constituent; <, less than the method reporting limit (MRL) or for total phosphorus, the new (October 1, 1998) long-term method detection limit (LT-MDL). Because mean flow-weighted concentrations are estimates from the mean annual discharge and the mean annual load, some constituents may have calculated concentrations less than the MRL or LT-MDL. A value flagged with "e" indicates a lower level of confidence in the reported concentration.

Map number	Station Name	Station ID	Station type	Mean Annual Runoff (cm)	Mean Annual Flow-Weighted Concentration (milligrams per liter)				
					NH4-N	NO3+NO2-N	Total N	PO4-P	Total P
20	Holiday Creek, VA	02038850	HBN	37.2	0.023	0.036e	0.21	0.008e	0.031e
21	S. Fork Potomac R., WV	01608000	nawqa	33.8	0.020	0.770	1.11	<0.010	0.037e
22	N. Fork Bens Creek, PA	---	research	72.2		0.534			
23	Jordan Creek, NC	---	research	21.1		0.021e			
24	Scape Ore Swamp, SC	02135300	HBN	43.8	0.035	0.068	0.61	0.007e	<0.030
25	Middle St. Marys R., FL	02229000	nawqa	26.4	0.030	0.02e	1.05	0.015	<0.030
26	Cataloochee Creek, NC	03460000	HBN	90.5	0.035	0.231	0.38	0.012	<0.030
27	Upper Twin Creek, OH	03237280	HBN	34.4	0.018e	0.312	0.42	0.007e	<0.030
28	Coweeta, NC	---	research	120		0.013e			
29	Little R, TN	03497300	HBN	103	0.010e	0.173	0.16e	0.008e	<0.030
30	Panola Mountain, GA	---	research	45.7		0.016e			
31	Sopchoppy R., FL	02327100	HBN	75.4	0.044	0.026e	0.74	0.012	<0.030
32	Snake Creek., GA	02337500	nawqa	46.9	0.030	0.170	0.43	0.010	0.093
33	Blackwater R., AL	02369800	HBN	63.3	0.026	0.099	0.37	0.010	<0.030
34	Sipsey Fork, AL	02450250	HBN	63.8	0.014e	0.050	0.19e	0.010	<0.030
35	Peshekee R., MI	04062085	nawqa	66.4	0.030	0.090	0.49	<0.010	<0.030
36	Popple R., WI	04063700	HBN, nawqa	28.7	0.058	0.091	0.70	0.007e	<0.030
37	Cypress Creek, MS	02479155	HBN	69.6	0.037	0.075	0.52	0.004e	<0.030
38	Washington Creek, MI	04001000	HBN	35.9	0.046	0.058	0.58	0.005e	<0.030
39	Trout Lake, WI	---	research	47.2		0.007e			
40	Kawishiwi R., MN	05124480	HBN	22.7	0.039	0.079	0.61	0.008e	<0.030
41	Paddy Creek., MO	06929315	nawqa	31.6	0.020	0.04e	<0.20	<0.010	0.042e
42	N. Sylamore Creek, AR	07060710	HBN, nawqa	29.8	0.019e	0.100	0.23	0.004e	<0.030
43	Big Crk, LA	07373000	HBN	51.5	0.022	0.075	0.87	0.007e	0.054
44	Buffalo R., AR	07056000	nawqa	55.0	0.020	<0.050	<0.20	<0.010	<0.030
45	Cossatot R., AR	07340300	HBN	88.1	0.013e	<0.050	0.11e	0.003e	<0.030
46	Kiamichi R., OK	07335700	HBN	93.1	0.014e			0.005e	
47	Menard Creek, TX	08066295	nawqa	55.1	0.020	0.050	0.44	0.004e	0.062
48	Kings Creek, KS	06879650	HBN	28.5	0.015e	0.085	0.18e	0.007e	0.032e
49	S. Fork Rocky Creek, TX	08103900	HBN	15.0	0.015e	0.223	0.72	0.007e	0.031e
50	Blue Beaver Creek, OK	07311200	HBN	24.3	0.013e			0.020	
51	Dismal R., NE	06775900	HBN, nawqa	7.5	0.016e	0.491	0.72	0.131	0.198
52	Castle Creek, SD	06409000	HBN	5.6	0.020	0.144	0.25	0.006e	0.034e
53	Lonetree Creek, CO	06753400	nawqa	0.1	0.030	0.210	0.47	<0.010	<0.030
54	Cache la Poudre R., CO	06752000	nawqa	10.6	0.020	0.070	0.28	<0.010	<0.030
55	Clear Creek., CO	06719505	nawqa	20.1	0.030	0.160	0.27	<0.010	0.081
56	Green Lakes Valley, CO	---	research	72.6		0.126			
57	Rio Mora, NM	08377900	HBN	31.0	0.026	0.036e	0.17e	0.005e	<0.030
58	Icy Brook, CO	---	research	75.5		0.289			
59	Andrews Creek, CO	---	research	94.2		0.326			

Data supporting the JAWRA article "**Nutrient concentrations and yields in undeveloped stream basins of the United States,**" by Clark and others, 2000 [in press]. Specific methods of computations are noted in that article. HBN, hydrologic benchmark network; ---, station ID not listed for research stations; Blank fields, insufficient data to compute mean-annual concentration of constituent; <, less than the method reporting limit (MRL) or for total phosphorus, the new (October 1, 1998) long-term method detection limit (LT-MDL). Because mean flow-weighted concentrations are estimates from the mean annual discharge and the mean annual load, some constituents may have calculated concentrations less than the MRL or LT-MDL. A value flagged with "e" indicates a lower level of confidence in the reported concentration.

Map number	Station Name	Station ID	Station type	Mean Annual Runoff (cm)	Mean Annual Flow-Weighted Concentration (milligrams per liter)				
					NH4-N	NO3+NO2-N	Total N	PO4-P	Total P
60	Rito de los Frijoles, NM	08313350	nawqa	3.4	0.020	<0.050	<0.20	0.031	0.042
61	Saguache Creek, CO	08227000	nawqa	4.3	0.020	<0.050	0.44	0.074	0.119
62	Halfmoon Creek, CO	07083000	HBN	36.4	0.016e	0.127	0.24	0.008e	<0.030
63	Encampment Creek, WY	06623800	HBN	46.2	0.019e	0.023e	0.18e	0.008e	<0.030
64	Rock Creek, MT	06169500	HBN	1.1	0.037	0.093	1.13	0.110	0.198
65	Vallecito Creek, CO	09352900	HBN	59.5	0.015e	0.119	0.22	0.007e	<0.030
66	Mogollan Creek, NM	09430600	HBN	21.8	0.023	0.022e	0.16e	0.017	<0.030
67	Snake R., WY	13010065	nawqa	53.8	0.020	0.080	0.24	<0.010	0.052
68	Cache Creek, WY	13018300	HBN	31.5	0.024	0.112	0.27	0.013	0.036e
69	Wet Bottom Creek, AZ	09508300	HBN	23.6	0.026	0.04e	0.25	0.005e	0.030e
70	Red Butte Creek, UT	10172200	HBN	13.5	0.013e	0.049e	0.17e	0.031	0.084
71	Big Lost R., ID	13120500	nawqa	25.2	0.020	0.050	<0.20	<0.010	0.042e
72	Steptoe Creek, NV	10244950	HBN	9.9	0.015e	0.147	<0.20	<0.010	<0.030
73	Big Jacks Creek, ID	13169500	HBN	0.4	0.030	0.264	0.58	0.108	0.149
74	Hayden Creek, ID	12416000	HBN	31.2	0.018e	0.235	0.20	<0.010	<0.030
75	South Twin Creek, NV	10249300	HBN	6.0	0.020	<0.050	<0.20	<0.010	<0.030
76	Minam R., OR	13331500	HBN	54.7	0.015e	0.031e	<0.20	0.011	<0.030
77	Merced R., CA	11264500	HBN	60.9	0.025	0.037e	0.21	0.009e	<0.030
78	E. Fork Carson R., NV	10309010	nawqa	41.4	0.01e	<0.050	<0.20	0.023	0.060
79	Truckee R., CA	10346000	nawqa	25.1	0.020	0.01e	<0.20	<0.010	<0.030
80	Andrews Creek, WA	12447390	HBN	39.4	0.014e	0.029e	0.40	0.009e	<0.030
81	Sagehen Creek, CA	10343500	HBN	21.3	0.009e	0.02e	0.17e	0.005e	<0.030
82	HJ Andrews Creek, OR	---	research	101		0.001e			
83	Little Abiqua Creek, OR	14200400	nawqa	108	0.020	0.540	0.54	0.010	<0.030
84	Gales Creek, OR	14203750	nawqa	163	0.020	0.270	0.49	0.014	0.050
85	Elder Creek, CA	11475560	HBN	47.5	0.012e	0.03e	0.10e	0.017	<0.030

# **Technical Assistance for Developing Nutrient Site-Specific Alternative Criteria in Florida**

**DRAFT**

June 2011

**Disclaimer:** This interim draft reflects input from comments received to date and is being made available in interim draft form to allow for additional comment and feedback while sharing EPA's current thinking regarding the SSAC process. The CWA provisions and EPA regulations described in this document contain legally binding requirements. This document does not substitute for those provisions or regulations, nor is it a regulation itself. Therefore, this document does not impose legally binding requirements on EPA, states, tribes, or the regulated community, and it may not apply to a particular situation based upon the circumstances. EPA's decision-makers retain the discretion to adopt approaches on a case-by-case basis that differ from this document, when appropriate. Any decisions regarding a particular submission will be made based on the applicable statutes and regulations. Therefore, interested parties are free to raise questions and objections about the appropriateness of the application of this document to a particular situation, and EPA will consider whether or not the recommendations or interpretations in the document are appropriate in that situation. EPA may change this document in the future.

Interim Draft

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Interim Draft

## I. Purpose

The purpose of this technical assistance document is to help the state of Florida and other stakeholders develop alternatives to EPA's numeric criteria for Florida's waters, called site-specific alternative criteria (SSAC), and to propose them to EPA for consideration. SSAC are values that would take the place of the total nitrogen, total phosphorus, nitrate+nitrite, and/or chlorophyll *a* criteria in 40 CFR 131.43. The final rule that established these criteria, "Water Quality Standards for the State of Florida's Lakes and Flowing Waters", was published in the *Federal Register* on December 6, 2010 (found in Vol. 75, No. 233, p. 75762) and goes into effect on March 6, 2012. The rule has a provision at 40 CFR 131.43(e) for establishing site-specific alternative criteria that would apply in lieu of the criteria established in 40 CFR 131.43(c); entities may submit proposed SSAC, accompanied by supporting documentation, for EPA to consider. The SSAC-related provision of the rule went into effect on February 4, 2011. This document outlines the process that a SSAC submission will go through and provides detailed information on the scientific approaches and analyses that can be used and on the documentation that should be submitted to support the proposed SSAC.

The key principles of this technical assistance document are the following:

- Site-specific alternative criteria must assure attainment of Florida's designated uses<sup>1</sup> with respect to nutrient-related causes of impairment.
- When reviewing proposed SSAC, EPA will adhere to existing applicable regulatory requirements related to water quality standards.
- The SSAC provision in 40 CFR 131.43(e) applies only to adjustments to the criteria values in 40 CFR 131.43(c).
- Such adjustments must be based on technically sound and detailed site-specific or watershed-specific data and analysis.

## II. What SSAC Are and When They Are Appropriate

EPA regulations at 40 CFR 131.11(a)(1) require that water quality criteria must protect applicable designated uses. Such criteria must be based on sound scientific rationale and must contain sufficient parameters or constituents to protect the designated use. As provided at 40 CFR 131.10(b), a state's water quality standards, which include water quality criteria, developed under the Clean Water Act (CWA) must also provide for the attainment and maintenance of water quality standards of downstream waters.

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<sup>1</sup> The designated uses established by Florida that are protected by criteria in 40 CFR 131.43 are:

- Class I – Potable Water Supplies.
- Class III – Recreation, Propagation and Maintenance of a Healthy, Well-Balanced Population of Fish and Wildlife.

SSAC are alternative values to the criteria for total nitrogen (TN), total phosphorus (TP), nitrate+nitrite, and/or chlorophyll *a* that are established in 40 CFR 131.43. SSAC do not modify the designated use(s) of a waterbody; rather, SSAC are alternatives to the existing criteria that protect the designated use(s) of the affected water. SSAC can apply to a single waterbody, waterbody segment, group of waterbodies with similar characteristics, or group of waterbodies in a watershed. These SSAC must meet the regulatory requirements of protecting the instream (or in-body) designated use of the affected waterbody, having a basis in sound science, and ensuring the attainment and maintenance of downstream water quality standards.

SSAC may be more or less stringent than the federal numeric nutrient criteria. In circumstances where an entity submits alternative criteria that are more stringent than those in 40 CFR 131.43, the entity must include an analysis showing that EPA's promulgated criteria are not sufficiently protective of the designated uses for that specific waterbody. When a proposed SSAC does not address all criteria established in 40 CFR 131.43 for a given waterbody, then any unadjusted criteria in 40 CFR 131.43 continue to apply to that waterbody. Consistent with EPA's final rule, a SSAC must be expressed in the form of a concentration along with its intended spatial application. The SSAC proposal may also include a criterion expressed as a corresponding load that is consistent with the proposed concentration, with the associated factors and assumptions used in the calculation or conversion. The entity proposing the SSAC should include documentation showing how the supplemental load information is consistent with the proposed SSAC concentration. Additional detail explaining concentration-based criteria and the supplemental loading information is described in section V.A. While a concentration-based criterion is expected to be applicable for all purposes of the Clean Water Act, EPA recognizes that an associated load could be useful in source control. For NPDES-permitted discharges, because the criteria at 40 CFR 131.43 are expressed as concentrations, resultant permit limits will generally be expressed as concentrations as well, with an option for the permitting authority to include a supplemental mass-based limit. Neither the regulations at 40 CFR 131.43 nor the SSAC process changes the terms of any NPDES permit, and deriving permit limits remains under the jurisdiction of the permitting authority. Similarly, for waters that have TMDL targets or allocations expressed as loads, neither the regulations at 40 CFR 131.43 nor the SSAC process changes the terms of the TMDL. However, it should be noted that the load associated with a point or nonpoint source discharge usually will not be the entire load for a given waterbody. Furthermore, EPA finds it reasonable to presume that basing NPDES permit limits on existing TMDLs will result in effluent limitations as stringent as necessary to meet the federal numeric nutrient criteria. In carrying out its permit review oversight responsibilities, EPA intends to exercise its discretion by presuming that NPDES permits proposed by FDEP that implement wasteload allocations in current TMDLs will result in effluent limitations that reflect the necessary loading reductions to assure attainment of the new criteria. Additional

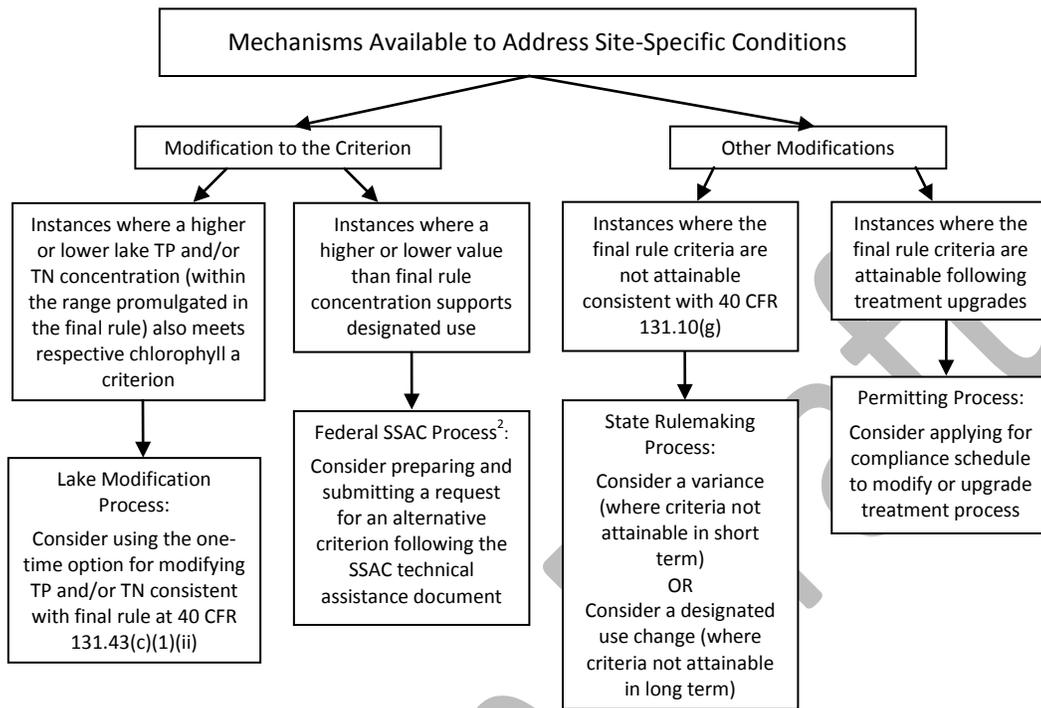
information related to SSAC and their relationship with TMDLs and NPDES permits is in sections V.B and C.

The SSAC process provides a mechanism to address situations when adjustments to criteria are appropriate to address site-specific conditions beyond the modification provision in 40 CFR 131.43(c)(1)(ii). This modification provision allows the state to calculate modified TN and/or TP criteria that fall within the range of values in Table 1 in 40 CFR 131.43(c)(1) for a lake when the chlorophyll *a* criterion is not exceeded. This modification provision is available one time for a given lake; any further adjustment to a lake's TN and/or TP criteria has to be done through the SSAC process. In addition, mechanisms such as variances, compliance schedules and designated use changes (via use attainability analyses (UAAs)) are available that also provide entities flexibility. Where criteria cannot be achieved for reasons of economic feasibility or other factors listed in 40 CFR 131.10(g), the state could adopt a variance or consider changing the designated use. Figure 1 illustrates when a certain mechanism might be appropriate for a given situation.

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<sup>2</sup> The federal SSAC process is separate and independent from Florida's SSAC process. The State has the option to submit a SSAC request to EPA under the federal process described in this document and set forth at 40 CFR 131.43(e). There is no requirement in the federal rule that the State go through its own state-level Type I or Type II SSAC process before submitting a proposed SSAC to EPA for consideration. Florida's rules that describe the process for obtaining a state-level Type I or II SSAC can be found in F.A.C Chapter 62-302.800. The federal SSAC process does not prevent the State from initiating and conducting its own rule making to develop new or revised criteria. Recently the State adopted new provisions for changing the designated use of its waterbodies. In any case where the State changes the designated use of a waterbody from Class I or III to something else, and EPA approves that change, EPA's federal criteria would no longer apply to that waterbody, and the federal SSAC provision would no longer be available for that waterbody. In any case where Florida adopts site-specific criteria for the revised non-Class I or III designated use, such revision would be subject to EPA's review under CWA section 303(c).

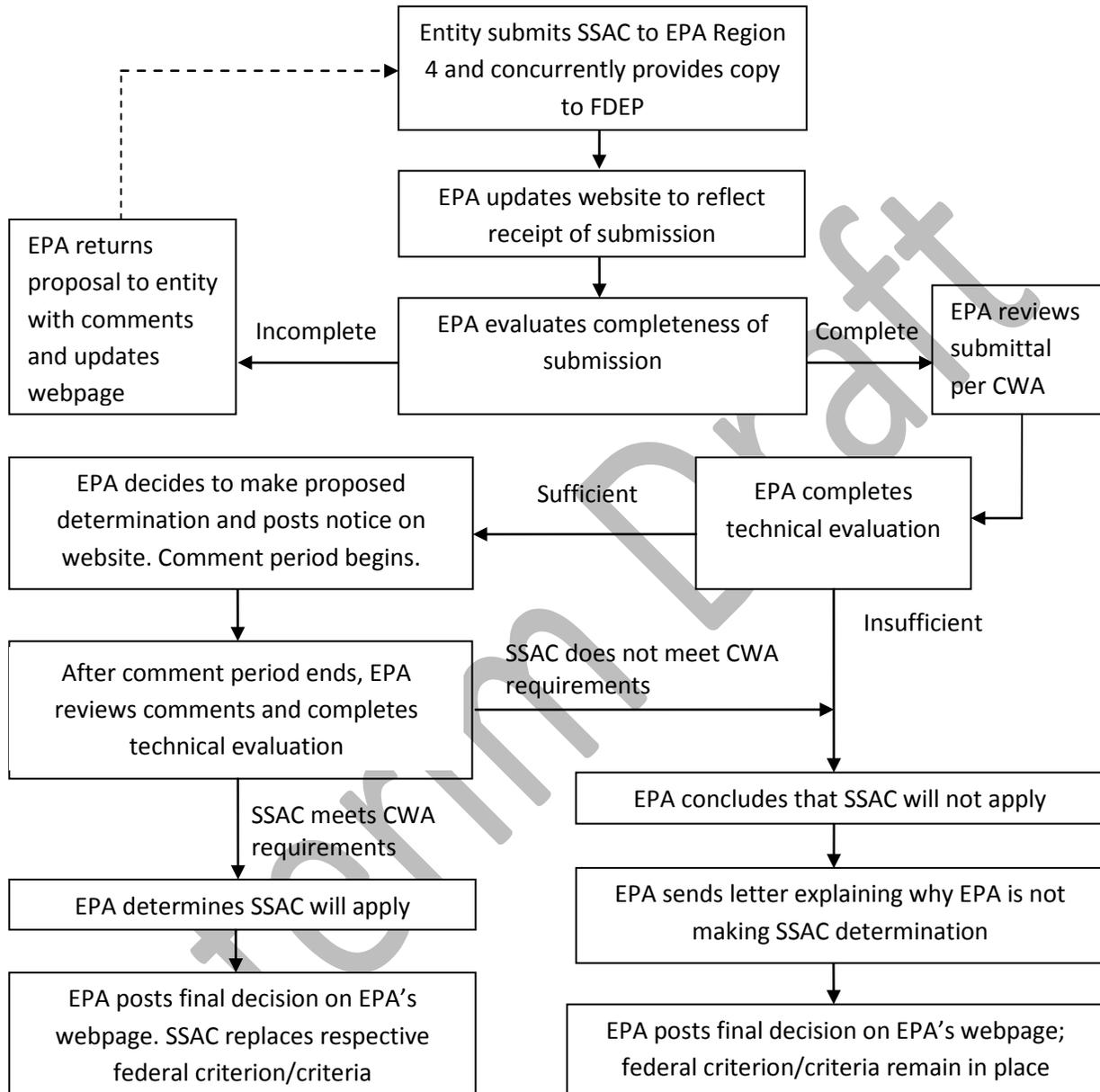
**Figure 1. Mechanisms for addressing site-specific conditions**



### III. Process for a Proposed SSAC

The process for a proposed SSAC is outlined in Figure 2 and described in subsection A. Subsections B and C provide details about who may submit a proposed SSAC and where those submissions should be sent. Section IV contains information on the data requirements, analyses, and documentation necessary to support a SSAC submission.

**Figure 2. Flow diagram of process for a proposed SSAC**



*A. Process Overview*

As stated in 40 CFR 131.43(e), a SSAC may be established by the Regional Administrator of EPA Region 4 after providing notice and opportunity for the public to comment. An entity proposing a SSAC must compile the supporting data, analyses, and any other relevant documentation to demonstrate that each alternative criterion is fully protective of the applicable designated use(s) and submit the package of information to EPA and Florida’s

Department of Environmental Protection. EPA will provide information on SSAC submissions and their review status on EPA's Florida Nutrient Rule webpage.<sup>3</sup>

EPA will evaluate the completeness of the submission and the technical basis of the proposed SSAC and determine whether the SSAC are protective of the designated use, based on sound science, and protective of downstream waters. Possible EPA actions include the following:

1. The Regional Administrator may decide to return the proposal to the entity with an explanation why the proposed SSAC submittal did not provide sufficient information for EPA to conduct a technical evaluation (i.e., submittal was incomplete).
2. The Regional Administrator may decide that the proposal from the entity contains sufficient information to conduct a technical evaluation but is not sufficient to meet Clean Water Act requirements. The Regional Administrator may then decide that the proposal does not support proposing a SSAC determination and soliciting public comment. EPA will send a letter to the entity explaining why EPA is not making a proposed SSAC determination.<sup>4</sup> This conclusion will be made publicly available.
3. If the Regional Administrator decides that the proposal contains sufficient information to propose making a determination, then EPA will prepare a technical evaluation summary<sup>5</sup> of the submitted materials and an explanation for EPA's proposed decision. EPA will post a public notice on its website, providing a link to the technical evaluation and submitted materials and soliciting comments on the proposed SSAC. Written comments can be submitted by email or standard postal delivery. After the comment period ends, the Regional Administrator will determine whether the SSAC meets the statutory and regulatory requirements for new or revised water quality standards, including 131.43(e) and 131.11. EPA's determination will be made publicly available with an explanation of the basis for the decision.

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<sup>3</sup> Details about submitted SSAC applications can found on EPA's webpage for the Florida Nutrient Rule at [http://water.epa.gov/lawsregs/rulesregs/florida\\_index.cfm](http://water.epa.gov/lawsregs/rulesregs/florida_index.cfm) or EPA Region 4's webpage for Water Quality Standards in the Southeast at <http://www.epa.gov/region4/water/wqs/index.html>.

<sup>4</sup> If the Regional Administrator concludes the SSAC does not meet the statutory and regulatory requirements, such action does not preclude or prohibit the entity from initiating another submission process in the future if additional data become available.

<sup>5</sup> In these cases, EPA's technical evaluation summary will include a compilation of relevant materials so that the public can access a short synopsis of the proposed SSAC, its coverage, its justification, and EPA's initial conclusions whether the SSAC appears to meet the statutory and regulatory requirements.

### *B. Who May Submit a SSAC Proposal*

Provisions in 40 CFR 131.43(e) allow any entity to submit proposed alternative numeric criteria and supporting documentation to the Regional Administrator. The entity that petitions for a SSAC may be the State of Florida, a city or county, a municipal or industrial discharger, a citizen group, an environmental organization, or any other individual or organization. The entity submitting a SSAC proposal bears the burden of demonstrating that the proposed SSAC meets the requirements of the CWA and EPA's implementing regulations, specifically 40 CFR 131.10 and 131.11.

### *C. Where Entities Should Submit SSAC Proposals*

Entities should submit SSAC proposals to EPA's Region 4 Regional Administrator. One method for submittal is that entities submit an electronic version of the SSAC proposal and all supporting materials to R4\_FL\_NutrientSSAC@epa.gov. If entities prefer, or also wish, to submit a paper version, then it can be sent to the following address:

Ms. Joanne Benante, Chief  
Water Quality Planning Branch  
US EPA Region 4  
Sam Nunn Atlanta Federal Center  
61 Forsyth Street, SW  
Atlanta, GA 30303-8960

If the entity submitting the proposal is not the State of Florida, the entity is also required to submit the proposed SSAC and supporting materials to the state at the same time those materials are submitted to EPA. This requirement ensures that the state has the opportunity to provide comments to EPA. Materials should be sent to the following address:

Mr. Eric Shaw, Environmental Manager  
Standards and Assessments Section  
Florida Department of Environmental Protection  
2600 Blair Stone Road Mail Stop 6511  
Tallahassee, FL 32399-2400

If the entity submitting the proposal is not a local government, EPA recommends that the entity submit a copy of the SSAC and supporting materials to the appropriate local government.

If the proposed SSAC could indirectly affect tribal waters and/or waters of other states, EPA recommends that the entity notify the relevant environmental management agencies. Materials should be sent to the following addresses, when applicable:

State/Tribe	Address
Alabama	Lynn Sisk Water Quality Branch Water Division Alabama Department of Environmental Management 1400 Coliseum Boulevard Montgomery, AL 36110-2059
Georgia	Elizabeth Booth, Program Manager Water Planning and Monitoring Program Georgia Environmental Protection Division 4220 International Parkway, Suite 101 Atlanta, GA 30354
Miccosukee Tribe of Indians of Florida	Truman E. Duncan, Director Environmental Protection Department Miccosukee Tribe of Indians of Florida P.O. Box 440021, Tamiami Station Miami, Florida 33144  An electronic copy can be emailed to gened@miccosukeetribe.com
Seminole Tribe of Florida	Craig Tepper, Director Environmental Resource Management Department Seminole Tribe of Florida 6300 Stirling Road Hollywood, Florida 33024  An electronic copy can be emailed to Ctepper@Semtribe.com  Mitchell Cypress, Chairman Seminole Tribe of Florida 6300 Stirling Road Hollywood, Florida 33024

#### **IV. Data Requirements, Analyses, and Other Information Necessary to Support a Proposed SSAC**

This section describes the information that entities should submit to support a proposed SSAC. Subsection B describes the fact sheet that should be submitted with the supporting documentation. Subsection C briefly describes the data requirements, which are more fully described in Appendix A, and subsection D explains the downstream protection requirements. Subsections E and F present details on how to develop SSAC for lakes and streams using the

three types of approaches briefly described in the following introduction. Although springs are not explicitly discussed, as are streams and lakes, EPA believes that the information contained in Subsections E and F provides pertinent information that can also be applied to developing SSAC for springs.

#### *A. Introduction*

As described in section V.C(1) in the preamble to EPA's final rule, *Water Quality Standards for the State of Florida's Lakes and Flowing Waters* (75 FR 75970-71) and listed in 40 CFR 131.43(e)(2), there are several approaches for developing SSAC to adjust the total nitrogen (TN), total phosphorus (TP), nitrate+nitrite, and/or chlorophyll *a* values in 40 CFR 131.43. One approach is to replicate the processes that EPA used to develop its lake (40 CFR 131.43(c)(1)) and stream (40 CFR 131.43(c)(2)(i)) criteria, and to apply these methods to a smaller subset of waters. Another approach relies on a biological, chemical, and physical assessment of lake and stream conditions. The regulation also has a general provision at 40 CFR 131.43(e)(2)(iv) for using other scientifically defensible approaches that are protective of the designated use.

An entity proposing SSAC must compile all of the supporting data, conduct the necessary analyses, develop the expression of alternative criteria, demonstrate that alternative numeric criteria values are fully protective of the applicable designated uses (i.e., both in the SSAC waterbodies and downstream waters), and prepare the supporting documentation to justify the change in criteria. The entity must demonstrate that any proposed SSAC meet the requirements of the CWA.<sup>6</sup> In circumstances where an entity submits alternative criteria that are more stringent than those in 40 CFR 131.43, they must include an analysis showing that EPA's promulgated criteria are not sufficiently protective of the designated uses for that specific waterbody.

Consistent with EPA's final rule, a SSAC must be expressed in the form of a concentration, along with its intended spatial application. The SSAC proposal may also include a corresponding load, with all associated factors and assumptions that is consistent with the proposed concentration. The entity proposing the SSAC should include documentation showing how the supplemental load information is consistent with the proposed SSAC concentration. Additional detail explaining concentration criteria and the supplemental loading information is described in section V.A.

As stated above, one approach for developing SSAC relies on the methodologies used by EPA in developing the water quality standards found in 40 CFR 131.43. For lakes, this approach keeps the same applicable value of chlorophyll *a*, based on lake color and alkalinity, and develops corresponding alternative TN and/or TP values. For streams, entities can use EPA's

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<sup>6</sup> EPA's implementing regulations include 40 CFR §§ 131.11 and 131.10(b).

reference-based methodology to define a sub-region within one of EPA's nutrient watershed regions and then (a) identify the subset of EPA reference sites located within the sub-region drawn from the broader regional set relied upon by EPA, or (b) develop a set of reference sites consisting of a combination of a subset of EPA's reference sites and additional sites that pass EPA's screening methodology to establish alternative TN and/or TP values.

A second general approach is to use a combination of biological, chemical, and physical assessment measures to demonstrate that the waterbody is meeting its designated uses or to demonstrate that the waterbody is not meeting its designated use due to factors unrelated to nutrients<sup>7</sup> (e.g., mercury). The entity can then propose concentrations of TN, TP, nitrate+nitrite, and/or chlorophyll *a* that reflect baseline conditions protective of the designated use and are calculated from at least three years<sup>8</sup> of data (consecutive if available) as alternative criteria. For lakes and streams, entities can use methods and data similar to those used by EPA to show how the designated use is being met. For example, all of the screening attributes used by EPA for defining the reference sites for streams can be applied to the data from an individual stream. Entities can also use alternate methods to show healthy conditions.

A third general approach provides for entities to use other scientifically defensible approaches to modify TN, TP, nitrate+nitrite, and/or chlorophyll *a*. For example, entities can use several approaches to develop a new chlorophyll *a* response value for lakes that reflects a site-specific or regionally-specific attainment of applicable designated uses, and then define TN and/or TP values based on the new chlorophyll *a* response value. When using this approach, the entity must show how the new chlorophyll *a* value represents attainment of the designated use. For streams, entities can use a number of methods to define a new relationship between a representative stream condition and attainment of the designated uses, which can then be translated into protective TN and TP criteria.

For some waterbodies in Florida, total maximum daily loads (TMDLs) have been developed as a result of the waterbody being listed as impaired. The SSAC proposal can take advantage of the data and analyses performed in the TMDL to support the SSAC submission. For example, a TMDL that used mechanistic modeling to establish the relationship among TN, TP, and chlorophyll *a* in a lake could augment a lake SSAC under the other scientifically defensible methods approach described above. Additional considerations for TMDLs in the SSAC process are presented in section V.

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<sup>7</sup> For waterbodies not meeting their designated uses due to factors unrelated to nutrients, SSAC for nutrients must allow for attainment of the designated use when the non-nutrient factor is corrected.

<sup>8</sup> Three consecutive years should incorporate the most recently available data. However, if a different time period is utilized due to data availability, an explanation should be provided as to why data older than the most recent three consecutive years is appropriate.

*B. Fact Sheet to Accompany the Proposed SSAC*

Each submission should have a “fact sheet” in addition to the required supporting documentation. An example fact sheet is included as Figure 3, but in general the following information should be included:

- Location (e.g., county name, specific identifying location information, current waterbody identification or WBID<sup>9</sup>, maps).
- For each waterbody or segment, identification of the applicable numeric nutrient criteria and the recommended numeric nutrient criteria proposed as an alternative.
- Identification of approach(es) used.
- Synopsis describing how the proposed SSAC would be fully protective of the applicable designated use(s) and based on a sound scientific rationale.
- Administrative history - Any assessment, 303(d) list, TMDL history, other prior interpretation of the narrative nutrient criteria, and/or previous permitting decisions/actions to document nutrient relevant history at the location. Note that an entity can submit a proposed SSAC for a waterbody that is or has been on the 303(d) impaired waters list, as long as the entity demonstrates that the proposed SSAC are protective of the designated use of the waterbody.
- Identification of any downstream waters that might be affected by the proposed SSAC.

**Figure 3. Example of "fact sheet" to include with a submittal**

<b>Fact Sheet: Proposed SSAC for Wet Creek</b>	
Location Information	Located in Clear Water State Park (Greene County, Florida) SSAC will apply to Wet Creek from its headwaters to River Mile 8.5 (Lat-Long info) Currently WBID 7000 Map enclosed
Numeric Nutrient Criteria Comparison	Wet Creek is located in the Panhandle West NWR. Currently applicable criteria are: TP=0.06 mg/L , TN=0.67mg/L SSAC proposed only for TP. No change proposed for TN of 0.67mg/L.

<sup>9</sup> WBIDs are mentioned here for informational purposes. For purposes of delineating the extent of the location or area for which a SSAC is being requested, identification information such as specific watershed or tributary locations at the upstream and downstream reaches of the area should be used to describe the spatial extent.

	Proposed TP SSAC: TP= 0.1 mg/L
Approach Used to Develop SSAC	Replicating EPA's methodology for streams
Synopsis of Protection of Designated Use	<i>See section IV for additional details on how to document use protection. Only a synopsis of this information is needed for the fact sheet.</i>
History of Assessment	This waterbody is in Group 1 and has been determined to be fully supporting its uses (for all water quality parameters) in the last 3 reporting cycles. Therefore it has never been listed as impaired nor had a TMDL completed.
Identification of Downstream Waters	Wet Creek flows into Wet Lake at River Mile 8.5. There are no streams that flow from Wet Lake.

### C. Data Requirements

Entities submitting SSAC should document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to Appendix A, which discusses the *Technical Support Document for U.S. EPA's Final Rule for Numeric Criteria for Nitrogen/Phosphorus Pollution in Florida's Inland Surface Fresh Waters* (USEPA 2010), data quality elements used by the Florida Department of Environmental Protection, and other details on data sufficiency and quality requirements. The appendix provides information that entities should use to evaluate existing data to determine if it is sufficient to develop SSAC. Appendix A also provides information that entities should use to plan field sampling and analyses in accordance with applicable requirements to ensure that the data collected will be of sufficient quality to develop SSAC. Examples of these considerations include:

- Age and quantity of data.
- Data limits to be evaluated (e.g., pH values > 14).
- Method detection limit considerations.
- Use of approved field methods.
- Analytical laboratory certifications.
- Sampling and analysis plans.
- Data validation considerations (e.g., holding time considerations, analytical data qualifiers, contamination problems).

Florida and EPA resources that are described in the data quality considerations for developing SSAC include the following:

- Florida's Quality Assurance Rule 62-160, F.A.C.
- Florida Department of Environmental Protection's (FDEP's) *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07).
- Section 2.2.2 of the *Technical Support Document for U.S. EPA's Final Rule for Numeric Criteria for Nitrogen/Phosphorus Pollution in Florida's Inland Surface Fresh Waters* (USEPA 2010).
- Florida's Impaired Waters Rule (IWR), 62-303, F.A.C.
- FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02).

EPA's intention is to make this information on how to develop SSAC for lakes and streams easily accessible and to illustrate what information should be documented in a SSAC proposal. The goal is not to require any additional burden for data quality on an entity beyond what EPA utilized in its own criteria development effort. All of the data quality consideration information included in Appendix A may not apply in every case. Lastly, the purpose for including these details is to provide entities with an idea regarding the types of data quality considerations that are already established by the State of Florida in its water quality standards program.

#### *D. Downstream Protection Requirements*

The SSAC proposal must demonstrate that the alternative criteria will ensure the attainment and maintenance of water quality standards of downstream waters, pursuant to 40 CFR 131.10(b). One potential way to do this is to compare the proposed SSAC to the criteria of downstream waters and explain how the downstream criteria will be met, especially if a downstream criterion is a lower concentration than the proposed SSAC.

Streams that flow into lakes are subject to both an instream protection value (IPV) to protect the designated uses of the stream and a downstream protection value (DPV) to protect the designated uses of the downstream lake. An entity proposing a SSAC to replace only the IPV for a stream that flows into a lake should provide a statement that the DPV remains applicable to the stream; that statement is sufficient to document how the SSAC is meeting the downstream protection requirement. In that circumstance, the effective criterion for the stream will be whichever is more stringent of the SSAC and the downstream protection value.

For SSAC that propose to adjust DPVs of streams that flow into lakes, EPA provides a flexible approach for calculating DPVs. If neither EPA nor the state has derived DPVs for the stream pursuant to 40 CFR 131.43(cc)(2)(ii)(B) when the SSAC is proposed, then the applicable DPV depends on the attainment status of the downstream lake. If the lake is attaining the chlorophyll *a*, TN and TP criteria, then the DPVs are the ambient instream levels of TN and TP at

the point of entry to the lake. If the lake is not attaining the criteria or has not been assessed, then the DPVs are the TN and TP criteria for the downstream lake. Alternatively, DPVs can be calculated using one of the following methods:

- Use U.S. Army Corps of Engineers' BATHTUB model when there is sufficient data and information available. It is appropriate for simplified downstream protection value calculations.
- Use other scientifically defensible models (e.g., WASP) that might provide additional capabilities, such as simulating water quality responses to natural and manmade pollutant inputs.

An entity proposing SSAC that adjusts a DPV should provide the data and/or analyses performed to calculate the DPV.

Streams that do not flow into a lake will presumably flow into another waterbody, such as another stream segment or stream reach, a river, a spring, and eventually to an estuary or coastal water. In the case of a stream flowing into a downstream segment, reach, river or spring, the entity must demonstrate that the proposed SSAC allows for the attainment and maintenance of the water quality standard in that downstream segment or reach, especially if there is evidence suggesting that the downstream water is more sensitive than the stream for which the SSAC is being proposed. Likewise, the entity must demonstrate that the SSAC allows for the attainment and maintenance of water quality standards in any receiving estuary or coastal waters. Until the numeric nutrient criteria for estuaries and coastal waters are established, the SSAC must provide for the attainment and maintenance of the narrative criteria applicable to those waters. After the numeric nutrient criteria for estuaries and marine coastal waters are established, those numeric criteria will be an interpretation of the narrative criteria.

The submittal of proposed SSAC for a lake must include a review and analysis of applicable downstream TN and TP criteria to confirm that a proposed SSAC for a lake will meet the instream protection value (found in 40 CFR 131.43(c)(2)(i)) of any stream leaving the lake.

#### *E. Developing Site-Specific Alternative Criteria for Lakes*

This subsection describes three general approaches for developing SSACs for lakes<sup>10</sup>:

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<sup>10</sup> EPA allows a one-time adjustment to lake criteria in accordance with 40 CFR 131.43(c)(1)(ii) without the need for a SSAC. Any subsequent adjustments are only available as SSAC.

1. Applying EPA's methodology while maintaining the applicable chlorophyll *a* values specified in 40 CFR 131.43 and deriving alternative TN and/or TP values based on local conditions.
2. Using site-specific biological, chemical, and physical data to demonstrate that the waterbody is meeting its designated uses or to demonstrate that the waterbody is not meeting its designated uses due to factors unrelated to nutrients and then using baseline conditions of TN, TP, and/or chlorophyll *a* levels as alternative criteria.
3. Using other scientifically defensible methods to derive chlorophyll *a*, TN, and/or TP values that can be shown to be protective of the designated use(s).

For all proposed alternative lake values, the SSAC submission must include a review and analysis of applicable downstream TN and TP criteria to confirm that the alternative lake values will meet the instream protection value (IPV) of any stream leaving the lake. Demonstration of downstream protection should be consistent with the approaches that EPA provided in 40 CFR 131.43(c)(2)(ii), unless another scientifically defensible method is appropriate.

#### 1. Replicating EPA's Methodology for Lakes

This approach involves replicating EPA's method of deriving lake criteria to adjust the federally promulgated TN and/or TP criteria to values *outside* of the range defined in the modification provision at 40 CFR 131.43(c)(1)(ii) while maintaining the promulgated chlorophyll *a* criterion. Under this process, a lake with a proposed SSAC would remain in the same class based on color and alkalinity as defined in 40 CFR 131.43, and keep the associated chlorophyll *a* value.

First, identify the appropriate lake classification and corresponding chlorophyll *a* criterion for the lake:

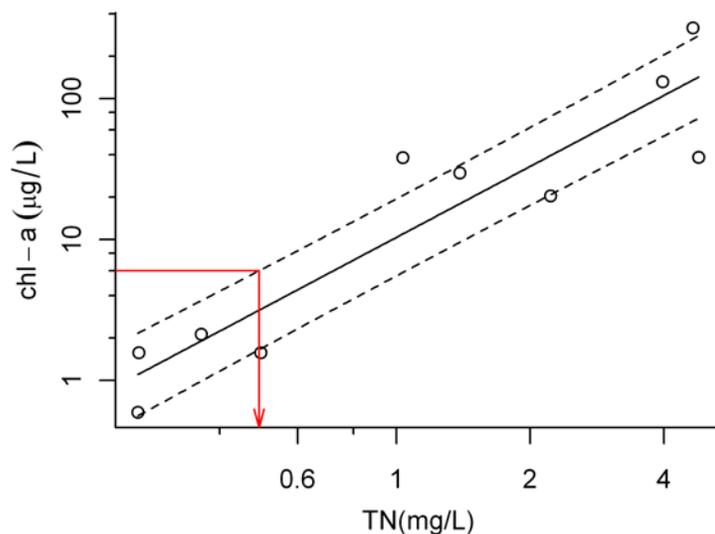
- Colored lakes (color > 40 platinum cobalt units (PCU)) – 20 µg/L chlorophyll *a*
- Clear lakes (color ≤ 40 PCU) with high alkalinity (alkalinity > 20 mg/L as CaCO<sub>3</sub>) – 20 µg/L chlorophyll *a*
- Clear lakes (color ≤ 40 PCU) with low alkalinity (alkalinity ≤ 20 mg/L as CaCO<sub>3</sub>) – 6 µg/L chlorophyll *a*

Next, establish a new stressor-response (empirical) relationship between chlorophyll *a* and TN and/or TP by using linear regression to relate TN/TP with chlorophyll *a* (see Figure 4 for an example). Identify the TN/TP concentration associated with the chlorophyll *a* criterion identified in the first step (i.e., where the chlorophyll *a* value intersects with the 75<sup>th</sup> percentile of predicted distribution of chlorophyll *a* values). This nutrient concentration becomes the

proposed SSAC. The red line in Figure 4 shows the derivation of TN corresponding to 6  $\mu\text{g/L}$  of chlorophyll  $a$ .

**Figure 4. Example of site-specific nutrient stressor-response relationship.**

Solid line: mean relationship, dashed lines: 25th and 75th percentiles of the predicted distribution of chlorophyll  $a$  values.



The new empirical relationship should be based on at least ten pairs of data<sup>11</sup>. Each data pair represents the annual average TN or TP and chlorophyll  $a$  for a particular lake or sampling location. Data used to compute annual averages should be collected over the course of the year to capture seasonal differences. When collecting data for multiple parameters, EPA prefers that the data for all of the parameters be collected concurrently, but at a minimum within a four-day period. The strength of the scientific defensibility of the SSAC increases with the number of data pairs and when the data points for each of the data pairs are collected close together in time. Moreover, the data should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis (refer to EPA's *Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs* (EPA-822-B-00-001) for examples of sampling recommendations).

The precision of the estimated relationships between nutrient concentrations and chlorophyll  $a$  should be evaluated by considering the range of candidate criterion values associated with different percentiles of the predicted distribution<sup>12</sup>. Relationships in which the

<sup>11</sup> Accurately estimating an empirical relationship between a stressor and a response requires at least 10 samples (Harrell FE, 2001. *Regression Modeling Strategies*. Springer-Verlag, Inc., New York, NY). Calculating 10 annual averages of TN or TP and chlorophyll  $a$  may be achievable by using long-term monitoring data or by combining data from nearby, similar lakes.

<sup>12</sup> See US EPA, 2010. *Using Stressor-response Relationships to Derive Numeric Nutrient Criteria*. EPA-820-S-10-001. Office of Water, U.S. Environmental Protection Agency, pp.38-39.

criterion associated with the 25<sup>th</sup> percentile of the predicted relationship differs substantially from the criteria associated with higher percentiles may be too imprecise to usefully inform criterion decisions.

Document all methods and assumptions associated with data collection, analysis, and SSAC derivation. Refer to section A.1 of Appendix A, which discusses the *Technical Support Document for U.S. EPA's Final Rule for Numeric Criteria for Nitrogen/Phosphorus Pollution in Florida's Inland Surface Fresh Waters* (USEPA 2010), Florida's Impaired Waters Rule (62-303 F.A.C.), Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07), and other details on data sufficiency and quality requirements.

## 2. Using Site-Specific Biological, Chemical, and Physical Data

Using this approach, first assemble a data set that includes biological, chemical, and physical data to show how the lake is presently attaining its designated use(s). Data should include at least three years of the most recent data (consecutive years where available). Calculate an annual average for each biological, chemical, and physical parameter, when applicable; these should include TN, TP, and chlorophyll *a* for a particular lake or sampling location. The data for computing the annual averages should be collected over the course of the year to capture seasonal differences, and should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis. Refer to EPA's *Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs* (EPA-822-B-00-001) for examples of sampling recommendations. Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section A.2 of Appendix A, which discusses Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07), and other details on data sufficiency and quality requirements.

Supporting physical, chemical and biological data may include the following:

- Historical quantitative water quality data (e.g., TN, TP, chlorophyll *a*, dissolved oxygen, clarity/turbidity, temperature, average depth).
- Qualitative information (e.g., long term observations of water for the presence of algal mats or fish kills, surrounding land uses).
- Presence of balanced native flora and fauna.
- Consideration of the range of diel fluctuations in dissolved oxygen (DO).
- Consideration of current and historical conditions to ensure full support of designated uses and consistency when comparing temporal data.

Here is an example of a data set that includes physical, chemical and biological parameters to support a demonstration of how a lake presently meets designated uses:

- Chemical water quality data including at least three consecutive years of DO, chlorophyll *a*, TN, and TP data.
- 2 Lake Vegetation Index (LVI) calculations (LVIs must both be > 46; assuming 2 samples from at least 3 consecutive years).
- Habitat assessment (including presence/absence of native flora and fauna).

Finally, propose the alternative numeric criteria (e.g., TN, TP, and/or chlorophyll *a*) based on concentrations that reflect baseline conditions calculated from at least three years of the most recent data (consecutive years where available) with a justification for the adjustment and explain how the changes will ensure maintaining the designated uses.

### 3. Using Other Scientifically Defensible Methods

EPA recognizes that there may be other scientifically defensible methods that can be used to develop an alternative chlorophyll *a* endpoint that is protective of designated uses and then relate TN and TP concentrations in one or more lakes to the alternative endpoint. The following are general examples using stressor-response, mechanistic modeling, and reference-based approaches.

#### *a. Stressor-Response Approach*

First, determine an alternative chlorophyll *a* response endpoint (i.e., different from those in 40 CFR 131.43), and clearly demonstrate how this response endpoint supports the protection of the designated use(s) of the lake using site-specific data. Then, determine the stressor-response (empirical) relationship<sup>13</sup> between the new chlorophyll *a* response endpoint and TN and TP. Data may include the following:

- Long-term data set (at least three years of the most recent data (consecutive years where available)) that includes the alternate chlorophyll *a* endpoint, TN, TP, and any other relevant data.
- Alternative scientifically defensible trophic status metric.

For relating the new chlorophyll *a* endpoint to TN and/or TP for a lake, the new empirical relationship should be based on at least three years of the most recent data (consecutive years where available). For statistical robustness, however, at least ten pairs of

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<sup>13</sup> U.S. EPA 2010. Using Stressor-Response Relationships to Derive Numeric Nutrient Criteria. EPA-820-S-10-001. U.S. Environmental Protection Agency, Office of Water, Washington DC.

data<sup>14</sup>, in which each data pair represents the annual average TN or TP and chlorophyll *a* for a particular lake or sampling location, are preferable if such data are available. Data used to compute annual averages should be collected over the course of the year to capture seasonal differences. Data should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis; refer to EPA's *Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs* for examples of sampling recommendations. Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section A.3 of Appendix A, which discusses Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07), FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02) and other details on data sufficiency and quality requirements.

Next, use statistical techniques, such as linear or multivariate regression, to relate TN and TP with chlorophyll *a*. Evaluate whether the accuracy and precision of the estimated stressor-response relationship<sup>15</sup> are sufficient to inform nutrient criteria derivation. Finally, pick the point at which the prediction interval value of chlorophyll *a* is equivalent to the new chlorophyll *a* criterion as the new TN and/or TP criterion, and justify the use of the point selected in the distribution (e.g., the 75<sup>th</sup> percentile). Then, translate this chlorophyll *a* value to the new TN and TP criterion. Justify and use valid stressor-response analysis to derive TN and TP based on the alternate chlorophyll *a* value.

#### *b. Mechanistic Modeling*

Well-calibrated environmental water quality or ecosystem models can be used to identify potential thresholds of biological and ecosystem responses and the associated level of nutrient inputs, and may be applicable to developing SSAC. In contrast to regression approaches that rely on empirical statistical analysis, mechanistic (or process-based) models more explicitly simulate the ecological processes that are operating in a given waterbody, and this may provide a greater ability to discern the reasons behind the observed biological responses. Mechanistic models can also examine proposed numeric nutrient criteria under a range of conditions to predict a system's response as an additional confirmatory step for a stressor-response relationship.

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<sup>14</sup> Accurately estimating an empirical relationship between a stressor and a response requires at least 10 samples (Harrell FE, 2001. *Regression Modeling Strategies*. Springer-Verlag, Inc., New York, NY). Calculating ten annual averages of TN or TP and chlorophyll *a* may be achievable by using long-term monitoring data available in some lakes or by combining data from nearby, similar lakes.

<sup>15</sup> U.S. EPA 2010. *Using Stressor-Response Relationships to Derive Numeric Nutrient Criteria*. EPA-820-S-10-001. U.S. Environmental Protection Agency, Office of Water, Washington DC.

Any model proposed for SSAC development should simulate nutrient processes and algal responses (e.g., phytoplankton in lakes). If possible, the model should account for the effects of confounding variables (e.g., suspended sediment, shading, flow, grazers).

Identify a sound scientific model<sup>16</sup> and justify why this model was chosen. Describe which biological, chemical, and/or physical characteristics were simulated, which endpoints were chosen, and how those endpoints are related to designated use protection. The description should also include:

- Ecological processes captured by the model.
- Time variable versus steady state.
- Primary simplifying assumptions.
- Metrics/endpoints that are able to be calculated from model output.

Entities should be prepared to provide the model software, its supporting documentation, and/or model runs for review, if EPA requests.

Document the important or sensitive model parameters and their sources. Document the sources of the driving data and the quality assurance procedures for the data collection. Data should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis; refer to EPA's *Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs* for examples of sampling recommendations. Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section A.3 of Appendix A, which discusses Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07), FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02) and other details on data sufficiency and quality requirements.

Provide a description of the modeled site. If the model does not simulate the entire waterbody, then describe how it can be considered a representative site, or that it was applied in enough sites to capture spatial heterogeneity. Use site-specific data for driving variables, if available. If the values are not direct measurements, indicate how the values were derived (e.g., flow data extrapolated from an upstream gage, time series, total suspended solids [TSS] data derived from a regression against flow).

Document the model calibration procedures along with a description of model performance (i.e., how well calibrated the model output was to the calibration endpoints). Also describe which verification and/or validation procedures were undertaken, and their results.

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<sup>16</sup> For example, use the TMDL compendium on models: U.S. EPA 1997. Compendium of Tools for Watershed Assessment and TMDL Development. EPA 841-B-97-006.

The model simulation should be run for existing conditions as well as the proposed nutrient regime to demonstrate that designated uses would be protected by the proposed SSAC. If it is a dynamic (time-variable) model, the simulation time period should include important variability (e.g., high-flow and low-flow years).

### *c. Reference Condition Approach*

Identify a group of lakes (or observations within a lake) with similar, naturally expected conditions to each other taking into consideration regional variability<sup>17</sup>. Screen sites/observations to identify the subset of reference lakes that is minimally impacted/least disturbed. Describe the data quality screening methodology used and show how it results in a set of reference conditions that are minimally impacted/least disturbed.

Demonstrate that adequate data are available to pursue this methodology. The data should include at least three years of the most recent data (consecutive years where available) for each of the biological, chemical, and physical parameters used in developing the reference condition, and include TN, TP, and chlorophyll *a* for a particular lake or sampling location. Data should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis (refer to EPA's *Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs* for examples of sampling recommendations).

Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section A.3 of Appendix A, which discusses Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07), FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02), and other details on data sufficiency and quality requirements.

Determine how many reference sites and observations are needed to represent natural variability of the lakes in the analysis, and then justify the number of reference sites selected (refer to EPA's *Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs*). Develop a distribution for chlorophyll *a*, TN and TP from the reference sites. Select and justify the appropriate percentile for deriving the alternative numeric nutrient criteria for TN, TP and/or chlorophyll *a* based on available data and document how the set of reference sites meets the designated uses.

### *F. Developing Site-Specific Alternative Criteria for Streams*

This subsection describes three general approaches for developing SSAC for streams:

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<sup>17</sup> U.S. EPA 2000. Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs. EPA-822-B-00-001. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

1. Applying EPA's methodology by using a set of reference conditions (i.e., a subset of reference sites from EPA's sites or a combination of EPA sites and additional sites).
2. Using site-specific biological, chemical, and physical data to show that a specific stream or watershed is meeting the designated stream uses.
3. Using other scientifically defensible methods to derive TN and TP values that can be shown to be protective of the designated uses.

In all cases, explain and demonstrate how the proposed alternative stream TN and TP values continue to provide for the attainment and maintenance of the water quality standards of downstream waters. For SSAC stream segments with downstream lakes, a statement that a SSAC seeks to adjust only the IPV for a stream while the DPV remains applicable is sufficient for this purpose. Where the SSAC seeks to adjust both the stream IPV and DPV, use the methodology described in 40 CFR 131.43(c)(2)(ii) and in section IV.D. For SSAC stream segments with downstream streams/rivers/canals, if the proposed alternative TN and/or TP criteria are less than or equal to the instream protective value (IPV) for the downstream stream segment, then the site-specific stream criteria meet the test for downstream protection. Otherwise, if the proposed SSAC stream criteria are greater than the IPV for the downstream stream segment, then the SSAC submission must include the analysis and data to demonstrate how the proposed alternative site-specific stream criteria will assure that the downstream IPV is met.

#### 1. Replicating EPA's Methodology for Streams

For streams, entities can use the EPA's reference-based methodology to define a sub-region within one of EPA's nutrient watershed regions and then (a) develop a subset of reference sites from the set of regional reference sites used by EPA or (b) develop a set of reference sites consisting of a combination of a subset of EPA's regional reference sites and additional sites that pass the EPA reference site screening methodology to establish alternative TN and/or TP values. The entity should use all reference sites in the sub-region.

First, identify the sub-region for which a refined TN and/or TP value is desired. If using the EPA set of reference sites, identify the subset of reference sites within the sub-region. If additional reference sites are being included, screen sites/observations, based on screening criteria identified in EPA's final rule, to identify the reference site set that is minimally impacted/least disturbed. Document that the reference sites are minimally impacted/least disturbed.

Demonstrate that adequate data are available to pursue this methodology. The data should include at least three years of the most recent data (consecutive years where available).

Each sample set of TN, TP, Stream Condition Index (SCI) and chlorophyll  $a^{18}$  should be independent and representative of the conditions for which the annual average for each of the biological, chemical, and physical parameters could be calculated. Data should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis. Refer to EPA's *Nutrient Criteria Technical Guidance Manual: Rivers and Streams* (EPA-822-B-00-002) for examples of sampling recommendations. Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section B.1 of Appendix A, which discusses the *Technical Support Document for U.S. EPA's Final Rule for Numeric Criteria for Nitrogen/Phosphorus Pollution in Florida's Inland Surface Fresh Waters* (USEPA 2010), Florida's Quality Assurance Rule (62-160 F.A.C), and other details on data sufficiency and quality requirements.

Determine the number of reference sites and observations that are adequate to represent natural variability. Develop a distribution of TN and/or TP using the reference sites, and select a percentile of the resulting distribution of reference sites for TN and/or TP. To replicate EPA's methodology for streams, use the 75<sup>th</sup> percentile for the SCI sites in the West Central region and use the 90<sup>th</sup> percentile for reference sites elsewhere in the state when deriving the alternative criteria.

## 2. Using Site-Specific Biological, Chemical, and Physical Data

Using this approach, first assemble a data set that includes biological, chemical, and physical data to show how the stream segment is presently meeting its designated use(s). Data should include at least three years of the most recent data (consecutive years where available). Calculate an annual average for each year for each of the biological, chemical, and physical parameters, if applicable; these should include TN and TP for a particular stream or sampling location. Data for computing annual averages should be collected over the course of the year to capture seasonal differences and should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis. Refer to EPA's *Nutrient Criteria Technical Guidance Manual: Rivers and Streams* (EPA-822-B-00-002) for examples of sampling recommendations. Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section B.2 of Appendix A, which discusses Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02), and other details on data sufficiency and quality requirements.

Supporting physical, chemical and biological data may include the following:

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<sup>18</sup> Chlorophyll  $a$  and SCI provide pertinent information on the condition of the waterbody, although they were not parameters included as stream criteria under this rule or subject to the alternative criteria derivation of this rule.

- Historical quantitative water quality data (e.g., TN, TP, chlorophyll *a*, dissolved oxygen (DO), total suspended solids, clarity, temperature, depth, flow rates).
- Qualitative information (e.g., long term observations of water for the presence of algal mats or fish kills, riparian habitat).
- Presence of balanced native flora and fauna.
- Stream Condition Index > 40 or other valid metric for streams and other flowing waters.
- Consideration of the range of diel fluctuations in dissolved oxygen.

Consideration of current and historical conditions to ensure full support of designated uses and consistency when comparing temporal data.

Here is an example of a data set that includes physical, chemical and biological parameters to support a demonstration of how a stream presently meets designated uses:

- Chemical water quality data including at least three consecutive years of DO, TN and TP data.
- 3 Stream Condition Index (SCI) samples (SCIs > 40; based on one or more samples from each of 3 consecutive years).
- Information on hydrologic disturbance/channelization.
- Landscape Development Intensity (LDI) score of  $\leq 2$  in the 100 m wide by 10 km upstream corridor and  $\leq 3$  within the watershed.
- Habitat assessment (including presence/absence of native flora and fauna).

Finally, propose the alternative numeric criteria (e.g., TN, TP, and/or chlorophyll *a*) based on concentrations that reflect baseline conditions calculated from at least three years of the most recent data (consecutive years where available) with a justification for the adjustment and explain how the changes will ensure maintaining the designated uses.

### 3. Using Other Scientifically Defensible Methods

EPA recognizes that there may be other scientifically defensible methods that can be used to develop alternative TN and TP concentrations for streams that are protective of designated uses. Stressor-response, reference, and mechanistic modeling approaches are described here as examples.

#### *a. Stressor-Response Approach*

Develop one or more response endpoints (e.g., chlorophyll *a*, periphyton, or metric/index) with links to nutrients that show that the stream designated uses are being met. First, determine the response endpoint using an empirical relationship that is scientifically justified by site-specific data. The alternative endpoint(s) must meet all existing Florida water

quality standards. Then, determine the stressor-response relationship<sup>19</sup> between the new response endpoint and TN and TP. Provide data to justify using the alternate endpoint value (i.e., how it protects designated use) and how the alternate TN and TP values were derived. Data may include:

- Long-term data set (at least three years of the most recent data (consecutive years where available)) that includes the alternate endpoint, TN, TP, and any other relevant data.
- Alternative scientifically defensible trophic status metric appropriate for this waterbody type.

Data should include at least three years of the most recent data (consecutive years where available). For statistical robustness, however, at least ten samples<sup>20</sup> are preferable if such data are available. Calculate an annual average for each year for each of the biological, chemical, and physical parameters used in developing the stressor-response relationship; these should include TN and TP for a particular stream or sampling location. Data used to compute annual averages should be collected over the course of the year to capture seasonal differences. Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section B.3 of Appendix A, which discusses Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07), FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02), and other details on data sufficiency and quality requirements.

Establish the relationship between the long-term data and/or trophic status metric and the endpoint in the SSAC stream(s). Use statistical techniques, such as linear or multivariate regression, to relate TN and TP with the response endpoint. Evaluate whether the accuracy and precision of the estimated stressor-response relationship<sup>21</sup> is sufficient to inform nutrient criteria derivation. Identify the point in the predicted distribution of the endpoint values that is equivalent to the desired endpoint threshold. Justify the use of the point selected in the distribution (e.g., the 75<sup>th</sup> percentile, see Figure 4). Then translate this endpoint value to the new TN/TP criterion. Justify and use valid stressor-response analysis to derive TN and TP based on the alternate endpoint value.

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<sup>19</sup> U.S. EPA 2010. Using Stressor-Response Relationships to Derive Numeric Nutrient Criteria. EPA-820-S-10-001. U.S. Environmental Protection Agency, Office of Water, Washington DC

<sup>20</sup> Accurately estimating an empirical relationship between a stressor and a response requires at least 10 samples (Harrell FE, 2001. Regression Modeling Strategies. Springer-Verlag, Inc., New York, NY). Calculating ten annual averages of TN or TP and chlorophyll *a* may be achievable by using long-term monitoring data available in some streams or by combining data from nearby, similar streams.

<sup>21</sup> U.S. EPA 2010. Using Stressor-Response Relationships to Derive Numeric Nutrient Criteria. EPA-820-S-10-001. U.S. Environmental Protection Agency, Office of Water, Washington DC.

### *b. Reference Condition Approach*

For streams, entities can develop reference sites that differ from those developed using EPA's reference-based methodology. For example, the entity could define a sub-region within one of EPA's nutrient watershed regions and then (a) develop a set of reference sites using a different screening methodology than that used by EPA or (b) develop a set of reference sites from outside of the region in which the SSAC stream segments are located. In all cases, if a new screening methodology is developed, document how the new screening methodology ensures that the reference sites represent minimally impacted/least disturbed conditions.

First, identify the sub-region for which a refined TN and/or TP value is desired. Show how the streams in this sub-region are similar. If using any of EPA's set of reference sites, identify the subset of reference sites. If additional reference sites are being included, screen sites/observations based on the desired screening criteria (either EPA's or a newly developed, scientifically defensible one), to identify the reference site set that is minimally impacted/least disturbed.

Next, demonstrate that adequate data are available to support this methodology. The data should include at least three years of the most recent data (consecutive years where available). Calculate an annual average for each year for each of the biological, chemical, and physical parameters used in developing the reference condition; these should include TN and TP for a particular stream or sampling location. Data should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis. Refer to EPA's *Nutrient Criteria Technical Guidance Manual: Rivers and Streams* (EPA-822-B-00-002) for examples of sampling recommendations. Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section B.3 of Appendix A, which discusses Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07), FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02), and other details on data sufficiency and quality requirements.

Determine the number of reference sites and observations that are adequate to represent natural variability. Develop a distribution of TN and TP using the reference sites, and select a percentile of the resulting distribution of reference sites. Derive the alternative criteria using that percentile, and justify the selection of the percentile based on the available data.

### *c. Mechanistic Models*

Well-calibrated environmental water quality or ecosystem models can be used to identify potential thresholds of biological and ecosystem responses and the associated level of nutrient inputs, and may be applicable to developing SSAC. In contrast to regression

approaches that rely on empirical statistical analysis, mechanistic (or process-based) models more explicitly simulate the ecological processes that are operating in a given waterbody, and this may provide a greater ability to discern the reasons behind the observed biological responses. Mechanistic models can also examine proposed numeric nutrient criteria under a range of conditions to predict a system's response as an additional confirmatory step for a stressor-response relationship.

Any model proposed for SSAC development should simulate nutrient processes and appropriate response endpoints (e.g., periphyton, dissolved oxygen, or metric/index) for the stream segment. The response endpoint(s) should have an established link to nutrients and reflect protection of the designated use. The endpoint(s) must meet existing Florida water quality standards for that parameter. If possible, the model should account for the effects of confounding variables (e.g., suspended sediment, shading, flow, grazers).

Identify a sound scientific model<sup>22</sup> and justify why this model was chosen. Describe which biological, chemical, and/or physical characteristics were simulated, which endpoints were chosen, and how those endpoints are related to designated use protection. The description should also include:

- Ecological processes captured by the model.
- Time variable versus steady state.
- Primary simplifying assumptions.
- Metrics/endpoints that are able to be calculated from model output.

Entities should be prepared to provide the model software, its supporting documentation, and/or model runs for review, if EPA requests.

Document the important or sensitive model parameters and their sources. Document the sources of the driving data and the quality assurance procedures for the data collection. Data should be collected at locations within the waterbodies to represent the variability of waterbodies used in the analysis; refer to EPA's *Nutrient Criteria Technical Guidance Manual: Lakes and Reservoirs* for examples of sampling recommendations. Document all methods and assumptions associated with data collection, analysis and SSAC derivation. Refer to section B.3 of Appendix A, which discusses Florida's Quality Assurance Rule (62-160 F.A.C), FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07), FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02) and other details on data sufficiency and quality requirements.

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<sup>22</sup> For example, use the TMDL compendium on models: U.S. EPA 1997. Compendium of Tools for Watershed Assessment and TMDL Development. EPA 841-B-97-006.

Provide a description of the modeled site. If the model does not simulate the entire waterbody, then describe how it can be considered a representative site, or that it was applied in enough sites to capture spatial heterogeneity. Use site-specific data for driving variables, if available. If the values are not direct measurements, indicate how the values were derived (e.g., flow data extrapolated from an upstream gage, time series TSS data derived from a regression against flow).

Document the model calibration procedures along with a description of model performance (i.e., how well calibrated the model output was to the calibration endpoints). Also describe which verification and/or validation procedures were undertaken, and their results.

The model simulation should be run for existing conditions as well as the proposed nutrient regime to demonstrate that designated uses would be protected by the proposed SSAC. If it is a dynamic (time-variable) model, the simulation time period should include important variability (e.g., high-flow and low-flow years).

## **V. Considerations for Using Loads and TMDL Targets when Deriving Proposed SSAC**

### *A. Use of Concentration-Based Criteria and Supplemental Load Information*

EPA established the TN and TP criteria in 40 CFR 131.43(c) as concentrations based on several factors. The ability to monitor and assess concentrations of TN and TP is a function of direct measures of the nitrogen and phosphorus constituents in a waterbody. This gives all interested parties, including water quality managers and the public, numeric values of nutrients that are easy to understand and use. In contrast, the ability to assess loads in a receiving waterbody requires the measurement of concentrations of all nitrogen and phosphorus constituents from each source (including sources such as urban and agricultural runoff and atmospheric deposition) and the associated flows from these sources. In addition, loads are often an estimated measurement due to the necessity of estimating concentrations from the various sources (in particular intermittent ones) and associated flows.

When EPA developed the criteria as concentrations, EPA also considered the ecological response of the effects of excess nutrients. For algal growth, the concentration of nutrients combined with favorable growing conditions results in algal production. Because loads of TN and TP can be delivered to a waterbody over varying time periods, the resulting concentration of TN and TP can vary as well. For example, a large load delivered over a short period of time will most likely result in a higher concentration than the same load delivered over a long period of time. Loads to waterbodies over time tend to integrate some of the fluctuations in nutrient inputs from various sources.

EPA recognizes how these criteria affect implementation of other Clean Water Act programs, such as the relationship of the TMDL program to point and nonpoint source discharges, and is allowing entities to also submit a supplemental load that is consistent with the proposed SSAC concentration. While the results of a TMDL are load and wasteload allocations to nonpoint and point sources, the basis for the TMDL target is ultimately a concentration of nutrients in a receiving waterbody. EPA's requirement that SSAC be expressed as concentrations, with or without optional supplemental loads, does not undermine existing or past TMDLs, NPDES permits, or other CWA actions that have load-based requirements. Additional information on TMDLs and NPDES permits is in subsections B and C.

#### *B. Considerations for Using TMDL Targets When Deriving Proposed SSAC*

A total maximum daily load (TMDL) establishes the maximum amount of a particular pollutant that a particular waterbody may receive while still meeting water quality criteria. TMDLs are based upon the best available data and information at the time that they are written to ensure that the waterbody will meet and continue to meet the water quality standards for the pollutant. The principles, data requirements and types of analyses needed for the development of TMDLs can be similar to those necessary for SSAC development. In this section, EPA provides some general guidelines for proposing a SSAC based on work underlying a previously established TMDL.

In order to use data and analyses developed for TMDLs in support of a proposed SSAC, the following questions should be addressed in the documentation supporting the SSAC:

- Do the data and analyses support the conclusion that the SSAC protects the designated use (i.e., translates the narrative nutrient criterion) in the subject water, based upon the most current available information?
- Is there adequate supporting documentation to demonstrate protection of the designated use?
- Does the SSAC ensure adequate protection of downstream water quality standards?

Regarding the question of designated use protection, there should be information on the following:

- How the conclusions indicate values that are protective of balanced natural populations of aquatic flora and fauna.
- What the initial assumptions were and whether the assumptions are still valid.
- What was being demonstrated at the time the TMDL was written.
- Whether the target was derived – directly or indirectly – from an impairment threshold.

Any new data about the system should be considered. If the TMDL did not address downstream effects, delay in the response to nutrient inputs, then those effects must be addressed.

EPA recommends that entities follow the expectations outlined in section IV in addition to those in this section in order to demonstrate that the proposed SSAC are fully protective of the designated use(s).

### *C. SSAC, Existing TMDLs and Resultant NPDES Permit Limits*

EPA finds that a reasonable way to move forward with reducing nutrient pollution is to presume that existing TMDLs and wasteload allocations are an appropriate basis on which to establish NPDES permit limits in the next round of permits after EPA established the standards in 40 CFR 131.43. Because the nutrient TMDLs that were existing when EPA published the final rule were established to protect Florida's waters from the effects of nitrogen and phosphorus pollution, the same goal as EPA's numeric nutrient criteria, the Agency finds that, absent specific new information to the contrary, it is reasonable to presume that basing NPDES permit limits on those TMDLs will result in effluent limitations as stringent as necessary to meet the federal numeric nutrient criteria. Therefore, in carrying out its permit review oversight responsibilities, EPA intends to exercise its discretion by presuming that NPDES permits proposed by FDEP that implement wasteload allocations in current TMDLs will result in effluent limitations that reflect the necessary loading reductions to assure attainment of the new criteria. As new information becomes available in the future or as FDEP examines over time the existing nutrient TMDLs, EPA recognizes that changes may be necessary for some TMDLs and NPDES permits to reflect revised analysis and updated data. However, due to the complexity and/or significance of a TMDL, the state or any other entity may decide that the results of that TMDL should be incorporated into site-specific alternative criteria. In those cases the state or other entity may submit a proposed SSAC to EPA.

## Appendix A. Data Quality

### A. Data Quality Considerations for Developing Site-Specific Alternative Nutrient Criteria for Florida's Lakes

As described in section V.C(1) of the preamble for EPA's final rule, *Water Quality Standards for the State of Florida's Lakes and Flowing Waters*, there are several approaches for developing SSAC for lakes. One approach is to replicate the one that EPA used to develop lake criteria and apply this method to a smaller subset of waters. Another approach is to conduct a biological, chemical, and physical assessment of lake conditions to develop SSAC. A general provision for using another scientifically defensible approach that is protective of the designated use is also provided. A description of the data quality considerations for developing SSAC for these approaches is provided below.

FDEP's *Quality Assurance Rule 62-160*<sup>23</sup> describes the minimum field and laboratory quality assurance (QA), methodological and reporting requirements used to assure that chemical, physical, biological, microbiological, and toxicological data used by FDEP are appropriate and reliable. It applies to all FDEP programs, projects, studies, and other activities that involve the measurement, use, or submission of environmental data or reports to FDEP with the exception of those activities related to air quality and meteorological studies that have no requirements for contamination of soil, water or tissue. Part II (*Field Procedures*) of Rule 62-160 discusses approved field procedures and recordkeeping and reporting requirements for field procedures. Part III (*Laboratory Certification Procedures*) of Rule 62-160 covers laboratory certification, approved laboratory methods, approval of new and alternative laboratory methods, and recordkeeping and reporting requirements for laboratory procedures. Part IV (*Miscellaneous*) discusses sample preservation and holding times, electronic signatures, research field and laboratory procedures, field and laboratory audits, and data validation. In addition to the data verification and validation procedures described in Rule 62-160.670(1) and (2), F.A.C., FDEP evaluates data quality using the data quality indicators described in FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07)<sup>24</sup>.

#### 1. Data Quality Objectives Used in EPA's Approach for Developing Lake Criteria

If an entity chooses to apply EPA's approach for developing lake criteria to a smaller subset of waters, it should use the same data quality objectives used by EPA for developing this approach. As described in section 2.2.2 of the *Technical Support Document for U.S. EPA's Final Rule for Numeric Criteria for Nitrogen/Phosphorus Pollution in Florida's Inland Surface Fresh Waters* (USEPA 2010), EPA downloaded chlorophyll *a* and selected water chemistry data (alkalinity, color, nitrogen species, phosphorus species, pH, dissolved oxygen) from Florida lakes from the Florida *Impaired Waters Rule*

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<sup>23</sup> Florida Department of Environmental Protection (FDEP). 2008. Rule 62-160. *Quality Assurance*. Effective 12-3-08.

<sup>24</sup> Florida Department of Environmental Protection (FDEP). 2008. DEP-EA 001/07 *Process for Assessing Data Usability*. Florida Department of Environmental Protection, Bureau of Standards and Special Projects, Environmental Assessment Section.

(IWR), 62-303, F.A.C.<sup>25</sup> database, which comprises all of the STORET data for Florida. The IWR data set includes several years of monitoring data from FDEP and other entities (public and private) in Florida. These data were augmented by FDEP with some of its own data not stored in the IWR database. FDEP queried its own Laboratory Information Management System (LIMS) for QA information not provided in IWR.

### 1.1 Impaired Waters Rule (62-303, Florida Administrative Code)

Florida's STORET database design is dictated by the *Impaired Waters Rule*, 62-303, F.A.C.<sup>26</sup>. This rule establishes a methodology to identify waters that will be included on Florida's verified list of impaired waters based on representative data. The rule covers assessment of aquatic life use support, biological assessment, interpretation of narrative nutrient criteria, primary contact and recreation use support, fish and shellfish consumption use support, drinking water use support and protection of human health.

For example, data sufficiency and quality requirements in section 62-303 include, but are not limited to, the following:

- Data from FDEP's STORET database or its successors should be used as the primary source of data for determining whether samples do not meet water quality criteria.
- In general, data older than 10 years should not be considered representative of current conditions.
- Values that exceed possible physical or chemical measurement constraints (e.g., pH > 14) and data transcription errors will be excluded from the assessment. If statistical procedures are used to identify outliers, FDEP will evaluate these outliers and determine whether they should be considered invalid and not included in the assessment. If the data are excluded, FDEP will note in the record that data were excluded and why they were excluded.
- FDEP will consider all readily available water quality data collected and analyzed in accordance with Chapter 62-160, F.A.C. If requested, the sampling agency must provide to the Department all of the data quality assessment elements listed in Table 2 of the Department's Guidance Document *Data Quality Assessment Elements for Identification of Impaired Surface Waters* (DEP EAS 01-01, April 2001).
- Surface Water data with values below applicable PQLs or MDLs will be assessed in accordance with rules 62-4.246(6)(b)-(d) and (8), F.A.C. If there are no analytical methods with MDLs below a criterion, then the method with the lowest MDL should be used.

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<sup>25</sup> Florida Department of Environmental Protection (FDEP). 2007. Chapter 62-303. *Identification of Impaired Surface Waters*. Effective 9-4-07.

<sup>26</sup> Florida Department of Environmental Protection (FDEP). 2007. Chapter 62-303. *Identification of Impaired Surface Waters*. Effective 9-4-07.

## 1.2. Florida's Data Quality Assessment Elements for Identification of Impaired Surface Waters (DEP EAS 01-01)

As described in Florida's *Impaired Waters Rule* (62-303, Florida Administrative Code)<sup>27</sup>, FDEP may request and evaluate all of the data quality assessment elements listed in Table 2 of Florida's *Data Quality Assessment Elements for Identification of Impaired Surface Waters*<sup>28</sup>. This data quality assessment elements document also provides in Table 1, the level of data quality assessment that should be conducted for data used for identifying impaired surface waters. The following recommended quality assessment checks are provided in Table 1 of Florida's *Data Quality Assessment Elements for Identification of Impaired Surface Waters*:

- Review to determine if analyses were conducted within holding times.
- Review for qualifiers indicative of problems.
- Screen comments for keywords indicative of problems.
- Review laboratory certification status for particular analyte at the time analysis was performed.
- Review data to determine if parts are significantly greater than the whole (e.g., ortho-P > total phosphorus, or NH<sub>3</sub> > TKN).
- Screen data for realistic ranges (e.g., is pH < 14?).
- Review detection limits and quantitation limits against Department criteria and program action levels to ensure adequate sensitivity.
- Review for blank contamination.

## 2. Recommended Data Quality Procedures for Conducting a Biological, Chemical, and Physical Assessment of Lake Conditions

### 2.1 Field Activities and Field Measurements

If an entity wants to conduct a biological, chemical, and physical assessment of lake conditions to support SSAC development, it should follow FDEP's approved Standard Operating Procedures (SOPs) for field activities and field measurements described in DEP-SOP-001/01 (March 31, 2008) (available from FDEP's website at <http://www.dep.state.fl.us/labs/bars/sas/qa/sops.htm>). Entities that conduct or support field activities and field measurements for FDEP are required to follow these SOPs under Rule 62-160.210 (*Approved Field Procedures*), F.A.C. If an entity would like to apply for a new or alternative field procedure, it should follow the requirements of Rule 62-160.220 (*Approval of New and Alternative Field Procedures*), F.A.C. It should be noted that alternative procedures cannot be approved for the following DEP-SOP-001/01 methods:

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<sup>27</sup> Florida Department of Environmental Protection (FDEP). 2007. Chapter 62-303. *Identification of Impaired Surface Waters*. Effective 9-4-07.

<sup>28</sup> Florida Department of Environmental Protection (FDEP). 2001. *Data Quality Assessment Elements for Identification of Impaired Surface Waters*. DEP EAS 01-01, April 2001.

- FS 7410 Rapid Bioassessment (Biorecon) Method.
- FS 7420 Stream Condition Index (D-Frame Dipnet) Sampling.
- FS 7460 Lake Condition Index Lake Composite Sampling.
- FT 3000 Aquatic Habitat Characterization.
- FS 7220 Qualitative Periphyton Sampling.
- FS 7230 Rapid Periphyton Survey.
- FS 7310 Lake Vegetation Index Sampling (LVI).

## 2.2 Analytical Laboratory Certification and Procedures

An entity planning to conduct a biological, chemical, and physical assessment of lake conditions to support SSAC development should ensure that samples are analyzed by a laboratory that is certified by Florida's Department of Health's Environmental Laboratory Certification Program, as described in Rule 62-160.300, F.A.C. Laboratories should comply with relevant FDEP-approved methods as provided in Rule 62-160.320 (*Approved Laboratory Methods*), F.A.C. In addition, the laboratory should operate a QA program consistent with the quality systems standards of the National Environmental Laboratory Accreditation Conference (NELAC), as described in Rule 62-160.300(6), F.A.C. A link to the NELAC website and standards and National Environmental Laboratory Accreditation Program (NELAP)-certified laboratory list pages is provided on FDEP's website at <http://www.dep.state.fl.us/labs/bars/sas/qa/sops.htm>.

If an entity would like to apply for the use of a new or alternative laboratory method, it should follow the requirements of Rule 62-160.330 (*Approval of New and Alternative Laboratory Methods*), F.A.C.

## 2.3 Florida Department of Environmental Protection's Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract (DEP-QA-002/02)

In addition to following DEP-SOP-001/01 methods, it is recommended that entities planning to conduct a biological, chemical and physical assessment of lake conditions to support SSAC prepare a Sampling and Analysis Plan (SAP) in accordance with *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract (DEP-QA-002/02)*<sup>29</sup>. This document describes the content that should be included in a SAP for collecting and analyzing data for FDEP as well as requirements for documentation and recordkeeping, reporting, and data quality control.

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<sup>29</sup> Florida Department of Environmental Protection (FDEP). 2002. *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract*. DEP-QA-002/02. Florida Department of Environmental Protection, Bureau of Laboratories, Environmental Assessment Section, Tallahassee, Florida.

### 3. Recommended Data Quality Procedures for Using Another Scientifically Defensible Approach for Developing SSAC that Is Protective of the Designated Use

An entity might decide to use another scientifically defensible approach for developing SSAC that is protective of the designated use *other than* (or *in addition to*) applying EPA's approach for developing lake criteria to a smaller subset of waters or conducting a biological, chemical, and physical assessment of lake conditions. For example, an entity might want to include additional monitoring data from non-FDEP sources that were collected for a purpose other than Florida nutrient criteria development for lakes (secondary data) instead of (or in addition to) Florida's IWR database (refer to section 2.2.2 of the TSD) to develop an SSAC. These secondary data should be checked to ensure that they are suitable and usable for developing SSAC.

As provided below, section 62-160.670 (*Data Validation by the Department*), F.A.C., describes what information should be checked to ensure that data are suitable and usable for a specific purpose.

- “(a) Completeness of the Department requested data package(s) and the response of involved parties to any Department requests for additional data;
- (b) Integrity of samples as determined by complete and proper sample transmittal documentation, and records that demonstrate adherence to proper preservation, transport or other sample handling protocols, as applicable;
- (c) Proper use of sample collection methods;
- (d) Proper selection and use of analysis methods;
- (e) Sufficient use and routine evaluation of quality control measures to establish the precision, accuracy, sensitivity, and potential bias associated with the analytical system and associated results;
- (f) Proper instrument calibration and verification procedures;
- (g) Documentation of all generated data as provided in Rules 62-160.240 and 62-160.340, F.A.C.;
- (h) Ability to reconstruct all field sampling and laboratory procedures through the documentation and records of the laboratory or field sampling organization as provided in Rules 62-160.240 and 62-160.340, F.A.C.;
- (i) Ability to trace data in the final report to a specific sampling site, date, and time;
- (j) Status of the laboratory's certification through the DOH ELCP as provided in Chapter 64E-1, F.A.C., for any given analyte or category of analytes; and
- (k) Appropriateness of the collected data as related to the specific data quality objectives of the Department program activity or project for which they were collected including those data being considered for secondary use.”

In addition, as described in 62-160.670(3), F.A.C., data should be evaluated against the following data quality indicators described in FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07)<sup>30</sup>:

- 3.0 Laboratory control sample or spike (LCS), including evaluation of LCS recovery
- 4.0 Matrix spikes (MS), including evaluation of MS recovery
- 5.0 Surrogate spikes
- 6.0 LCS duplicates or replicates (LCSD) and matrix spike duplicates (MSD)
- 7.0 Sample duplicates (SD)
- 8.0 Calibrations
- 9.0 Method blanks or other analytical blanks
- 10.0 Field quality control blanks (trip blanks, field blanks or equipment blanks)
- 11.0 Holding times
- 12.0 Quality control check samples for BOD, chlorophyll, and matrix-specific evaluation for known or suspected interferences
- 13.0 Sample preservation checks
- 14.0 Evaluation of the reported MDL
- 15.0 Evaluation of the reported PQL
- 16.0 Evaluation of reversals (parts versus whole comparison), where sample results are evaluated to determine whether the sum of reported parts or fractions for a sample analyte result exceed 120 percent of the corresponded reported or calculated whole.

It is also recommended that secondary data be evaluated against the documentation and recordkeeping requirements, reporting requirements, and quality control requirements of FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract* (DEP-QA-002/02)<sup>31</sup>.

If it is determined during the data evaluation process that secondary data do not meet the data quality objectives described above for nutrient criteria development, those data should not be used for SSAC development.

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<sup>30</sup> Florida Department of Environmental Protection (FDEP). 2008. *DEP-EA 001/07 Process for Assessing Data Usability*. Florida Department of Environmental Protection, Bureau of Standards and Special Projects, Environmental Assessment Section.

<sup>31</sup> Florida Department of Environmental Protection (FDEP). 2002. *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract*. DEP-QA-002/02. Florida Department of Environmental Protection, Bureau of Laboratories, Environmental Assessment Section, Tallahassee, Florida.

## *B. Data Quality Considerations for Developing Site Specific Alternative Nutrient Criteria for Florida's Rivers and Streams*

As described in section V.C(1) of the preamble for EPA's final rule, *Water Quality Standards for the State of Florida's Lakes and Flowing Waters*, there are several approaches for developing SSAC for rivers and streams. One approach is to replicate the one that EPA used to develop river and stream criteria and apply this method to a smaller subset of waters. Another approach is to conduct a biological, chemical, and physical assessment of river and stream conditions to develop SSAC. A general provision for using another scientifically defensible approach that is protective of the designated use is also provided. A description of the data quality considerations for developing SSAC for these approaches is provided below.

FDEP's *Quality Assurance Rule 62-160*<sup>32</sup> describes the minimum field and laboratory QA, methodological and reporting requirements used to assure that chemical, physical, biological, microbiological, and toxicological data used by FDEP are appropriate and reliable. It applies to all FDEP programs, projects, studies, and other activities that involve the measurement, use, or submission of environmental data or reports to FDEP with the exception of those activities related to air quality and meteorological studies that have no requirements for contamination of soil, water or tissue. Part II (*Field Procedures*) of Rule 62-160 discusses approved field procedures and recordkeeping and reporting requirements for field procedures. Part III (*Laboratory Certification Procedures*) of Rule 62-160 covers laboratory certification, approved laboratory methods, approval of new and alternative laboratory methods, and recordkeeping and reporting requirements for laboratory procedures. Part IV (*Miscellaneous*) discusses sample preservation and holding times, electronic signatures, research field and laboratory procedures, field and laboratory audits, and data validation. In addition to the data verification and validation procedures described in Rule 62-160.670(1) and (2), F.A.C., FDEP evaluates data quality using the data quality indicators described in FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07)<sup>33</sup>

### 1. Data Quality Considerations that EPA Used in Developing Nutrient Criteria for Florida Rivers and Streams

If an entity chooses to apply EPA's approach for developing river and stream criteria to a smaller subset of waters, it should use the same data quality objectives that EPA used for this approach. As described in section 1.3.1 of the *Technical Support Document for U.S. EPA's Final Rule for Numeric Criteria for Nitrogen/Phosphorus Pollution in Florida's Inland Surface Fresh Waters* (USEPA 2010), EPA used the *All Streams Data Set* (see Appendix A3 of the Technical Support Document [TSD], *Data*

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<sup>32</sup> Florida Department of Environmental Protection (FDEP). 2008. Rule 62-160. *Quality Assurance*. Effective 12-3-08.

<sup>33</sup> Florida Department of Environmental Protection (FDEP). 2008. DEP-EA 001/07 *Process for Assessing Data Usability*. Florida Department of Environmental Protection, Bureau of Standards and Special Projects, Environmental Assessment Section.

*Supporting EPA's Reference Approach for Deriving Numeric Nutrient Criteria for Florida Streams*) to develop river and stream nutrient criteria. The *All Streams Data Set* contains all available nutrient data from Florida's STORET and GWIS databases that meet FDEP data quality requirements, as described in FDEP QA rule 62-160 and their "*Process for Assessing Data Usability*." EPA reviewed these FDEP data quality assurance procedures and determined that they were consistent with EPA quality assurance policies.

## 2. Recommended Data Quality Procedures for Conducting a Biological, Chemical, and Physical Assessment of River and Stream Conditions

### *2.1 Field Activities and Field Measurements*

If an entity wants to conduct a biological, chemical, and physical assessment of river or stream conditions to support SSAC development, it should follow FDEP's approved Standard Operating Procedures (SOPs) for field activities and field measurements described in DEP-SOP-001/01 (March 31, 2008) (available from FDEP's website at <http://www.dep.state.fl.us/labs/bars/sas/qa/sops.htm>). Entities that conduct or support field activities and field measurements for FDEP are required to follow these SOPs under Rule 62-160.210 (*Approved Field Procedures*), F.A.C. If an entity would like to apply for a new or alternative field procedure, it should follow the requirements of Rule 62-160.220 (*Approval of New and Alternative Field Procedures*), F.A.C. It should be noted that alternative procedures cannot be approved for the following DEP-SOP-001/01 methods:

- FS 7410 Rapid Bioassessment (Biorecon) Method.
- FS 7420 Stream Condition Index (D-Frame Dipnet) Sampling.
- FS 7460 Lake Condition Index Lake Composite Sampling.
- FT 3000 Aquatic Habitat Characterization.
- FS 7220 Qualitative Periphyton Sampling.
- FS 7230 Rapid Periphyton Survey.
- FS 7310 Lake Vegetation Index Sampling (LVI).

### *2.2 Analytical Laboratory Certification and Procedures*

An entity planning to conduct a biological, chemical, and physical assessment of river or stream conditions to support SSAC development should ensure that samples are analyzed by a laboratory that is certified by Florida's Department of Health's Environmental Laboratory Certification Program, as described in Rule 62-160.300, F.A.C. Laboratories should comply with relevant FDEP-approved methods as provided in Rule 62-160.320 (*Approved Laboratory Methods*), F.A.C. In addition, the laboratory should operate a QA program consistent with the quality systems standards of the National Environmental Laboratory Accreditation Conference (NELAC), as described in Rule 62-160.300(6), F.A.C. A link to the NELAC website and standards and National Environmental Laboratory Accreditation Program (NELAP)-certified laboratory list pages is provided on FDEP's website at <http://www.dep.state.fl.us/labs/bars/sas/qa/sops.htm>.

If an entity would like to apply for the use of a new or alternative laboratory method, it should follow the requirements of Rule 62-160.330 (*Approval of New and Alternative Laboratory Methods*), F.A.C.

### *2.3 Florida Department of Environmental Protection's Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract (DEP-QA-002/02)*

In addition to following DEP-SOP-001/01 methods, it is recommended that entities planning to conduct a biological, chemical, and physical assessment of river or stream conditions, prepare a Sampling and Analysis Plan (SAP) in accordance with FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract (DEP-QA-002/02)*<sup>34</sup>. This document describes the content that should be included in a SAP for collecting and analyzing data for FDEP as well as requirements for documentation and recordkeeping, reporting, and data quality control.

### 3. Recommended Data Quality Procedures for Using Another Scientifically Defensible Approach for Developing SSAC that Is Protective of the Designated Use

An entity might decide to use another scientifically defensible approach for developing SSAC that is protective of the designated use *other than* (or *in addition to*) applying EPA's approach for developing river and stream criteria to a smaller subset of waters or conducting a biological, chemical, and physical assessment of river or stream conditions. For example, an entity might want to include additional monitoring data from non-FDEP sources that were collected for a purpose other than Florida nutrient criteria development for rivers and streams (secondary data), instead of (or in addition to) EPA's *All Streams Data Set* (see Appendix A3 of the TSD) to develop an SSAC. These secondary data should be checked to ensure that they are suitable and usable for developing SSAC.

As provided below, section 62-160.670 (*Data Validation by the Department*), F.A.C., describes which information should be checked to ensure that data are suitable and usable for a specific purpose.

“(a) Completeness of the Department requested data package(s) and the response of involved parties to any Department requests for additional data;

- (b) Integrity of samples as determined by complete and proper sample transmittal documentation, and records that demonstrate adherence to proper preservation, transport or other sample handling protocols, as applicable;
- (c) Proper use of sample collection methods;
- (d) Proper selection and use of analysis methods;

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<sup>34</sup> Florida Department of Environmental Protection (FDEP). 2002. *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract*. DEP-QA-002/02. Florida Department of Environmental Protection, Bureau of Laboratories, Environmental Assessment Section, Tallahassee, Florida.

- (e) Sufficient use and routine evaluation of quality control measures to establish the precision, accuracy, sensitivity, and potential bias associated with the analytical system and associated results;
- (f) Proper instrument calibration and verification procedures;
- (g) Documentation of all generated data as provided in Rules 62-160.240 and 62-160.340, F.A.C.;
- (h) Ability to reconstruct all field sampling and laboratory procedures through the documentation and records of the laboratory or field sampling organization as provided in Rules 62-160.240 and 62-160.340, F.A.C.;
- (i) Ability to trace data in the final report to a specific sampling site, date, and time;
- (j) Status of the laboratory's certification through the DOH ELCP as provided in Chapter 64E-1, F.A.C., for any given analyte or category of analytes; and
- (k) Appropriateness of the collected data as related to the specific data quality objectives of the Department program activity or project for which they were collected including those data being considered for secondary use."

In addition, as described in 62-160.670(3), F.A.C., data should be evaluated against the following data quality indicators described in FDEP's *Department of Environmental Protection Process for Assessing Data Usability* (DEP-EA-001/07)<sup>35</sup>:

- 3.0 Laboratory control sample or spike (LCS), including evaluation of LCS recovery
- 4.0 Matrix spikes (MS), including evaluation of MS recovery
- 5.0 Surrogate spikes
- 6.0 LCS duplicates or replicates (LCS/D) and matrix spike duplicates (MSD)
- 7.0 Sample duplicates (SD)
- 8.0 Calibrations
- 9.0 Method blanks or other analytical blanks
- 10.0 Field quality control blanks (trip blanks, field blanks or equipment blanks)
- 11.0 Holding times
- 12.0 Quality control check samples for BOD, chlorophyll, and matrix-specific evaluation for known or suspected interferences
- 13.0 Sample preservation checks
- 14.0 Evaluation of the reported MDL
- 15.0 Evaluation of the reported PQL
- 16.0 Evaluation of reversals (parts versus whole comparison), where sample results are evaluated to determine whether the sum of reported parts or fractions for a sample analyte result exceed 120 percent of the corresponded reported or calculated whole.

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<sup>35</sup> Florida Department of Environmental Protection (FDEP). 2008. *DEP-EA 001/07 Process for Assessing Data Usability*. Florida Department of Environmental Protection, Bureau of Standards and Special Projects, Environmental Assessment Section.

It is also recommended that secondary data be evaluated against the documentation and recordkeeping requirements, reporting requirements, and quality control requirements of FDEP's *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract (DEP-QA-002/02)*<sup>36</sup>.

If it is determined during the data evaluation process that secondary data do not meet the data quality objectives described in this section for nutrient criteria development for Florida's rivers and streams, those data should not be used for SSAC development.

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<sup>36</sup> Florida Department of Environmental Protection (FDEP). 2002. *Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract*. DEP-QA-002/02. Florida Department of Environmental Protection, Bureau of Laboratories, Environmental Assessment Section, Tallahassee, Florida.



WATER QUALITY AND WATERSHED CONDITIONS IN  
THE UPPER ILLINOIS RIVER WATERSHED

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MSC Publication 359 | Arkansas Water Resources Center

## Water Quality and Watershed Conditions in the Upper Illinois River Watershed

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The Illinois River and its tributaries have many uses that have been designated by the Arkansas Department of Environmental Quality including fisheries, aquatic life, primary contact waters, secondary contact waters, drinking water supply, and agricultural and industrial water supply, and water quality affects whether these uses can be supported. Since water quality can be quite complex, many types of measurements can be used as water quality indicators; some common water quality measurements include pH, dissolved oxygen concentration, and conductivity. More complicated measurements include determining nutrients, sediment and bacteria in the water, as well as assessing the aquatic life—aquatic insects, fish, algae and plants that are present within a stream. Most of these parameters are related to the type and use of land surrounding the stream and thus can be impacted by human activities. This publication details stream use classification and use support, impaired reaches in the Arkansas portion of the Illinois River, general water quality conditions across the Upper Illinois River Watershed, and trends in water quality in the Illinois River over the past decade. This publication serves as companion material to MSC Publication 355, Final Report to the Illinois River Watershed Partnership: Recommended Watershed Based Strategy for the Upper Illinois River Watershed, Northwest Arkansas.

**Keywords:** Water Quality, Illinois River, Designated Uses, Trends

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# ARKANSAS WATER RESOURCES CENTER – UNIVERSITY OF ARKANSAS

## TECHNICAL PUBLICATION NUMBER MSC 359 – YEAR 2010

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### STREAM CLASSIFICATIONS AND USE SUPPORT

Arkansas has established designated uses for all waters of the State including streams and publicly-owned lakes in the Upper Illinois River Watershed (UIRW). The definitions of these designated uses are based on Regulation 2, which establishes water quality standards for the State of Arkansas.

- ◆ *Extraordinary Resource Waters (ERWs):* These waters are designated for their scenic beauty, aesthetics, scientific values, broad recreation potential and social values based on a combination of chemical, physical, and biological characteristics. Any and all areas in the UIRW that support the Arkansas darter, least darter, Oklahoma salamander, and cave fish, snails and crawfish would be considered ERWs.
- ◆ *Natural and Scenic Waterways (NSWs):* These waters have been legislatively adopted into a state or federal system of natural and scenic waterways. No streams in the UIRW are designated with this use by the State of Arkansas.
- ◆ *Ecologically Sensitive Waterbodies (ESWs):* These waters are known to provide habitat within the existing range of threatened, endangered or endemic species of aquatic or semi-aquatic organisms. In the UIRW, the following portions are considered ESWs: 1) Illinois River (From the Arkansas – Oklahoma state line upstream to its confluence with Muddy Fork), and any other portion where the Neosho mussel is known to inhabit 2) Little Osage (From its confluence with Osage Creek approximately 2.5 miles upstream) 3) Numerous springs and spring-fed tributaries, which support threatened, endangered or endemic species (11 locations within the UIRW).
- ◆ *Primary Contact Recreation:* These waters are designated for primary contact recre-

ation, or full body contact, use. All streams with drainage areas greater than 10 square miles and all lakes and reservoirs are designated with this use within the UIRW; this designated use typically applies from May 1<sup>st</sup> through September 30<sup>th</sup>.

- ◆ *Secondary Contact Recreation:* These waters are designated for secondary recreational activities including boating, fishing, or wading. All waters are designated with this use in the UIRW.
- ◆ *Domestic, Industrial Agricultural Water Supply:* These waters are designated for use as domestic, industrial or agricultural water supply. All waters are designated with this use in the UIRW.
- ◆ *Fisheries:* These waters are designated for the protection and propagation of fish, shellfish and other forms of aquatic life. In the UIRW, the following waterbodies are designated with this use or subsets of the use: 1) all lakes and reservoirs; 2) perennial fisheries—all streams with drainage area equal to or greater than 10 square miles; and 3) seasonal fisheries—all streams with drainage area less than 10 square miles during the primary season (generally mid-September to mid-May). Seasonal fishery streams may be designated as perennial fisheries with further evaluation of water sources or aquatic communities.

Tables 1 and 2 identify stream reaches and lakes in the UIRW are meeting their designated uses as monitored, assessed and evaluated by Arkansas Department of Environmental Quality (ADEQ).

### IMPAIRED STREAM REACHES IN THE ILLINOIS RIVER

ADEQ submits a list of waterbodies that do not meet current water quality standards, assessment criteria, and designated beneficial uses

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**Table 1.** Designated uses and use assessment for select stream reaches in the Upper Illinois River Watershed (ADEQ, 2008)

Stream	Reach	Length (miles)	Assessment Method	Monitoring Station	Fisheries	Aquatic Life	Designated Use Supported?			
							Primary Contact	Secondary Contact	Drinking Water	Agricultural and Industrial Use
Evansville Creek	012	9	Unassessed							
Baron Fork	013	10	Monitored	ARK07	Yes	Yes	Yes	Yes	Yes	Yes
Illinois River	020	1.6	Monitored	ARK06	Yes	<b>No</b>	Yes	Yes	Yes	
Cincinnati Creek	021	9	Monitored	ARK141	Yes	Yes	Yes	Yes	Yes	
Illinois River	022	10.8	Monitored	ARK06A	Yes	Yes	Yes	Yes	Yes	Yes
Illinois River	023	8.1	Evaluated		Yes	Yes	Yes	Yes	Yes	Yes
Illinois River	024	2.5	Monitored	ARK40	Yes	<b>No</b>	Yes	Yes	Yes	Yes
Muddy Fork	025	3.2	Monitored	MF104+	Yes	Yes	Yes	Yes	Yes	
Moore's Creek	026	9.8	Unassessed							
Muddy Fork	027	11	Monitored	MF102B+	Yes	Yes	Yes	Yes	Yes	
Illinois River	028	19.9	Monitored	III01	Yes	Yes	Yes	Yes	Yes	
Clear Creek	029	13.5	Monitored	ARK10C	Yes	Yes	<b>No</b>	Yes	Yes	Yes
Osage Creek	030	15	Monitored	ARK41	Yes	Yes	Yes	Yes	Yes	Yes
Osage Creek	930	5	Monitored	OSC03+	Yes	Yes	Yes	Yes	Yes	
Spring Creek	931	6	Monitored	SPG03+	Yes	Yes	Yes	Yes	Yes	
Flint Creek	031	9.6	Monitored	ARK04A	Yes	Yes	Yes	Yes	Yes	Yes
Sager Creek	932	8	Monitored	ARK05	Yes	Yes	Yes	Yes	<b>No</b>	Yes

From ADEQ's perspective and assessment, these selected stream reaches in the UIRW are generally meeting the designated uses – there were four of the selected stream reaches that were monitored where one designated use (e.g., aquatic life, primary contact, or drinking water) were not supported. Thus, these stream reaches were placed on the 303(d) list submitted by ADEQ to EPA in 2008.

**Table 2.** Designated uses and use assessment for select lakes in the Upper Illinois River Watershed (ADEQ, 2008)

Lake	Size (acres)	Depth* (ft)	Purpose	Assessment Method	Fisheries	Aquatic Life	Designated Use Supported?			
							Primary Contact	Secondary Contact	Drinking Water	Agricultural and Industrial Use
Wedington	102	16	Recreation	Monitored	Yes	Yes	Yes	Yes	Yes	
Elmdale	180	8	Recreation	Monitored	Yes	Yes	Yes	Yes	Yes	Yes
Fayetteville	196	15	Recreation	Monitored	Yes	Yes	Yes	Yes		
Bobb Kidd	200	13	Fishing	Monitored	Yes	Yes	Yes	Yes		
SWEPCO	531	17	Water Supply	Monitored	Yes	<b>No</b>	Yes	Yes	Yes	Yes

\*Average depth; the select lakes or small reservoirs monitored and assessed by ADEQ were supporting the designated uses, with one exception – Lake SWEPCO, which was not supporting the its designated aquatic life use and the cause for this impairment was unknown.

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called the 303(d) list to U.S. Environmental Protection Agency (EPA). ADEQ submitted the most recent list to EPA in 2008 based on evaluation of data collected between July 1, 2002 and June 30, 2007 (Tables 1 and 2). ADEQ indicated that four segments within the UIRW

were impaired; however, EPA added additional segments to this list for a total of 14 stream reaches or reservoirs in the UIRW, and the map of the UIRW depicts the location of these stream reaches and the single reservoir (Figure 1, Table 3).

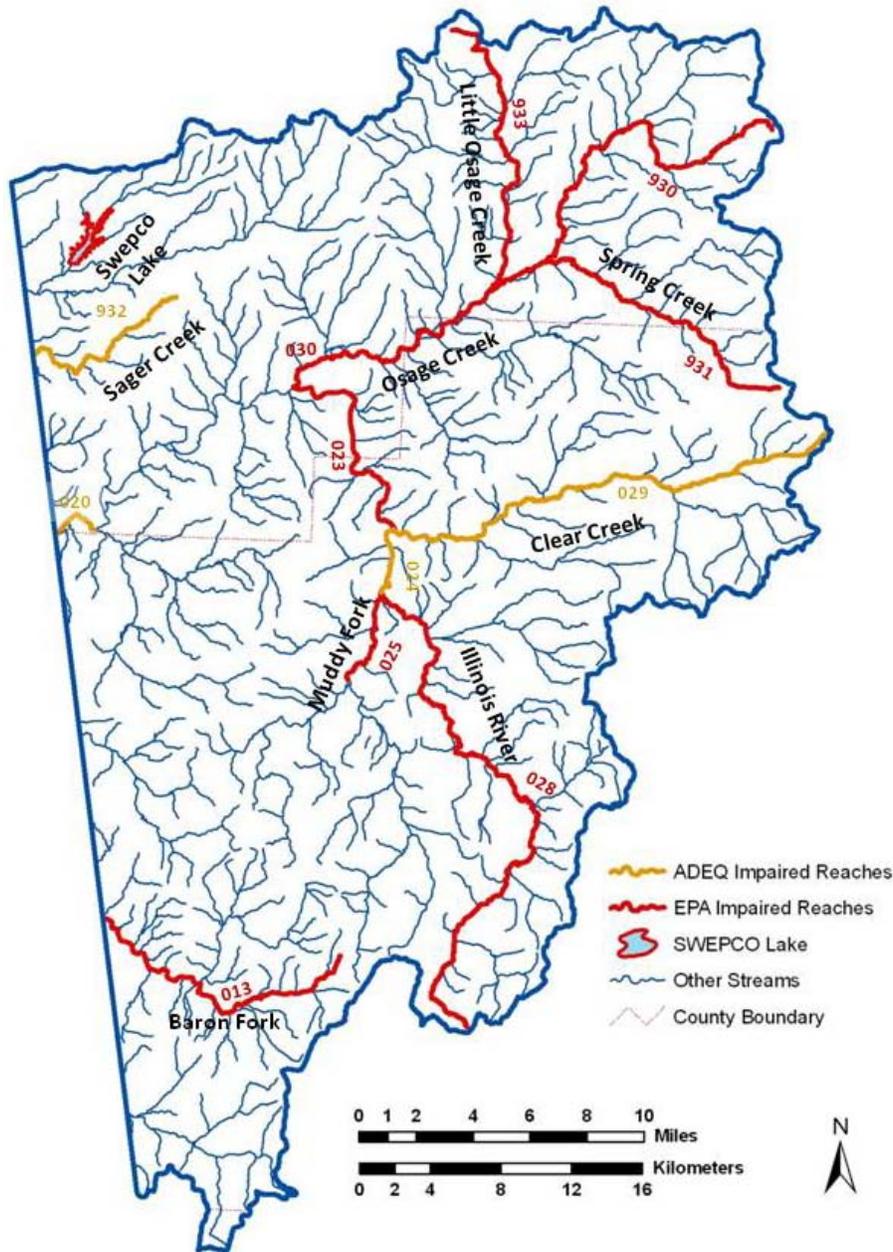


Figure 1. 303(d) listed reaches within the Upper Illinois River Watershed (provided by the UA Center for Advanced Spatial Technology)

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**Table 3.** 303(d) listed stream segments or reservoirs within the Upper Illinois River Watershed in 2008

Stream Name	Reach	Length (miles)	Pollutant	Category	Priority <sup>4</sup>
Illinois River	020	1.6	Siltation	5d <sup>1</sup>	Low
Illinois River	024	2.5	Siltation	5d <sup>1</sup>	Low
Clear Creek	029	13.5	Pathogen	5d <sup>1</sup>	Low
Sager Creek	932	8.0	Nitrate	5e <sup>2</sup>	Low
Baron Fork	013	10.0	Pathogen	5g <sup>3</sup>	Low
Illinois River	023	8.1	Pathogen	5g <sup>3</sup>	Low
Illinois River	024	2.5	Pathogen	5g <sup>3</sup>	Low
Muddy Fork	025	3.2	Pathogen	5g <sup>3</sup>	Low
Muddy Fork	025	3.2	Total Phosphorus	5g <sup>3</sup>	Low
Illinois River	028	19.9	Pathogen	5g <sup>3</sup>	Low
Osage Creek	030	15.0	Total Phosphorus	5g <sup>3</sup>	Low
Osage Creek	030	15.0	Pathogen	5g <sup>3</sup>	Low
Osage Creek	930	10.2	Total Phosphorus	5g <sup>3</sup>	Low
Little Osage Creek	933	10.2	Pathogen	5g <sup>3</sup>	Low
Spring Creek	931	8.4	Total Phosphorus	5g <sup>3</sup>	Low
Swepco Lake	Lake	NA	Unknown	5g <sup>3</sup>	Low

<sup>1</sup> Additional data is needed to determine the extent of impairment

<sup>2</sup> Future permit restrictions are expected

<sup>3</sup> Reach listed by the US Environmental Protection Agency

<sup>4</sup> The priority status for these segments was provided by ADEQ.

### Explanation of the 303(d) listed reaches

**Baron Fork (Reach 013).** EPA added Reach 013 of Baron Fork to the 303(d) list as not supporting its primary contact recreation use due to elevated bacteria concentrations, specifically *Escherichia coli*. The impairment was listed under Category 5g meaning that the reach was added by EPA.

**Illinois River (Reaches 020, 023, 024, and 028).** ADEQ listed Reaches 020 and 024 of the Illinois River due to siltation that impaired the aquatic life designated use. The listed source of the impairment is surface erosion. The impairment is listed under Category 5d meaning that additional data is needed to verify the use impairment.

EPA added Reaches 023, 024, and 028 of the Illinois River to the 303(d) list as not supporting its primary contact recreation use due to elevated bacteria concentrations, specifically *Escherichia coli*. The impairment was listed

under Category 5g meaning that the reach was added by EPA.

**Muddy Fork (Reaches 025 and 027).** EPA added Reach 025 of the Muddy Fork to the 303(d) list as not supporting its primary contact recreation use due to elevated bacteria concentrations, specifically *Escherichia coli*. The impairment was listed under Category 5g meaning that the reach the reach was added by EPA.

EPA added Reach 027 of the Muddy Fork to the 303(d) list as not supporting the aquatic life designated use due to elevated total phosphorus (TP) concentrations. The impairment was listed under Category 5g meaning that the reach the reach was added by EPA.

**Clear Creek (Reach 029).** ADEQ listed Reach 029 of Clear Creek due to elevated fecal coliform concentrations impairing the primary contact recreation designated use. The listed

source of the impairment is urban runoff, and the impairment is listed under Category 5d meaning that additional data is needed to verify the use impairment.

**Osage Creek (Reaches 030 and 930).** EPA added Reach 030 of Osage Creek to the 303(d) list as not supporting the primary contact recreation use due to elevated bacteria concentrations, specifically *Escherichia coli*. The impairment was listed under Category 5g meaning that the reach was added by EPA.

EPA added Reaches 030 and 930 of Osage Creek to the 303(d) list as not supporting the aquatic life designated use due to elevated TP concentrations. The impairment was listed under Category 5g meaning that the reach was added by EPA.

**Little Osage Creek (Reach 930).** EPA added Reach 930 of the Little Osage Creek to the 303(d) list as not supporting the primary contact recreation designated use due to elevated bacteria concentrations, specifically *Escherichia coli*. The impairment was listed under Category 5g meaning that the reach was added by EPA.

**Spring Creek (Reach 931).** EPA added Reach 931 of Spring Creek to the 303(d) list as not supporting the primary contact recreation designated use due to elevated bacteria concentration, specifically *Escherichia coli*. Reach 931 was also listed as not supporting the aquatic life designated use due to elevated concentrations of TP. Both impairments were listed under Category 5g meaning that the reach was added by EPA.

**Sager Creek (Reach 932).** ADEQ listed Reach 932 of Sager Creek due to elevated nitrate (NO<sub>3</sub>) concentrations impairing the drinking water designated use. The listed source of the impairment is municipal point source(s). The impairment is listed under Category 5e meaning that future permit restrictions on the municipal

point source(s) are expected to eliminate the impairment.

**Swepco Lake.** EPA added Swepco Lake to the 303(d) list for unspecified pollutants. The impairment is listed under Category 5d meaning that additional data is needed to verify the use impairment, and its source.

The above list and brief explanations focus on stream reaches and one reservoir listed as impaired for not meeting one of its designated uses; however, these listings do not give a sense as to general water quality trends across the UIRW.

#### GENERAL WATER QUALITY CONDITIONS IN THE UPPER ILLINOIS RIVER WATERSHED

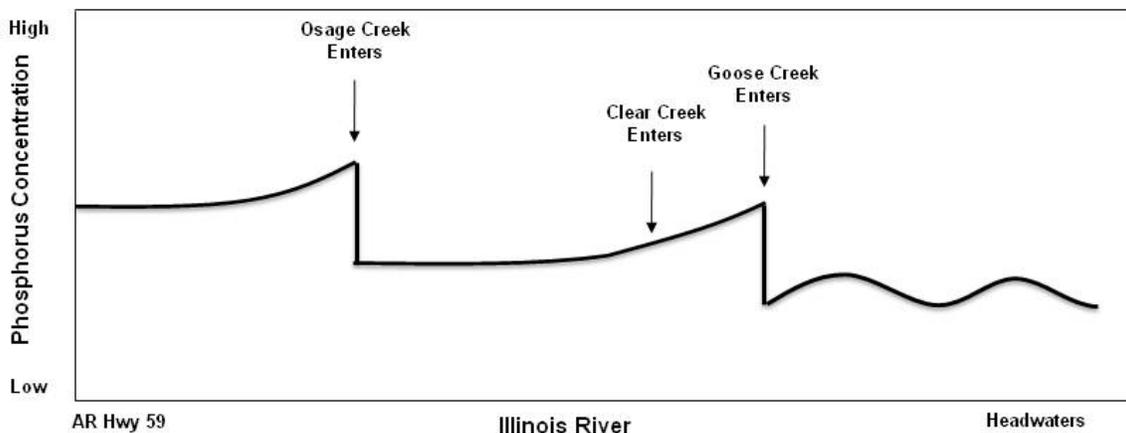
##### *Concentrations, Loads and Sources within the Upper Illinois River Watershed*

Water flowing in the Illinois River and its tributaries comes from groundwater flow, runoff from adjacent land, and from water discharged from pipes such as effluent discharges. Often, stream flow or discharge is discussed in terms of *Base Flow* and *Surface Runoff*. Base flow describes the stream flow contributed from groundwater inflows, as well as water that flows laterally below the soil surface. Surface runoff describes the elevated water levels that occur when storm water runoff from the surrounding land flows into the stream channel. Stream flow is an important aspect of water quality, because the flowing water is the mechanism for downstream transport. During storm events, runoff carries materials from the adjacent landscape into streams, and the elevated stream flow may scour the stream bottom resuspending materials into the overlying water. This may elevate nutrients (nitrogen (N) and phosphorus (P)), sediment and bacteria concentrations in the stream; many constituent concentrations often increase with increases in stream flow. At the same time, higher stream flows can dilute

concentrations of other constituents in streams if the source of the constituent is not from runoff.

The Illinois River has been monitored near the Arkansas–Oklahoma state line for many years, and specifically, constituent loads have been estimated at the Illinois River south of Siloam Springs on Arkansas Highway 59. Several different agencies have collected water samples at this site including ADEQ, the Arkansas Water Resources Center (AWRC), U.S. Geological Survey (USGS), and other entities. The two most important databases come from the AWRC and USGS, where the AWRC has estimated constituent loads based upon water samples collected manually and using automated equipment and the USGS has maintained a stream discharge monitoring station. The water samples and continuous recording of stream flow can be combined to estimate constituent loads at the Illinois River, representing the amounts of N, P and sediment transported from its drainage area in northwest Arkansas. Other sites are being or have been monitored by the AWRC and USGS to estimate constituent loads within the UIRW, including Ballard Creek, Baron Fork, Flint Creek, Moores Creek, and Osage Creek. In 2009, the concentrations of N, P and sediment during base flow conditions near the Arkansas–Oklahoma border ranged from 2.6–5.2 mg L<sup>-1</sup>, 0.05–0.08 mg L<sup>-1</sup>, and 1.6–20.8 mg L<sup>-1</sup>,

respectively (based on data from the HUC 12 monitoring program, Haggard et al., 2010), but historic P concentrations in the Illinois River have been as high as 0.4 mg L<sup>-1</sup> near the Arkansas–Oklahoma border during base flow conditions over the last decade. The concentrations of P show some distinct patterns with distance, e.g., river miles, upstream from the state line (Figure 2), where-as N does not show a strong longitudinal gradient (e.g., pattern from the watershed outlet upstream) and sediment concentrations are especially low during base flow within the Illinois River. The pattern with P concentrations from the Illinois River at Arkansas Highway 59, south of Siloam Springs, upstream to its headwaters near Hogeye show the influence of two specific tributaries—one large tributary, i.e. Osage Creek, and one smaller tributary, i.e. Goose Creek; each tributary significantly increases the P concentration in the Illinois River. P concentrations generally increase from the Arkansas–Oklahoma border upstream to Osage Creek and then decrease substantially upstream from the confluence with Osage Creek. Phosphorus concentrations in the Illinois River generally increase upstream to its confluence with Goose Creek; decreasing again above this smaller tributary, remaining relatively low up-stream to its headwaters. These two tributaries have one thing in common; both receive effluent discharge from major wastewater treatment



**Figure 2.** A conceptual model of the longitudinal gradient in phosphorus concentrations along the Illinois River and how select tributaries influence these concentrations during base flow conditions.

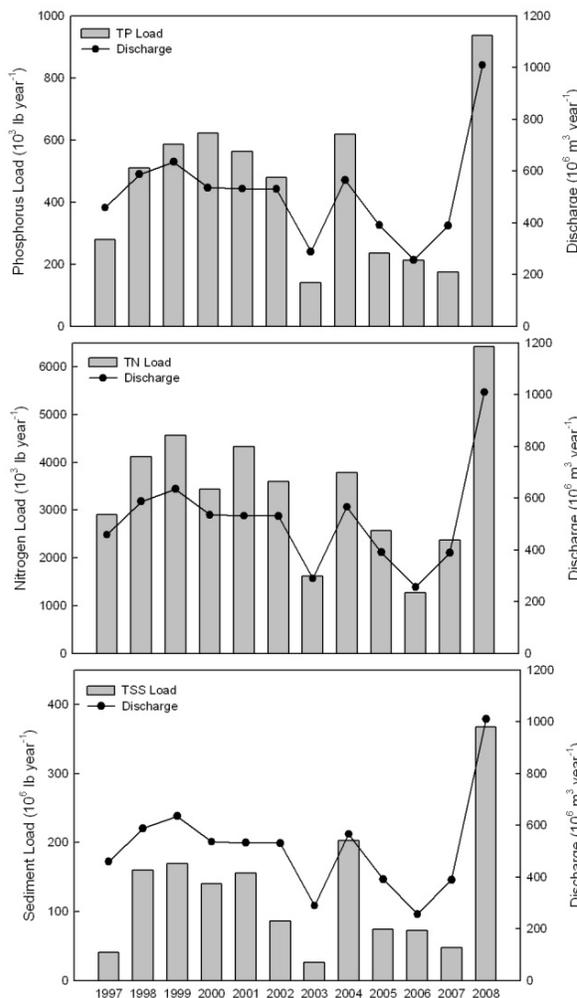
facilities within the UIRW, e.g. effluent discharges from Fayetteville, Rogers and Springdale. The influence of these effluent discharges may be seen in the P concentrations observed during base flow conditions within the Illinois River.

The annual loads for N, P and sediment are variable between years (Figure 3), and these loads generally follow the same pattern as the water volume or discharge within a given year (Massey et al., 2009a). The similar patterns between annual constituent load and water volume illustrate how important the connection is between rainfall, runoff and constituent transport within the UIRW. Therefore, it is difficult to set goals regarding selected percent reductions in annual loads because the transport of the target constituents is strongly tied to climatic conditions and how much rainfall and runoff occurs. The link between rainfall, runoff and constituent loads is further demonstrated in the proportion of the load occurring during base flow or surface runoff conditions, and the partitioning of the loads between stream flows differs between constituents.

*How are Nutrients and Sediment Typically Transported through the Watershed?*

**Nitrogen:** About half of N transport in the Illinois River occurs during base flow conditions, because the majority of N is transported in the form of  $\text{NO}_3$  which is readily soluble and moves easily via ground-water and stormwater runoff from the landscape.

**Phosphorus:** Unlike N, less than 25 per-cent of the annual P load is transported during base flow conditions because the dissolved form of P is highly reactive and it has the ability to bind to sediments within the stream channel delaying its transport downstream; the remaining 75 percent or more of the load is transported during surface runoff conditions from nonpoint sources and the resuspension of P stored within the stream channel.



**Figure 3.** Annual discharge volume and loads of phosphorus, nitrogen and suspended sediments have varied in the Illinois River over the past decade. In the figures above, the bars represent the total load and the line the total discharge during the calendar year (data from Massey et al., 2009a).

**Sediment:** Almost all of the sediment moved downstream within the UIRW will occur during surface runoff conditions, as the Illinois River and its tributaries have low suspended sediment concentration (or turbidity) in the water column during base flow.

The high flows that occur during the storm events have the ability to resuspend sediment and P stored within the fluvial channel, and then transport these materials downstream. The percent of these constituents moved down-

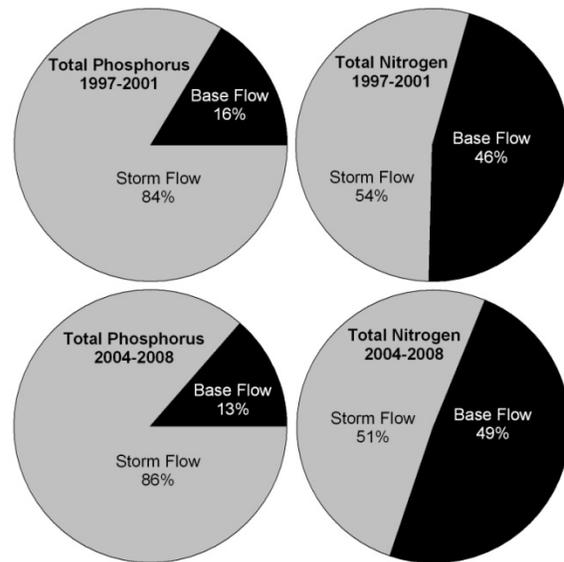
stream during surface runoff conditions depends greatly on the amount of rainfall and runoff that occurs within a given year.

When the Illinois River experiences more water movement downstream during a given year the annual constituent loads will be increased, and the proportion of the load transported during surface runoff conditions will likely be much greater than that occurring during base flow (Figure 4). This dynamic process needs to be kept in mind when evaluating differences between constituent loads on a year to year basis (e.g., see Figure 3), and when designing monitoring programs to measure load reductions resulting from the implementation of best management practices or other watershed management changes.

There are several ways that constituent transport in streams is often presented, including loads, yields and flow-weighted concentrations. While these terms may look technical, the definitions are easily explainable:

- ◆ **Loads** – the total amount of a constituent transported during a time period, e.g., lb year<sup>-1</sup>;
- ◆ **Yield** – the load divided by the size of the watershed, e.g., lb mile<sup>-2</sup> year<sup>-1</sup>; and
- ◆ **Flow-Weighted Concentration** – the load divided by the total amount of runoff, e.g., mg L<sup>-1</sup>.

**Yields.** Yields represent constituent loads on a unit area basis (e.g., lb mile<sup>-2</sup> year<sup>-1</sup>) which allows comparisons across basins of relatively similar size; however, constituent yields are not necessarily independent of the size of the watershed because yields typically increase in magnitude as the watershed gets smaller. So, it is not as simple as comparing yields across watersheds with largely different drainage areas—but yields do provide a value with which to compare across watersheds.



**Figure 4.** Average phosphorus and nitrogen loads transported during base flow and storm events at the Highway 59 Bridge just upstream of the Arkansas-Oklahoma border from 1997-2001 and 2005-2008.

**Flow-Weighted Concentrations.** Flow-weighted concentrations are the constituent loads divided by the water volume during a given period of time (e.g., mg L<sup>-1</sup>), which represents an average concentration for the constituent and theoretically would remove the influence which increased rainfall and runoff would have on constituent loads. So, it would be possible to evaluate how flow-weighted concentrations changed over time where the change in load over time reflects changes in overall stream flow.

In the UIRW, there are many sources that can contribute to constituent loads, particularly for N, P and sediment. The non-point or diffuse sources include runoff from urban areas, agricultural lands and the application of manure, whereas point sources represent a discrete source such as the effluent discharges in this watershed. Basically, the constituent load can be partitioned between nonpoint and point sources when it is assumed that the constituents entering the Illinois River from point sources are conservatively transported down-

stream to the watershed outlet. ‘*Conservatively*’ simply means that the amount input from point sources leaves the watershed on an annual basis. Making this assumption, the proportion of the constituent load from nonpoint sources can be estimated.

The partitioning between nonpoint and point source constituent loads is not as simple when substantial management changes have occurred throughout the time period of interest. For example, P loads from wastewater treatment plants (WWTPs) have been significantly reduced from 2003 to present day. The average P load from WWTPs was  $\sim 200,000$  lb year<sup>-1</sup> from 1997 through 2000, and it decreased over 75 percent after 2003; the average load was only 48,000 lb year<sup>-1</sup> from 2004 through 2006 (Figure 5). This large decrease in WWTP loading was from facility improvements at the Springdale WWTP; the other major WWTPs (e.g. Fayetteville and Rogers) had undergone upgrades to reduce P loads prior to 1997.

Looking at the data from the Illinois River prior to WWTP changes in late 2002, it is possible to estimate that on average approximately 45 percent of the annual P load (on average  $\sim 200,000$  lb year<sup>-1</sup>) may be attributed to inputs from WWTPs (see also Green and Haggard, 2001), particularly the major effluent discharges in Fayetteville, Rogers and especially Springdale. The remaining 55 percent (on average  $\sim 244,000$  lb year<sup>-1</sup>) would be assumed to be from nonpoint sources of P within the UIRW, including urban development, animal agriculture and the management of pastures. Thus, the historic focus should have been on the management of both point and nonpoint sources because of the near equal contributions to annual P loads. The reduction in P concentrations and loads from Springdale’s WWTP effluent discharge was a substantial first step to reducing P output from the UIRW.

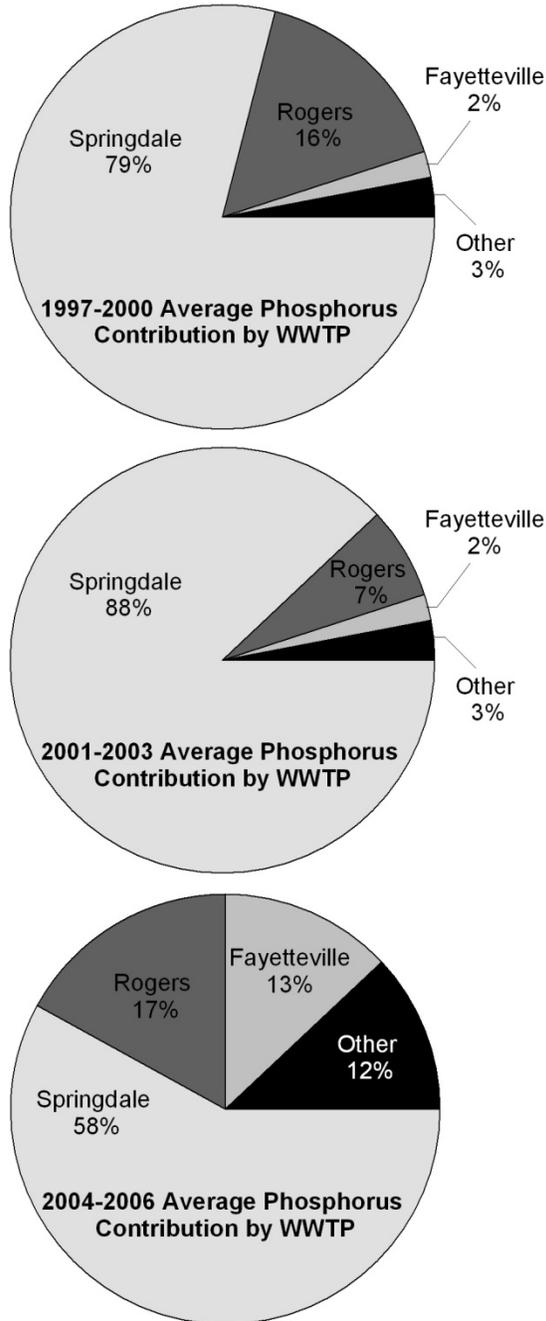
Following the management change and facility improvements at Springdale’s WWTP, the pro-

portion of the P load between nonpoint and point sources changed dramatically with the 75 percent reduction in WWTP P inputs. But, this change in P inputs from effluent discharges also raised questions related to the storage of these historic P inputs within the fluvial channel and especially Lake Frances near the Arkansas–Oklahoma border on the Illinois River. After 2003, the P load from WWTPs was less than 14 percent of the total annual P load on average from 2004 through 2006—when the average annual load at the Illinois River was  $\sim 356,000$  lb year<sup>-1</sup>. However, one important question would be how much of this load transported at the Illinois River would be from P stored from historical WWTP inputs, often referred to as legacy P. Historical P contributions may be stored within the stream channel and definitely Lake Frances along the Illinois River, and this legacy P could be released into the water column during base flow or even resuspended during the high flow events from rainfall and runoff.

#### *What is Legacy Phosphorus?*

This term often refers to dissolved P that has been adsorbed or taken up by bottom sediments in streams, especially downstream from effluent discharges; this stored or legacy P can be released later when dissolved P concentrations in the stream are reduced or during high flow events which scour the stream bottom. Thus, legacy P can delay decreases in stream concentrations to the levels expected by watershed management changes.

Therefore, some of the annual P loads in recent times might represent release of the legacy P within the UIRW—thus, the loads attributed to nonpoint sources may be lower than the estimates presented here. Unfortunately, it is difficult or nearly impossible to trace the exact source of the P in the Illinois River as it crosses from Arkansas into Oklahoma. Watershed-scale assessment models are often used to partition P loads measured in streams into sour-



**Figure 5.** Annual phosphorus load contributed by wastewater treatment plants (WWTPs) in the Upper Illinois River Watershed from 1997-2000, 2001-2003 and 2004-2006. Average annual phosphorus load from the WWTPs was 200,000 lb year<sup>-1</sup> from 1997-2000; 160,000 lb year<sup>-1</sup> from 2001-2003; and 48,000 lb year<sup>-1</sup> from 2004-2006.

ces may be lower than the estimates presented here. Unfortunately, it is difficult or nearly impossible to trace the exact source of the P in the Illinois River as it crosses from Arkansas into Oklahoma. Watershed-scale assessment models are often used to partition P loads measured in streams into sources, such as WWTPs, urban development, pasture and land application of animal manure or commercial fertilizers. However, these models are only as good as the parameters and other inputs used during the simulations and much of the time there is limited measured data available or coarse spatial data used. The use of watershed-scale assessment models should not exclude the use of actual water quality monitoring to measure P concentrations and loads in streams within the UIRW. In fact, these two approaches should be used in concert, as the approach of widespread monitoring and watershed-scale modeling would provide a more complete assessment of the distribution of P sources within the UIRW.

*Surface Water Chemistry across the Upper Illinois River Watershed*

The following sections describe how select constituents in the UIRW are related to the surrounding land use during base flow and surface runoff conditions. Figures 6 and 9 depict how strongly the constituent concentration is related, either positively or negatively, to surrounding land use. Positive relations suggest that constituent concentrations increase as the amount of the selected land use category (e.g., pasture and urban) increases, whereas negative relations show that the constituent tends to decrease as the selected land use categories (e.g., forest and herbaceous areas) increases. In Figures 6 and 9, the r value of the linear trend line indicates the strength of the relation. The closer the r value is to one, the stronger the relationship between land use classification and constituent concentration, where the concentrations from various streams would fall closer to the line showing less variability across the land use category. These

graphs represent a visual display of how constituent concentrations change with land use across the UIRW, and recently collected data were used to develop these graphs.

**Phosphorus.** Streams need nutrients to support plant and animal growth in the ecosystem, but excessive P levels may also become an environmental concern—excess P can lead to algae blooms and the depletion of dissolved oxygen in the water; otherwise known as accelerated eutrophication. P occurs in both dissolved and particulate (within organic matter or attached to sediment or soil particles) forms in stream water. TP describes both the dissolved and particulate P in the water. Dissolved P can be taken up immediately by algae and aquatic plants and is the bioavailable form of P; thus, dissolved P is often removed from the water becoming particulate P in organic matter. On the other hand, particulate P can be a long-term source when organic matter, sediment and soils are deposited in stream beds of lakes and reservoirs; they can slowly release P to overlying waters for several years.

Dissolved P concentrations during base flow conditions in the UIRW range from less than  $0.005 \text{ mg L}^{-1}$ , levels observed in relatively pristine Ozark streams, to historic concentrations greater than  $0.5 \text{ mg L}^{-1}$  (Haggard et al., 2010), levels seen downstream of WWTP effluent discharges before facility improvements. The dissolved P concentrations observed in the UIRW during base flow conditions are strongly correlated to pasture and urban land use within the watershed—the more pasture and urban lands surrounding the stream, the higher the observed dissolved concentrations in the water (Figure 6). Dissolved P concentrations in streams show some variability during base flow conditions and downstream from effluent discharges often decrease with increasing discharge, showing the effects of dilution. During storm events, P concentrations in streams would generally follow the same patterns with land use categories as expressed

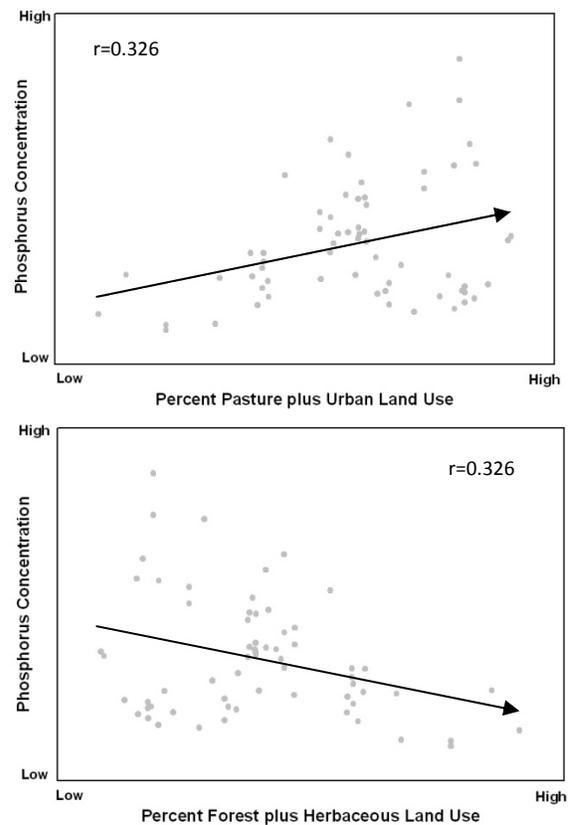


Figure 6. In the Upper Illinois River Watershed, phosphorus concentrations increase in streams as the amount of pasture and urban area within the watershed increases; the opposite relationship is true when streams are surrounded by forests—phosphorus concentrations decrease as the amount of forest area surrounding the streams increases.

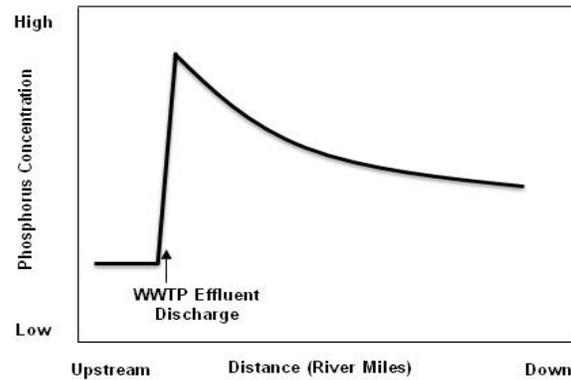
during base flow conditions—however, the strength of the relation might be slightly less.

Total P concentrations in stream water during base flow and storm flow also increase as the amount of pasture and urban land surrounding the water increases. Total P concentrations in streams draining the UIRW range from  $0.006 \text{ mg L}^{-1}$  to historic concentrations greater than  $0.5 \text{ mg L}^{-1}$  during base flow conditions and from  $0.1 \text{ mg L}^{-1}$  to over  $0.8 \text{ mg L}^{-1}$  during storm flow (Haggard et al., 2010). However, TP concentrations are often more variable between streams across land use gradients, and even within individual streams reflecting changes of P

uptake into organic matter, phosphorus storage within sediments, and the effect of stream discharge on P concentrations. Dissolved P concentrations decrease, increase or remain similar during storm events compared to base flow conditions while TP concentrations increase with increasing stream flow. The dynamics of P transport and uptake add to the variability in TP concentrations observed throughout the streams draining the UIRW.

Point sources also have an influence on P concentrations in streams within the UIRW, especially during base flow conditions. In fact, streams downstream from WWTPs often have P concentrations that are greater than what concentrations would usually be for a watershed with its urban and agricultural land use signature. Four major WWTPs in Fayetteville, Springdale, Rogers, and Siloam Springs and several minor plants (Gentry, Prairie Grove, Lincoln, and other locations) discharge their treated effluent to tributaries to the Illinois River. P concentrations increase downstream from these effluent discharges compared to that measured upstream from the effluent discharge (see Figure 7). Permit limits have been established for the amount of TP that the major WWTPs can discharge in treated effluent, which are based on a discharge concentration threshold of  $1 \text{ mg L}^{-1}$  for the major four WWTPs. Before these limits, some plants were discharging effluent with concentrations over  $10 \text{ mg L}^{-1}$  TP and elevated P concentration in the Illinois River could be traced over 28 river miles upstream to one individual WWTP, i.e. Springdale's facility, in spring 2002. Prior to 2003, P concentrations at the Illinois River near the Arkansas–Oklahoma border were often as high as  $0.4 \text{ mg L}^{-1}$  during base flow conditions in the summertime.

But since the late 1990's and early 2000's, most of the major WWTP have undergone plant upgrades which have allowed the facilities to meet established permit limits and significantly reduced P concentrations in the effluent dis-



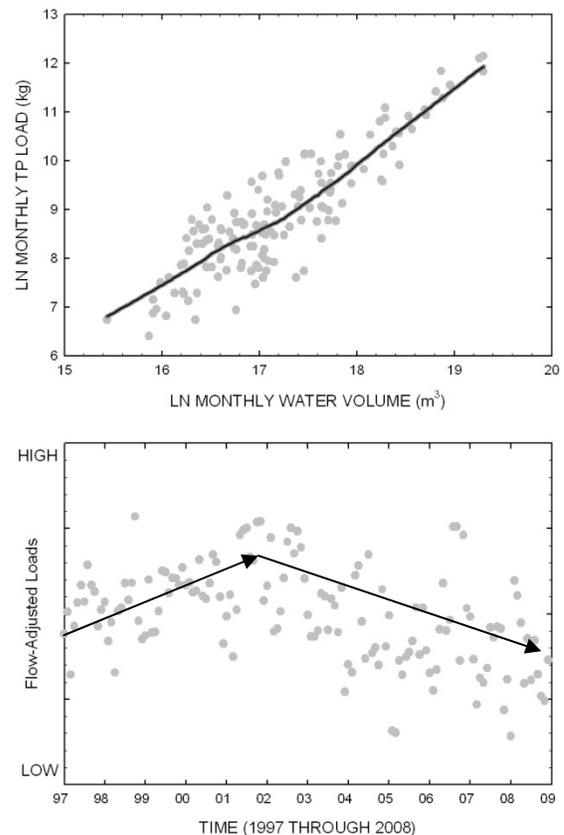
**Figure 7.** Conceptual model of the effect of wastewater treatment plants in the Upper Illinois River Watershed. Effluent discharges increase phosphorus concentrations in streams and then the concentrations generally decrease with increasing distance downstream from the point source. Phosphorus concentrations often stay greater than upstream or background concentrations for several miles down-stream.

charge and the streams receiving these discharges. Specifically, Springdale's facility made substantial improvements reducing effluent concentrations from as high as  $10 \text{ mg L}^{-1}$  in 2002 to less than  $0.5 \text{ mg L}^{-1}$  by the end of 2003. Springdale's effluent P concentrations have remained low (relative to historic effluent concentrations) averaging less than  $0.4 \text{ mg L}^{-1}$  in recent years, and these reductions in effluent concentrations have resulted in subsequent reductions in P concentrations within Spring Creek, Osage Creek and even the Illinois River (Haggard, 2005). The improvement in P management by all the major WWTPs within the UIRW have contributed to the decrease in base flow concentrations observed over the last decade or more. However, bottom sediments within the fluvial channel of the streams downstream from the effluent discharges have stored much of the dissolved P released from the WWTPs (e.g., legacy P), because as dissolved P moves downstream it may bind to sediments or even be consumed by microbes living on the stream bottom. So, even though WWTPs continue to reduce the amount P these facilities discharge, the sediments and or organic matter may continue to slowly release P to the water

column making the WWTP reductions less in the streams compared to that measured directly in the effluent. It is then likely that P concentrations at the Illinois River near the state line will continue to slowly decrease until the majority of this legacy P has been released from the stream bottom sediments and then transported downstream (See Haggard, 2010).

P concentrations during base flow conditions at the Illinois River have decreased significantly over the last decade, and a distinct seasonal pattern is visible which relates to the dilution of the WWTP effluent discharge during elevated base flow during the wet season, e.g. late winter through spring. P concentrations are least at the Illinois River during elevated base flow conditions, where concentrations have reduced from more than  $0.2 \text{ mg L}^{-1}$  observed in spring 2002 to less than  $0.05 \text{ mg L}^{-1}$  observed in spring 2004 and each year elevated seasonal base flow discharge was observed since (Haggard, 2005). So, the current message would be that P concentrations in the Illinois River flowing from Arkansas into Oklahoma have significantly decreased over the last decade—however, further decreases are likely possible with the implementation of best management practices within the UIRW, particularly targeted at riparian areas that are not currently forested, because P can be taken up by plants or infiltrated within the riparian zone. However, in 2008 the EPA listed four stream segments within the UIRW as being impaired due to elevated phosphorus concentrations despite the fact that ADEQ does not have numeric criteria for P in streams and that ADEQ did not list those stream reaches for P within the submitted 303(d) list to EPA.

The best way to determine how P loads have changed over time is to look at trends in monthly P loads normalized for changes in monthly water volumes, since loads are closely tied to discharge volume at the Illinois River (Figure 8). The residuals from the locally weighted scatterplot smoothing (LOESS) tech-



**Figure 8.** Monthly phosphorus loads as a function of monthly discharge at the Illinois River near the Arkansas and Oklahoma border, and the change in flow adjusted loads over time from 1997 through 2008 (data from Haggard, 2010).

nique represent the monthly loads as adjusted for changes in monthly water volumes, referred to as flow-adjusted loads. The flow adjusted loads show a distinct pattern in P over time where loads increased from 1997 to 2002 and then decreased from 2002 to 2008 (Haggard, 2010). This is consistent with the changes in P management at the wastewater treatments within the watershed, as well as other changes in poultry litter application, management and transport in this watershed.

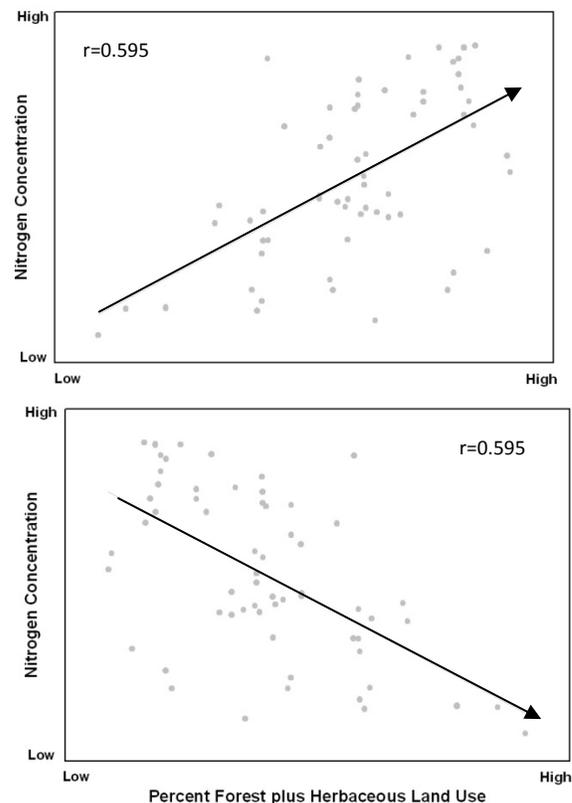
**Nitrogen.** Like P, N is also a necessary component for plant and animal growth in aquatic ecosystems, but excessive concentrations of N can also lead to water quality concerns. While P, tends to be more of a regional concern,

nitrogen is also the focus nationally within the Mississippi River Basin and its influence on Gulf hypoxia as recently reported. In the UIRW, N is contributed by both point and non-point sources (e.g., groundwater inflows and surface runoff from agriculture and fertilizers and WWTP effluent discharges). N, unlike P, may be removed from aquatic systems through the process of denitrification. Despite this potential loss pathway, approximately 3,300,000 lbs (i.e., 1,500,000 kg) of N are exported from the watershed annually which is basically split evenly between base flow conditions and high flow events during storms.

NO<sub>3</sub> is usually the most abundant form of N in water, and it is generally much more mobile or less reactive than dissolved P. NO<sub>3</sub> concentrations in streams often show a seasonal pattern reflective of seasonal base flow discharge and the potential for denitrification as water moves through groundwater inflows and downstream. The general pattern in stream NO<sub>3</sub> concentrations is elevated concentrations during spring when seasonal base flow discharge is greater and lower concentrations during summer when biological activity is high. Because NO<sub>3</sub> is more mobile, N concentrations generally show stronger relationships with watershed land use than P. NO<sub>3</sub> concentrations generally increase as the percentage of agricultural land increases and decreases as the percentage of forest land increases (Figure 9); this relation holds true during both base flow conditions and storm flow events. NO<sub>3</sub> concentrations in streams within the UIRW generally range from less than 0.5 mg L<sup>-1</sup> to more than 5.0 mg L<sup>-1</sup> (as N) during storm flow (based on data from Haggard et al., 2010). ADEQ does not have numeric N criteria in streams, other than EPA established a maximum contaminant level of 10 mg L<sup>-1</sup> for NO<sub>3</sub> (as N) in drinking water—streams rarely, if ever, exceed this water quality standard in the UIRW.

Total N concentrations (TN; particulate and dissolved N) in the streams draining the watershed typically range from approximately 0.5 mg L<sup>-1</sup> to more than 5.0 mg L<sup>-1</sup> during base flow and 0.5 mg L<sup>-1</sup> to more than 5.0 mg L<sup>-1</sup> during storm flow (based on data from Haggard et al., 2010). Like NO<sub>3</sub>, TN concentrations increase as pasture and urban land use increases and decrease as forest land use increases (Figure 9) and the strength of this relation is often similar to that of NO<sub>3</sub>, because NO<sub>3</sub> generally makes up the largest fraction of TN.

Again, this relation between TN and the various land use categories holds true during base flow conditions and even elevated discharge occurring during storm events.



**Figure 9.** In the Upper Illinois River Watershed, stream nitrogen concentrations increase as the amount of pasture and urban areas increases within the watershed; nitrogen levels typically decrease in streams as forest area increases within its catchment or riparian zone (data from Haggard et al., 2010 and Massey et al., 2009b).

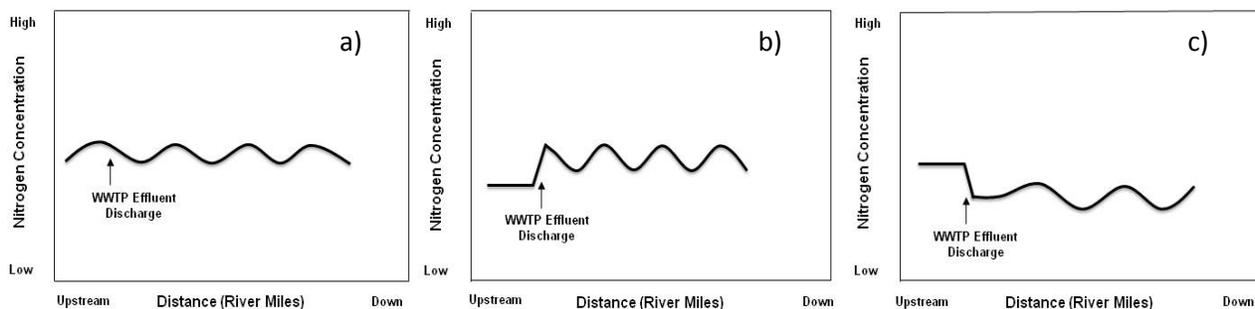
Point sources such as WWTPs also have the ability to influence N concentrations in streams, although the impact of effluent discharges may be highly variable and would be dependent on the background or upstream N concentrations. The effluent discharge might (figure 10):

- a) Have relatively little influence on the observed N concentrations because effluent and the stream have relatively similar concentrations;
- b) Increase the observed N concentrations, because the effluent has more N in it than the stream water; however, the gradient with increasing distance downstream from the effluent discharge does not necessarily mimic that of P (or chloride); or
- c) Decrease the observed N concentrations, because the background concentrations in the stream might be greater than that seen in the effluent.

The majority of the N released in effluent discharge is in the form of  $\text{NO}_3$  and organic N, especially in the major WWTPs—whereas smaller facilities may discharge more N in the reduced form such as dissolved ammonia ( $\text{NH}_3$ ) and organic N. This reduced N is usually quickly converted to  $\text{NO}_3$  in aquatic systems through nitrification, a natural biologically-mediated process. Within the UIRW, the impact of WWTP effluent discharge on stream N concentrations

is variable (see Figure 10) and the N concentrations observed further downstream are more reflective of landscape influences and less influenced by WWTPs.

**Chloride.** Chloride (Cl) is a conservative element in streams, meaning that Cl does not react with anything within the stream channel and it is simply transported downstream with the flowing water after it enters the stream. Why should we measure Cl in streams? Well, Cl is an excellent indicator of human impacts on streams within watersheds because of its conservative nature in streams—the various sources of Cl that might enter streams includes salts used to deice roads during winter, animal manure and commercial fertilizer applied to the landscape, and effluent discharges from WWTPs. The range in Cl concentrations during base flow conditions within the streams draining the UIRW was from  $4.0 \text{ mg L}^{-1}$  in a primarily forested stream to  $8.0 \text{ mg L}^{-1}$  in a stream draining a watershed with primarily pasture land use to  $22.0 \text{ mg L}^{-1}$  downstream an effluent discharge (based on data from Haggard et al., 2010). Within the UIRW, stream Cl concentrations generally increase as the proportion of pasture and urban development increases within the watershed, as likewise concentrations decrease with more forest and herbaceous lands within the catchment.

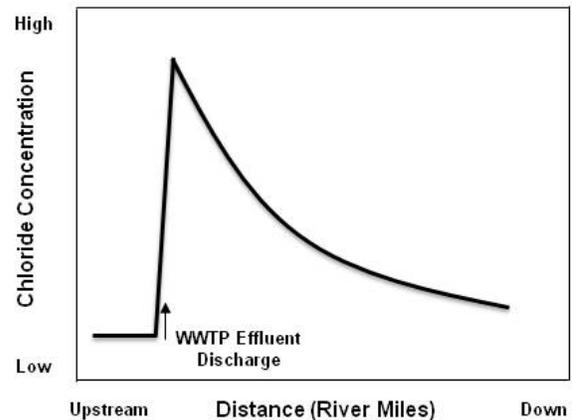


**Figure 10.** Conceptual model of the effect of WWTP effluent discharge on nitrogen concentrations in streams can be highly variable, where the effluent might have no influence, increase or even decrease observed concentrations downstream; nitrogen concentrations much further downstream are generally more reflective of the influence of the catchment land use than the effluent discharge.

Regulation 2 from ADEQ states that monthly average Cl concentrations should not exceed 20 mg L<sup>-1</sup> in the Illinois River itself, and Cl concentrations are generally less than 10 mg L<sup>-1</sup>. Effluent discharge from WWTPs often have high concentrations of Cl, because chlorine is used as a disinfection agent during the treatment process. Chloride concentrations are often as high as 50 mg L<sup>-1</sup> downstream from some effluent discharges and eventually return to background levels, because of dilution from groundwater and other lateral inflows from other streams (Figure 11).

**Sediments and Turbidity.** Sediment is the loose sand, clay, silt and other particles that settle to the bottom of the streams or sometimes stay suspended within the water column, and the EPA lists sediment as the most common pollutant in rivers and streams across the US. The natural process of erosion causes some sedimentation to occur, but accelerated erosion from human activities and alterations of the hydrologic cycle (e.g., peak stream flow) contributes much more sediment to waterbodies than natural processes. In fact, the top three sources of sediment in the northwest Arkansas are all linked to human activities, such as urban and sub-urban land uses.

Sediment is commonly measured as total suspended solids (TSS) within the water column of streams for water quality assessment. In the UIRW, TSS concentrations are weakly related to surrounding land use suggesting that TSS concentrations increase as the percentage of pasture and urban area increases within a watershed; the opposite relation is true for percent forest. Overall, TSS concentrations during base flow conditions in the UIRW are low relative to other waters across the state and the U.S. Average TSS concentrations range from 0.1 mg L<sup>-1</sup> to almost 20 mg L<sup>-1</sup> throughout the UIRW during base flow conditions and as high as 500 mg L<sup>-1</sup> during storm flow (based on data from Haggard et al., 2010). Sediment concentrations



**Figure 11.** Wastewater treatment plant effluent increases chloride concentrations in tributaries to the Illinois River; elevated chloride concentrations persist for several miles downstream from the effluent discharge point, showing the length of influence and how dilution may decrease concentrations.

in stream water increase with increasing stream flow, because the faster water moves the more sediment it can carry (i.e., carrying capacity) and the more force it has to cause erosion of the streambank and channel. On average, the UIRW exports approximately 46,000,000 lbs TSS annually, ranging from 12,000,000 lbs during relatively dry years to more than 70,000,000 lbs during wet years (data from Massey et al., 2009a).

Sediments may influence water quality of streams in two different ways—1) turbidity within the water column of streams, and 2) sediment embeddedness of the stream bottom. Turbidity is an indicator of the amount of solids suspended in water, whether algae, detritus (dead organic matter) or inorganic, suspended sediment. Turbidity measures the amount of light scattered within a water sample—the more suspended particles, the more light is scattered. Turbidity is relatively easy to measure and is measured in Nephelometric Turbidity Units (NTUs) where higher values indicate more cloudy, turbid waters.

Turbidity levels in streams vary naturally based on the stream characteristics (e.g., flow, bank slope, riparian soils), although human activities

can play an important role. Regulation 2 from ADEQ sets turbidity limits during base flow conditions at 10 NTUs for the Illinois River and its tributaries, which reflects the relative natural clarity of streams in this region of the Ozark Highlands and Boston Mountains. Average turbidity measurements in the Illinois River and its tributaries are below 10 NTUs, ranging from less than one to 8 NTUs during base flow conditions across the UIRW (data from Haggard et al., 2010). If turbidity was a problem within the UIRW, then it would be related to its impacts on the biological community of the streams as high levels of turbidity may impact the aquatic ecosystem.

High turbidity may cause light limitation of algal and plant growth within the stream and the decreased clarity may interfere with fish and aquatic insects that feed by sight. Ultimately, the increased turbidity would alter the biological community from its natural conditions, i.e., its aquatic life designated use.

When the sediment settles to the stream bottom, it may cause embeddedness—meaning that there are a lot of fine sediments in between the larger gravel substrate on the stream bottom. These smaller size or fine sediments fill in the spaces between the larger gravel, limiting the suitable habitat for some fish and aquatic insects. A few studies in the UIRW have suggested that the designated beneficial use of aquatic life may be threatened by increased sedimentation, or siltation, within the stream channel, which changes bottom habitat and the biological community from its natural assemblage. In fact, two stream reaches along the Illinois River are on the 303(d) for siltation as placed by ADEQ.

**Bacteria.** Fecal coliform bacteria live in the intestines of warm-blooded animals, and the presence of these bacteria in streams is indicative of contamination by fecal matter from some source—either pets, wildlife, animal manure, wastewater treatment plants and or septic

systems. Although fecal bacteria are not necessarily pathogens (i.e., disease causing organisms), these bacteria may indicate the presence of pathogenic organisms. For example, *Escherichia coli* (*E. coli*) is a type of fecal coliform that is an indicator organism for other pathogens that may be present in feces. Regulation 2 from ADEQ provides information on the water quality standards related to fecal coliform bacteria, and *E. coli*. The water quality standard specific to *E. coli* is between May 1 and September 30, *E. coli* colony counts should not exceed a geometric mean of more than 126 colonies per 100 mL or a monthly maximum value of not more than 410 colonies per 100 mL. During the remainder of the calendar year, *E. coli* values should not exceed the geometric mean of 630 colonies per 100 mL or a monthly maximum of 2050 colonies per 100 mL.

Overall, there is relatively little bacterial data available from the streams draining the UIRW—or at least little data widely available to the general public. Little information is also available from the scientific literature; however, the publications available in the general literature would suggest that the potential bacterial sources include land application of animal manure (e.g., poultry litter), direct deposition of manure from cattle or wildlife within the stream or riparian corridor and septic systems or other wastewater drainage systems within the watershed. It is not likely that effluent discharges from municipal WWTPs would be a major source of fecal coliform, because each facility would have more stringent permitted levels for coliform in the effluent discharge than that allowable in the streams under secondary or primary contact standards. Several stream reaches have been included on the 303(d) list for bacteria (i.e., pathogens) by ADEQ and EPA, where ADEQ included Clear Creek and EPA added reaches along the Baron Fork, Illinois River, Little Osage Creek and the Muddy Fork to the list.

**Biological Data.** Biological monitoring is a valuable tool for watershed assessment and management, because biological organisms integrate the cumulative impacts from point and nonpoint sources. Thus, biological monitoring provides a more complete picture of environmental condition from its habitat to general physico-chemical conditions than simple grab water samples alone. Fish, aquatic insects (i.e., macroinvertebrates), and algae are commonly used in biological monitoring. These organisms provide a robust measure of the integrated chemical, physical and biological condition of the water body.

The community structure of the fish, aquatic insects, and algae are evaluated to determine what particular species are present. Then, assessments of the biological community would be based on structure and function:

- ◆ **Structure:** The composition of the biological community looking at the number of organisms, individual species, and distribution of populations
- ◆ **Function:** The biological community based upon the feeding characteristics of groups of organisms and how the biological communities consume organic carbon (e.g., periphyton, plants, decaying organic matter or other animals) and dissolved oxygen over several days.

Both structural and functional indicators of the biological community should be used in the overall assessment, and the most common approach to integrating these two factors together would be the Rapid Bioassessment Protocol (RBP) developed and then revised by the EPA. This is the type of assessment often used to determine if a water body is meeting its designated beneficial use of aquatic life per ADEQ's Regulation 2.

There have been few published or available large-scale evaluations of the biological community integrating chemical and physical

assessments within the UIRW, but these study and other ancillary projects have suggested that biological communities and ecological integrity are threatened by alteration of the landscape, modification of hydrologic flow regime, loss of riparian zones, and enhanced primary production from nutrient enrichment.

The physical changes occurring in streams within the UIRW are that the stream bottoms are shifting from gravel-cobble substrate (i.e., larger bottom material) to sand-gravel (i.e., large material filled in with finer sediments), and that the channel morphology (i.e., structure) is shifting from riffle-pools to runs. The role of stream habitat, especially riparian zones, in protecting and maintaining aquatic life use in the UIRW cannot be overstated, as it is the riparian zone which controls how streams might express nutrient-enriched (or eutrophic) conditions. The lack of a riparian zone would allow an enriched stream to have increased algal growth and shifts in algal communities to filamentous organisms, which then shifts the fish and aquatic insect communities to those that may not support the designated aquatic life use.

#### *Groundwater*

Nutrient and bacteria concentrations in groundwater are affected by hydrologic and geologic factors. The Illinois River Watershed largely drains the Springfield Plateau area, which is characterized by karst geology where there are frequent solution channels, sinkholes, caves, and springs. These subsurface pathways provide a quick and close transportation between surface and groundwater, and can rapidly introduce constituents found in surface water into the groundwater system during rainfall events (Tables 4 and 5).

Like in surface water, nutrient and bacteria concentrations in groundwater are often related to nearby land use, where NO<sub>3</sub> concentrations in groundwater are generally greater under pastures compared to other land uses

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**Table 4.** Physico-chemical parameters of groundwater in the Upper Illinois River Watershed

Land use	Water Temperature (°C)		pH		Conductivity ( $\mu\text{s cm}^{-1}$ )	
	Range	Mean	Range	Mean	Range	Mean
Pasture	12.8-25.0	15.0	6.0-7.4	6.8	214-258	329.1
Mixed	14.1-21.0	16.4	6.6-7.5	7.1	102-522	280.7
Other	15.5-16.7	16.1	7.1-8.9	6.0	322-405	361.1

**Table 5.** Constituent concentrations in groundwater across Benton and Washington Counties, northwest Arkansas

Land use	Ammonia		Nitrate		Phosphorus		Chloride	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Pasture	<0.01-0.15	0.02	<0.05-8.30	2.13	<0.01-0.17	0.01	1.2-28.0	6.6
Mixed	<0.01-0.11	0.02	<0.05-4.90	0.28	<0.01-0.08	0.02	1.2-61.0	6.0
Other	<0.01	<0.01	1.40-3.90	2.34	<0.01	<0.01	2.7-7.9	4.6

(e.g., forested areas). Because of the close interaction between surface water and groundwater in the area, springs exhibit elevated concentrations of  $\text{NO}_3$  but well below the drinking water criterion for  $\text{NO}_3$  of  $10 \text{ mg L}^{-1}$  (as N). For the same reason, springs in the area often exhibit elevated bacteria (fecal coliform) levels during storm events as suggested by studies which have followed the transport of bacteria through groundwater into springs within the UIRW. The presence of karst also increases the risk of introduction of pesticide and herbicides into groundwater. While the use of pesticides and herbicides in the region is minimal, several herbicides have been detected in groundwater samples including atrazine, prometon, desethyl-atrazine and simazine at concentrations below Maximum Contaminant Levels (MCL) or health advisory levels set by the EPA for drinking water. These compounds were more prevalent in agricultural areas than in forested areas.

Groundwater also supports unique cave ecosystems in the karst terrain of northwest Arkansas. The Cave Springs Cave Natural Area supports several endangered species and other species of concern; the Ozarks has the largest population of the threatened Ozark cavefish (*Amblyopsis rosael*). The presence of these endangered species and other aquatic species of concerns have designated several areas within the UIRW as Ecologically Sensitive Waters (ESWs) as defined by ADEQ.

### EXISTING WATER QUALITY DATA IN THE ILLINOIS RIVER WATERSHED

The waterbodies in the UIRW are monitored by agencies including Arkansas Department of Environmental Quality, U.S. Geological Survey, Arkansas Water Resources Center, municipalities, and volunteers. The collected data is used to characterize waters, identify trends in water quality over time, identify emerging problems, predict future problems, and determine if pollution control programs are working.

#### *Arkansas Department of Environmental Quality*

ADEQ has been monitoring select reaches of the Illinois River and its tributaries since the early 1990's. ADEQ's surface water quality monitoring stations data files are available on the web at [http://www.adeq.state.ar.us/techsvs/water\\_quality/monitors.asp](http://www.adeq.state.ar.us/techsvs/water_quality/monitors.asp).

#### *U.S. Geological Survey*

The U.S. Geological Survey (USGS) has been monitoring several of the same sites that ADEQ monitors, as well as additional sites in the watershed. Data from the USGS is available online at the USGS National Water Quality Assessment Data Warehouse (NAWQA; [http://infotrek.er.usgs.gov/traverse/f?p=NAWQA:H\\_OME:0](http://infotrek.er.usgs.gov/traverse/f?p=NAWQA:H_OME:0)). The USGS measures stream discharge continuously at seven sites within the UIRW.

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These sites include Mud Creek tributary at Township Road (USGS Station No. 07194809), on Osage Creek near Elm Springs (USGS Station No. 07195000), on the Baron Fork near Dutch Mills (USGS Station No. 07196900), on Flint Creek near West Siloam Springs (USGS Station No. 07195855) and at Springtown (USGS No. 07195800), on the Illinois River at Arkansas Highway 59 (USGS Station No. 07195430) and at Savoy (USGS Station No. 07194800).

### *Arkansas Water Resources Center*

The AWRC has been monitoring water quality at the Illinois River since 1995 and at Ballard Creek, a tributary to the Illinois River since 2002. The available data is viewable online at <http://www.uark.edu/depts/awrc/pubs-MS.C.htm>.

### **HISTORIC AND ONGOING STUDIES OF WATER QUALITY IN THE UPPER ILLINOIS RIVER WATERSHED**

#### *Literature Cited and Completed Scientific Studies*

Water quality studies in the UIRW primarily began in the early 1980s and have become more frequent and in-depth as the watershed has changed from its natural characteristics to an urban and agricultural dominated watershed; the following are citations of water quality studies that have been completed in the UIRW.

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- ◆ Green, W.R. and B.E. Haggard. 2001. Phosphorus and Nitrogen Concentrations and Loads at Illinois River South of Siloam Springs, Arkansas, 1997-1999. U.S. Geological Survey, Water Resources Investigations Report No. 4217.
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# **Nutrient Concentrations and Yields in Undeveloped Stream Basins of the United States**

*Gregory M. Clark, David K. Mueller, and M. Alisa Mast*

## **Abstract**

Data from 85 sites across the United States were used to estimate concentrations and yields of selected nutrients in streams draining relatively undeveloped basins. Flow-weighted concentrations during 1990-95 were generally low with median basin concentrations of 0.020, 0.087, 0.26, 0.010, and 0.022 milligrams per liter (mg/L) for ammonia as N, nitrate as N, total nitrogen, orthophosphate as P, and total phosphorus, respectively. The flow-weighted concentration of nitrate exceeded 0.6 mg/L in only three basins. Total nitrogen exceeded 1 mg/L in only four basins, and total phosphorus exceeded 0.1 mg/L in only four basins. The median annual basin yield of ammonia as N, nitrate as N, total nitrogen, orthophosphate as P, and total phosphorus was 8.1, 26, 86, 2.8, and 8.5 kilograms per square kilometer, respectively. Concentrations and yields of nitrate tended to be highest in northeastern and mid-Atlantic coastal states and correlated well with areas of high atmospheric nitrogen deposition. Concentrations and yields of total nitrogen were highest in the southeastern part of the nation and in parts of the upper Midwest. In the northeast, nitrate was generally the predominant form of nitrogen, and in the southeast and parts of the upper Midwest, organic nitrogen was the dominant form. Concentrations of total phosphorus were generally highest in the Rocky Mountain and Central Plain states.

## **Introduction**

Population growth and industrial activities in the United States during the 20<sup>th</sup> century have affected, and will continue to affect the quality of the nation's water resources. Although natural processes and anthropogenic activities affect water quality in streams, past water-quality studies primarily have been designed to evaluate the anthropogenic affects. To fully evaluate the extent of anthropogenic activities, however, it is also important to describe water quality in streams draining relatively undeveloped environments and to understand the factors that control it. Natural variations in water quality occur among different regions of the nation because of differences in geology, vegetation, and climate, yet standards typically do not account for these differences. For example, some of the most pristine streams in parts of the southeastern United States have dissolved oxygen concentrations that are substandard according to national water-quality criteria (Omernik and Griffith, 1991). Attempting to meet criteria in parts of the nation where they may not be attainable is technically and economically unrealistic. Thus, an understanding of regional patterns in natural water quality provides for a more valid baseline for setting objective, attainable water-quality goals and ultimately will provide a more rigorous tool for separating natural and anthropogenic factors affecting water quality in streams across the nation.

The chemistry of natural waters varies both spatially and temporally and is controlled by factors such as atmospheric deposition, biological activity in soils, and chemical weathering of soils and bedrock (Likens and others, 1977). Approaches used to

describe regional water-quality characteristics in natural environments include physiographic provinces (Biesecker and Leifeste, 1975), hydrologic drainage basins (Smith, 1969), and ecoregions (Omernik and Gallant, 1986; Hughes and Larsen, 1988; Larsen and others, 1988). Although these frameworks are useful for describing natural spatial variations that occur in different regions of the nation, water quality in natural environments also may be influenced by anthropogenic factors that cross basin and regional boundaries. For example, atmospheric deposition introduces sulfur, nitrogen, base cations, and acidity to relatively undeveloped basins in the northeastern United States (Likens and others, 1996), which in turn may influence the weathering rate and buffering capacity of underlying soils and bedrock (Murdoch and others, 1998; Clow and Mast, 1999; Lawrence and Huntington, 1999). Stoddard (1994) and Williams and others (1996) suggest that the biologic demand for nitrogen has been exceeded by atmospheric inputs in a number of forested basins in the eastern United States and in the Rocky Mountains of Colorado. Atmospheric deposition of nitrogen can account for nearly all the downstream nitrogen load in some Midwestern and Northeastern streams (Smith and others, 1987; Puckett, 1995). Other studies in the northeast have documented the relation between air temperature and nitrogen mineralization and suggest that climate change may be influencing nitrification rates in undeveloped basins where excess nitrogen is accumulating (Murdoch and others, 1998).

The purpose of this paper is to evaluate concentrations and yields of selected nutrients (nitrogen and phosphorus species) in streams draining relatively undeveloped basins across the nation and to identify broad regional and national patterns. No attempt was made to describe concentrations and yields in relation to a defined regional or national framework, such as physiographic province, hydrologic drainage basin, or ecoregion. Nutrient data collected as part of three U. S. Geological Survey (USGS) programs were used for this assessment. To ensure data comparability, differences in selected physical and nutrient characteristics between the basins in each program were assessed. Nutrients were selected for study because of their long-standing role not only as constituents of concern for aquatic health in streams and coastal areas of the nation, but also in ground water. Nitrogen and phosphorus are known to be primary factors that can initiate the excessive growth of algae and macrophytes in freshwater systems. Under the guidelines of the Clean Water Action Plan, the U. S. Environmental Protection Agency (USEPA) is developing regional nutrient criteria for surface-water bodies across the nation. Findings from this assessment will provide baseline data as part of that effort.

## **Methods**

Nutrient data collected from 85 streams draining relatively undeveloped basins from across the United States were used for this assessment. Basins were selected from three programs of the USGS; the Hydrologic Benchmark Network (HBN), the National Water-Quality Assessment (NAWQA), and the Research Program. Drainage basins of size useful to characterize regional patterns in natural conditions are difficult to find or are not being monitored in many parts of the nation. In order to fill these gaps, some of the basins used for this assessment may be slightly affected by residential development, selective logging, grazing, and other agricultural disturbances. Even with the inclusion of these minimally affected basins, some areas of the nation are poorly represented in this

assessment. This is especially apparent in the “Corn Belt” region of the upper Midwest and in the Southern Plains states of Kansas, Oklahoma, and Texas (figure 1).

The HBN program was initiated in 1958 to track water-quality trends in streams draining basins free from anthropogenic influence and to study cause and effect relationships between various physiographic, meteorologic, and hydrologic variables (Cobb and Biesecker, 1971). The HBN network is primarily comprised of relatively undeveloped basins encompassing a wide variety of natural environments from across the nation (Clark and others, 1999; Mast and Turk, 1999a,b). To ensure minimal anthropogenic affects, many of the HBN basins are in wilderness areas, national and state parks, national forests, and in areas set aside for scientific study. For this assessment, 43 basins from the HBN network were used, with individual basins ranging in area from about 6.1 to about 2,500 km<sup>2</sup>.

The USGS NAWQA program, initiated in 1990, was designed to identify and describe major factors that affect observed water-quality conditions over large spatial and temporal scales (Hirsch and others, 1988). Thus, streams sampled as part of the NAWQA represent water-quality conditions influenced by a wide range of land- and water-use conditions. Of the 200 stream sites sampled as part of the NAWQA during 1992-95, 22 drain relatively undeveloped basins. These latter sites were included in this assessment (figure 1). The range in area of NAWQA basins included in this study is similar to the range in area of the HBN basins, 18 to about 2,700 km<sup>2</sup>.

The 20 USGS research basins used in this assessment were selected from the Water, Energy, and Biogeochemical Budgets (WEBB) program (USGS, 1999a), the Long Term Ecological Research (LTER) program, and other USGS research (O. Bricker, D. Burns, P. Murdoch, and K. Rice, USGS, written commun., 1999). The research basins included in this assessment are predominantly located in the Appalachian and Rocky Mountains (figure 1). The periods of data collection for the research basins varied, but all research data used for this assessment were collected during water years (October 1 to September 30) 1982-97. The primary focus of study in the research basins used in this assessment is the affects of atmospheric deposition on biogeochemical cycling within small, undisturbed watersheds. The research basins used in this assessment range in size from 0.1 to about 22 km<sup>2</sup> and are about 1-2 orders of magnitude smaller than the NAWQA and HBN basins.

Samples from most basins were collected on a weekly to bimonthly schedule. Research basins typically had the highest sampling frequency while HBN basins typically had the lowest. Samples from all of the basins were analyzed for nutrient concentrations at either the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado or USGS research laboratories. Analyses of samples collected at NAWQA and HBN basins included:

- Dissolved nitrate plus nitrite as nitrogen (nitrate),
- Dissolved ammonia plus ammonium as nitrogen (ammonia),
- Dissolved orthophosphate as phosphorus (orthophosphate), and
- Total phosphorus.

In addition, concentrations of total nitrogen were computed as the sum of nitrate and total Kjeldahl nitrogen (ammonia plus organic nitrogen). For the research basins, only nitrate data were used in this assessment.

Nutrient concentrations generally vary in relation to streamflow. For example, in some areas of the country, concentrations of nitrate and total phosphorus are greatest during high streamflow and are generally smaller during low streamflow (Murdoch and Stoddard, 1992; Mueller and others, 1995). This variability creates some difficulties for data analysis:

- Summary statistics, such as mean concentration, used to characterize a basin might be biased because of variations in sampling frequency during the period of data collection, and
- Comparisons among basins might be biased because of different sampling frequencies and total numbers of samples collected at different basins.

These data issues were overcome by estimating a concentration value for each day of a common period of record and computing a flow-weighted concentration based on the daily estimates. There is a long history of statistical models that have been used to make such estimates. The model selected for this analysis is based on the rating-curve method (Cohn and others, 1989 and 1992; Crawford, 1991). This method uses multiple regression to estimate constituent transport (load or mass discharge) in relation to streamflow and time. Separate regression models were calibrated for each constituent in each basin. The dependent variable in each case was the natural logarithm of the daily constituent load, computed as the product of the sample concentration and the mean streamflow on the day of sampling. The explanatory (independent) variables for each model were selected from a set of potential predictor variables:

- natural logarithm of mean streamflow for the day of sample collection,
- logarithm of streamflow, squared,
- time, in decimal years,
- sine of time, and
- cosine of time.

Because nutrient concentrations included censored values (values less than the method detection limit (mdl)), model coefficients were estimated by the maximum-likelihood method (Dempster and others, 1977; Wolynetz, 1979). In the absence of censored values, the maximum-likelihood method is equivalent to ordinary least-squares regression.

For each nutrient species in each basin, models were calibrated using the natural logarithm of streamflow plus all possible combinations of other variables. For NAWQA basins, the calibration period was 1992-95; for HBN and research basins the calibration period was 1976-97 or whatever data were available within the time period. The best model for each species-basin combination was selected based on the Akaike Information Criteria (Akaike, 1981; Judge and others, 1985).

Estimates of logarithms of daily constituent load were computed using the selected model and daily mean streamflow for a period of several water years. Estimates were converted to load values (in kilograms). Bias introduced by this conversion was corrected using the Bradu-Mundlak method (Bradu and Mundlak, 1970; Cohn and others, 1989; Crawford, 1991). For NAWQA basins, loads were estimated for water years 1994-95. For HBN and research basins, loads were estimated for water years 1990-95, although in some basins data were not collected for the entire period and estimates reflect only a

subset of those years. Although some annual variability in nutrient concentrations and yields occurred in these basins, the annual variability was relatively small as compared to the annual variability in nutrient concentrations and yields in more intensively developed basins sampled by the NAWQA during 1992-95. The small amount of annual variability in relatively undeveloped basins is probably the result of small, but consistent inputs of nutrients. For this reason, it was deemed that although not all of the basins in this assessment had a complete data record during water years 1990-95, a comparison of basins with slightly different periods of analysis during 1990-95 was appropriate.

Annual loads, in kilograms (kg), were estimated as the sum of the daily loads for each year. Annual yields represent the load per unit area of drainage basin and were estimated as the annual load divided by the contributing basin area, in kilograms per square kilometer ( $\text{kg}/\text{km}^2$ ). Flow-weighted concentration, in milligrams per liter (mg/L), was estimated as the total load over the entire estimation period divided by the total stream discharge during the estimation period.

For some of the nutrient species in some basins, concentrations were less than the mdl in almost all of the samples. In these cases, it was not possible to calibrate a regression model; however, this affected only 34 of the 361 combinations of nutrient species and basins. Flow-weighted concentrations for these nutrients in these basins were estimated as less than the mdl; loads and yields for these basins were estimated using a concentration of one-half the mdl.

## Results and Discussion

Flow-weighted concentrations of nutrients in the relatively undeveloped basins varied across the nation, but, in most basins, they were generally low. The median flow-weighted concentrations for all basins were 0.020 mg/L, ammonia as N; 0.087 mg/L, nitrate as N; 0.26 mg/L, total nitrogen; 0.010, orthophosphate as P; and 0.022 mg/L, total phosphorus (table 1). Median flow-weighted nutrient concentrations in the relatively undeveloped basins ranged from 3 times less for ammonia to 13 times less for nitrate as compared to concentrations in samples collected from a variety of land use settings across the nation by the NAWQA program during 1992-95 (USGS, 1999b).

### *Nitrate*

Flow-weighted concentrations of nitrate in relatively undeveloped basins tended to be highest in the northeastern part of the United States (figure 2). Twelve of 21 basins with flow-weighted nitrate concentrations exceeding 0.21 mg/L (the 75<sup>th</sup> percentile value for all basins; table 1) were located in the northeastern or mid-Atlantic coastal states. However, only three of the relatively undisturbed basins had a flow-weighted nitrate concentration that exceeded 0.6 mg/L. The highest flow-weighted nitrate concentration of 0.77 mg/L was found in the South Fork of the Potomac River in northeastern West Virginia. The southeastern and southwestern parts of the nation, in general, tended to have the lowest flow-weighted nitrate concentrations (figure 2). The median flow-weighted concentration of nitrate for all basins, 0.087 mg/L, was exceeded in only one of the 12 basins located in Arizona, California, Nevada, New Mexico, and Utah.

For basins in the northeastern part of the nation, and in Colorado's Rocky Mountains, the above-average concentrations of nitrate were coincident with areas of elevated nitrate concentrations in atmospheric deposition. Precipitation-chemistry data collected in 1994 as part of the interagency National Atmospheric Deposition Program

(NADP) indicate that volume-weighted concentrations of nitrate in wet deposition exceeded 0.27 mg/L over the Rocky Mountains in Northern Colorado, a large part of the central plains, and most of the northeastern United States (NADP, 1999) (figure 2). Some areas of Ohio, Pennsylvania, and New York received wet deposition with nitrate concentrations exceeding 0.40 mg/L. The lowest concentrations of nitrate in precipitation were in the western and southeastern parts of the United States (NADP, 1999) where the concentration generally ranged from 0.02-0.27 mg/L. Although some annual variability may occur, NADP data indicate that concentrations and total deposition of nitrogen from wet deposition remained relatively consistent over most of the nation from 1983-94 (Lynch and others, 1996).

The spatial pattern of annual nitrate yields from undeveloped basins across the nation was similar to the pattern of flow-weighted nitrate concentrations (figure 2). Annual nitrate yields correlated well with wet deposition of total inorganic nitrogen (nitrate plus ammonia as N) from the atmosphere (figure 2). Annual deposition of inorganic nitrogen over the entire eastern United States during 1994 exceeded 300 kg/km<sup>2</sup>, and in most of the northeastern United States exceeded 500 kg/km<sup>2</sup> (NADP, 1999). For 11 basins in Maryland, New York, Ohio, Pennsylvania, and West Virginia (the area of largest atmospheric deposition of inorganic nitrogen) the annual basin yield of nitrate averaged about 250 kg/km<sup>2</sup>. In contrast, the average annual basin yield of nitrate from 12 basins in Arizona, California, Nevada, New Mexico, and Utah (the area of smallest inorganic nitrogen deposition) was only 8.3 kg/km<sup>2</sup>. For nearly all basins, annual deposition of inorganic nitrogen exceeded annual nitrate yield indicating that some nitrogen is retained within basins. However, in two Oregon basins annual nitrate yield averaged almost 400 kg/km<sup>2</sup>, or more than two times the amount of inorganic nitrogen introduced by wet deposition. Because these two predominantly forested basins are essentially free of anthropogenic effects, excess nitrate yield is probably derived from localized atmospheric inputs or higher rates of organic decomposition within the basin relative to vegetative growth.

Because the HBN, NAWQA, and Research Programs contain basins with dramatically different physical characteristics, comparisons were made to examine the differences in nitrate concentrations and yields between programs. A statistical comparison between programs for drainage basin area, mean streamflow, mean annual runoff, nitrate concentrations, and nitrate yields is shown in figure 3. Although some significant differences ( $p < 0.05$ ) between programs were apparent for drainage basin area, mean streamflow, and mean annual runoff, differences in flow-weighted nitrate concentrations were not statistically significant ( $p > 0.05$ ). However, annual nitrate yield from research basins was significantly larger than yields from HBN ( $p = 0.002$ ) and NAWQA ( $p = 0.049$ ) basins. These differences in nitrate yield are primarily attributable to higher annual runoff from research basins. There was no statistically significant difference in annual nitrate yield between NAWQA and HBN basins (figure 3).

### ***Total nitrogen***

Only 4 of 63, or 6 percent, of the relatively undeveloped basins had a flow-weighted total nitrogen concentration exceeding 1 mg/L. By comparison, 83 percent of 97 NAWQA basins sampled during 1990-95 in areas dominated by agricultural and urban residential land had a flow-weighted concentration of total nitrogen exceeding 1.0 mg/L (USGS, 1999b). Flow-weighted concentrations and mean annual yields of total nitrogen

tended to be largest in basins in the eastern half of the United States, particularly in southeastern basins and four north-central basins in Michigan, Minnesota, and Wisconsin (figure 4). In basins in the northeastern United States, nitrate generally comprised about 70-80 percent of the total nitrogen concentration and annual yield, and in the southeastern and four north-central basins, nitrate generally comprised less than 25 percent of the total nitrogen concentration and annual yield. Organic forms of nitrogen accounted for most of the total nitrogen concentration and annual yield in the southeastern and four north-central basins. Southeastern and north-central basins also had some of the highest ammonia concentrations of all the relatively undeveloped basins in the nation. Higher concentrations of ammonia in north-central basins probably result from high rates of atmospheric ammonia deposition over large parts of the upper midwest (NADP, 1999). Of the basins for which both total nitrogen and ammonia data were available, Van Swamp in eastern North Carolina had the highest flow-weighted concentration and mean annual yield of total nitrogen (2.6 mg/L and 840 kg/km<sup>2</sup>, respectively) and ammonia (0.10 mg/L and 33 kg/km<sup>2</sup>, respectively).

### ***Total phosphorus***

The median flow-weighted concentration of total phosphorus in the relatively undeveloped basins was 0.022 mg/L, about 5 times less than the concentration threshold, 0.1 mg/L, generally recommended for prevention of nuisance aquatic growth in streams (USEPA, 1986). Of 63 basins analyzed nationwide for total phosphorus only 4, or 6 percent, had a flow-weighted concentration of total phosphorus exceeding 0.1 mg/L. By comparison, 70 percent of 97 NAWQA basins sampled during 1992-95 in areas dominated by agricultural and urban residential land had a flow-weighted concentration of total phosphorus exceeding 0.1 mg/L (USGS, 1999b). Flow-weighted concentrations of total phosphorus were generally highest in the Rocky Mountain and Central Plain states and parts of the southeast (figure 5). Flow-weighted concentrations of total phosphorus exceeding 0.10 mg/L occurred in basins of the Dismal River in central Nebraska (0.20 mg/L), Rock Creek in northern Montana (0.20 mg/L), Big Jacks Creek in southwestern Idaho (0.15 mg/L), and Saguache Creek in southern Colorado (0.12 mg/L). In these four basins, orthophosphate, on average, accounted for about 65 percent of the total phosphorus concentration and yield. In contrast, in basins in the southeastern United States, orthophosphate generally accounted for less than 35 percent of the total phosphorus concentration and yield, with organic and particulate forms accounting for the rest. Larger flow-weighted concentrations of total phosphorus in some of the western basins may result from mineral weathering of phosphorus enriched sediments. For instance, the Dismal River, Rock Creek, and Big Jacks Creek basins are underlain by either marine shale or mafic volcanic rocks (Clark and others, 1999) that are typically enriched in phosphorus. Land use factors such as rangeland grazing of cattle may also contribute to higher phosphorus concentrations in some western basins (Clark and others, 1999). Some of the lowest flow-weighted concentrations of total phosphorus were found in the northeastern part of the United States (figure 5). Of the seven basins located in Maine, Massachusetts, New Hampshire, New Jersey, New York, and Pennsylvania, six had flow-weighted concentrations of total phosphorus less than 0.01 mg/L, the mdl for total phosphorus analysis. Annual basin yields of total phosphorus ranged from less than 1 kg/km<sup>2</sup> from a number of basins to 82 kg/km<sup>2</sup> from Gales Creek in Western Oregon. Gales Creek also had the highest mean annual yield of orthophosphate (23 kg/km<sup>2</sup>). As

with total nitrogen, basins in the southeastern part of the United States had above-average concentrations of organic forms of phosphorus and some of the highest mean annual yields of total phosphorus (figure 5). The large fraction of organic forms of nitrogen and phosphorus in southeastern basins probably results from higher rates of organic decomposition as compared to western basins. The difference in flow-weighted total phosphorus concentrations and mean annual yields between NAWQA and HBN basins was not statistically significant.

## **Conclusions**

The U.S. Environmental Protection Agency has recognized natural variability of nutrient levels throughout the nation and is developing nutrient criteria for protection of surface-water bodies based on regional background conditions. This study provides a description of background conditions for nutrients in a number of relatively undeveloped basins of the United States. These results can be used to determine achievable baseline conditions for nutrients in basins with similar geographic and hydrologic conditions and to evaluate human effects on water quality in more intensively developed basins. To permit a nationally consistent analysis, only data collected by the USGS were used for this study.

Data from 1990-95 indicate that background concentrations and yields of nitrate are controlled more by anthropogenic inputs from the atmosphere rather than natural factors. Concentrations and yields of nitrate were highest in the northeastern and mid-Atlantic coastal states and correlated well with wet deposition of nitrate and total inorganic nitrogen from the atmosphere. In contrast, background concentrations and yields of total nitrogen and total phosphorus seem to be controlled by natural factors such as the rates of organic decomposition and mineral weathering. Concentrations and yields of total nitrogen were highest in the southeastern part of the nation and in parts of the upper Midwest. Concentrations and yields of total phosphorus were highest in the western and southeastern United States.

Although some national and regional patterns for nutrients were identified in this study, the number of basins was inadequate to define nutrient conditions in any type of established regional framework such as ecoregions or physiographic provinces. Filling in monitoring gaps, such as the upper Midwest and south-central United States may provide necessary data to define regions of similar baseline water-quality conditions. A regional delineation in natural concentrations of nutrients in surface water would be a valuable tool for agencies at the local, regional, and national scale to adopt attainable water-quality goals and management strategies.

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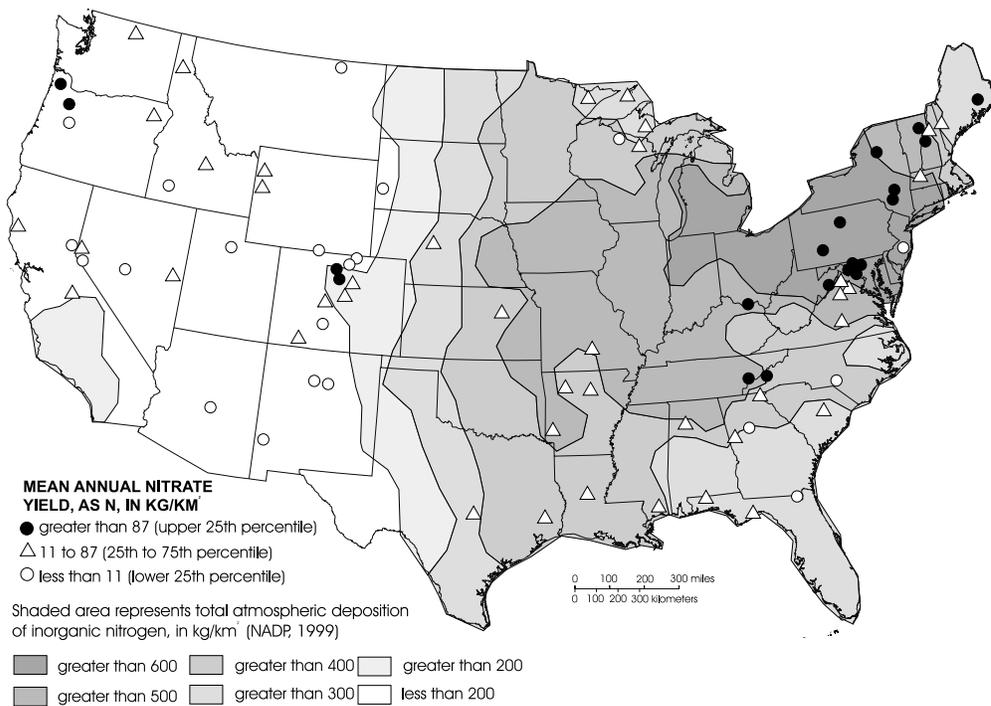
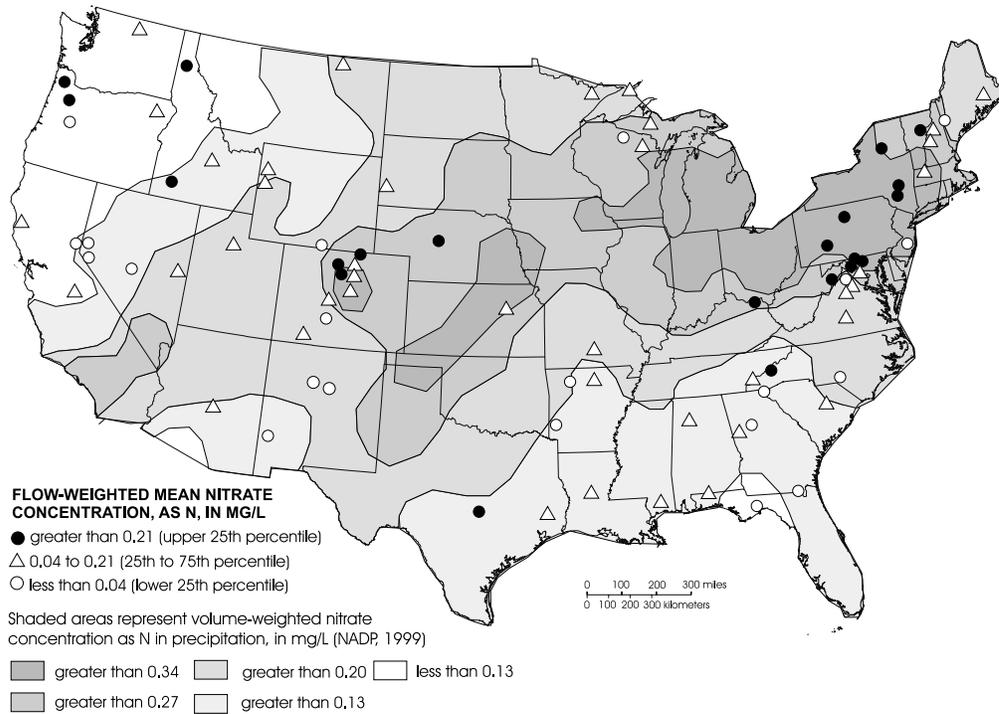
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Table 1 - Statistical summary of flow-weighted nutrient concentrations and mean annual nutrient yields for relatively undeveloped stream basins in the United States. Values are based on available data for water years 1990-95. Basin locations are shown in figure 1. Note: for Research basins, only data for nitrate concentrations and yields were available. 5/4/2001: 90th percentile values for nutrient concentrations were added to the table.

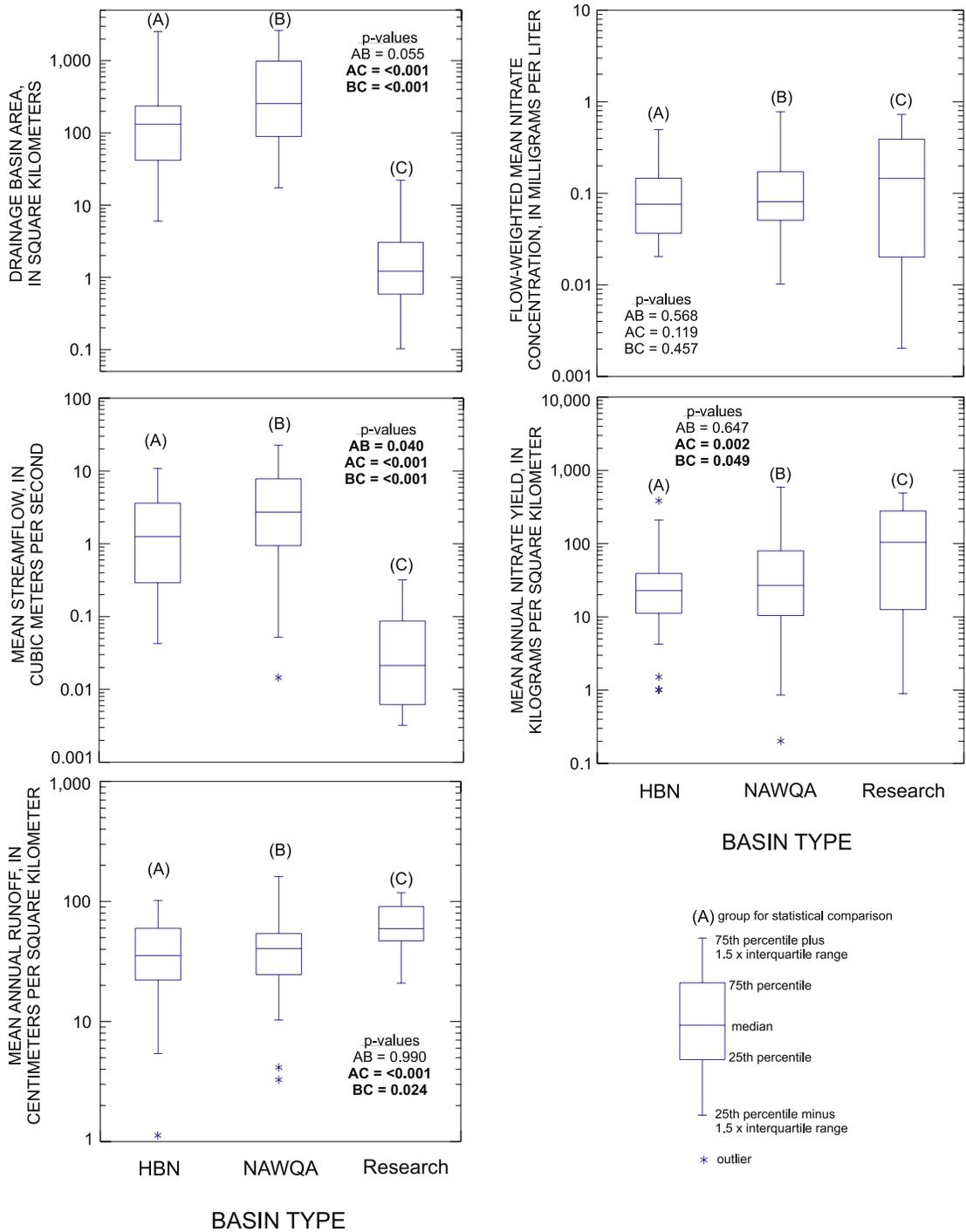
Basins	Number of basins	Minimum	Percentile				Maximum
			25 <sup>th</sup>	50 <sup>th</sup> (median)	75 <sup>th</sup>	90 <sup>th</sup>	
<b>Flow-weighted concentration, in milligrams per liter</b>							
<u>Dissolved ammonia, as N</u>							
All	65	<0.01	0.016	0.020	0.026	0.039	0.10
HBN	43	<0.01	0.015	0.019	0.026	0.041	0.058
NAWQA	22	0.010	0.020	0.020	0.030	0.030	0.10
<u>Dissolved nitrate+nitrite, as N</u>							
All	82	<0.01	0.040	0.087	0.21	0.43	0.77
HBN	41	0.020	0.036	0.075	0.14	0.27	0.49
NAWQA	21	0.010	0.050	0.080	0.17	0.27	0.77
Research	20	<0.01	0.020	0.15	0.40	0.52	0.73
<u>Total nitrogen</u>							
All	63	0.10	0.20	0.26	0.50	0.72	2.6
HBN	41	0.10	0.19	0.24	0.52	0.69	1.1
NAWQA	22	0.20	0.20	0.32	0.49	1.00	2.6
<u>Dissolved orthophosphate, as P</u>							
All	65	<0.01	<0.01	0.010	0.011	0.022	0.13
HBN	43	<0.01	<0.01	<0.01	0.010	0.021	0.13
NAWQA	22	<0.01	<0.01	0.010	0.014	0.023	0.074
<u>Total phosphorus</u>							
All	63	<0.01	0.014	0.022	0.037	0.091	0.20
HBN	41	<0.01	0.014	0.020	0.030	0.085	0.20
NAWQA	22	0.010	0.013	0.037	0.052	0.092	0.12
<b>Mean annual yield, in kilograms per square kilometer</b>							
<u>Dissolved ammonia, as N</u>							
All	65	<1.0	4.4	8.1	12		33
HBN	43	<1.0	4.6	8.1	12		33
NAWQA	22	<1.0	4.1	7.8	13		33
<u>Dissolved nitrate+nitrite, as N</u>							
All	82	<1.0	11	26	87		580
HBN	41	1.0	11	23	39		380
NAWQA	21	<1.0	10	27	79		580
Research	20	<1.0	13	110	290		510
<u>Total nitrogen</u>							
All	63	<1.0	45	86	220		840
HBN	41	2.1	50	94	170		560
NAWQA	22	<1.0	30	62	280		840
<u>Dissolved orthophosphate, as P</u>							
All	65	<1.0	1.6	2.8	4.8		23
HBN	43	<1.0	1.6	3.1	4.7		10
NAWQA	22	<1.0	1.2	2.7	5.4		23
<u>Total phosphorus</u>							
All	63	<1.0	4.8	8.5	12		82
HBN	41	<1.0	4.7	7.5	11		28
NAWQA	22	<1.0	5.1	11	25		82



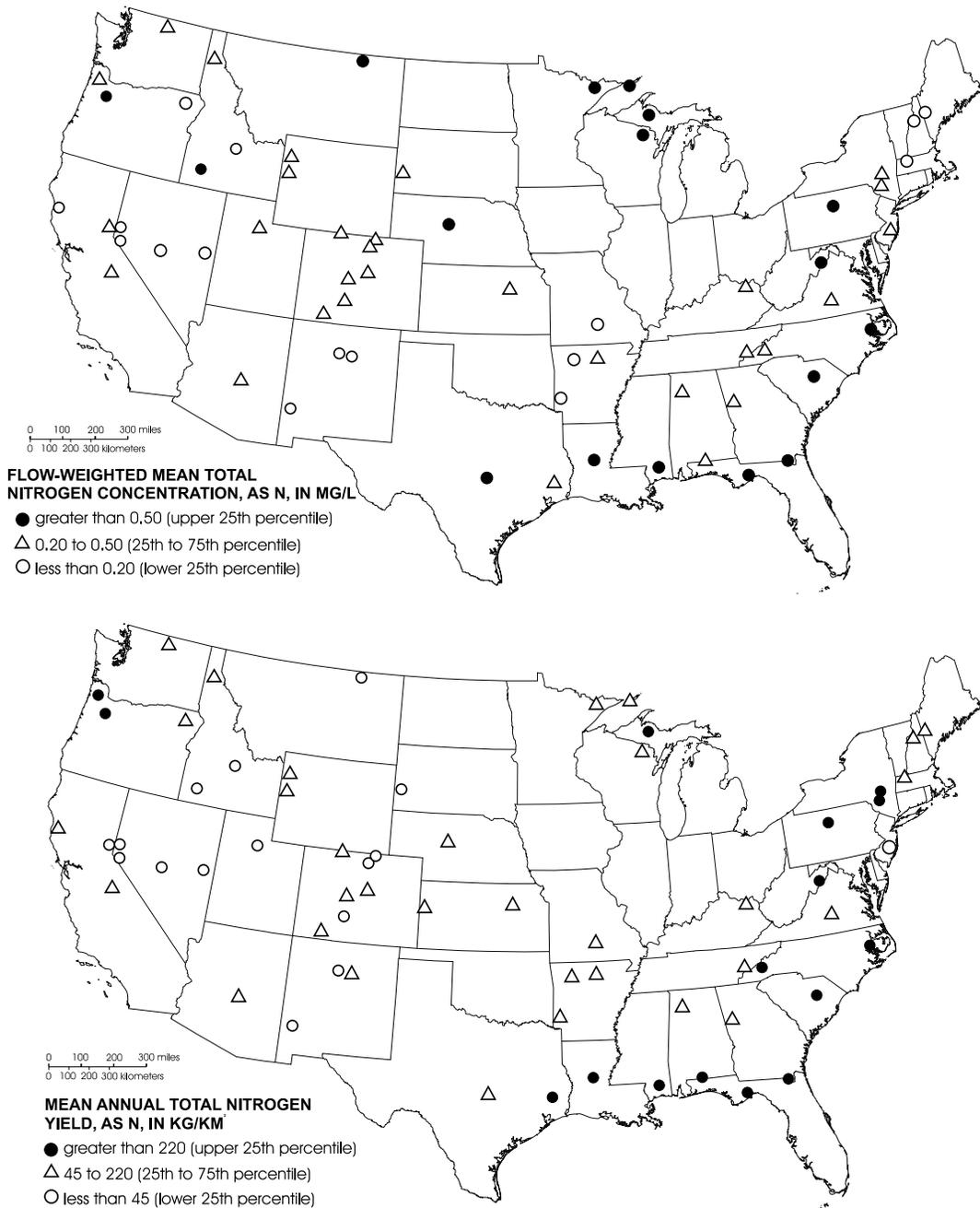
**Figure 1** – Location of Hydrologic Benchmark Network (HBN), National Water-Quality Assessment (NAWQA) and research sites used for assessment of nutrient concentrations and yields in relatively undeveloped stream basins of the United States.



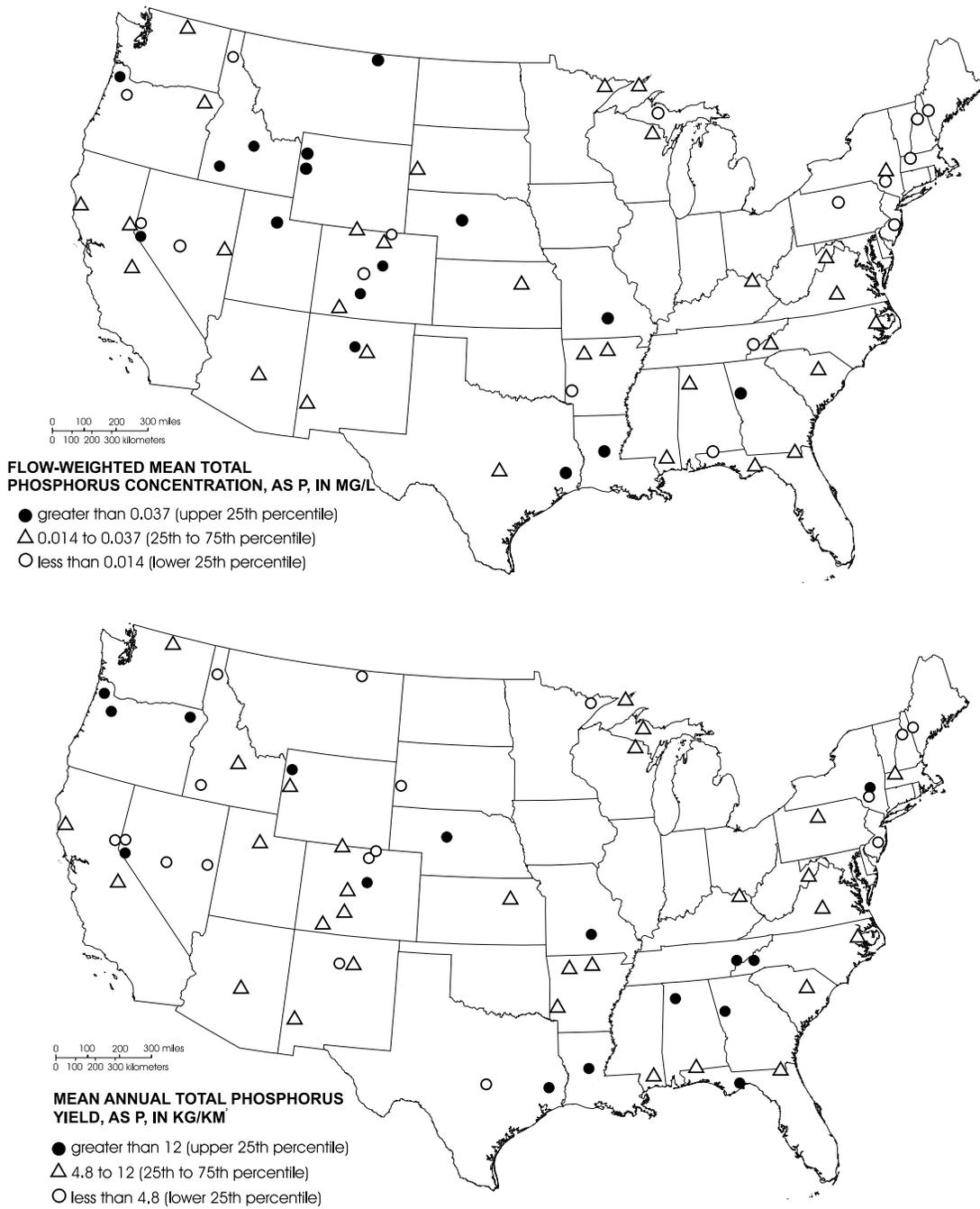
**Figure 2** – Flow-weighted concentrations and mean annual yields of nitrate in relatively undeveloped HBN, NAWQA, and research basins and their relation to atmospheric deposition of nitrogen. Basin concentration and annual yield values are based on available data for water years 1990-95. Atmospheric deposition data are from 1994.



**Figure 3** – Physical and hydrologic characteristics and flow-weighted nitrate concentrations and mean annual yield in HBN, NAWQA, and research basins. Values are based on available data for water years 1990-95. P-values of less than 0.05 (bolded) indicate a significant difference between basin type using a Wilcoxon signed-rank test at a 95 percent confidence level.



**Figure 4** – Flow-weighted concentrations and mean annual yields of total nitrogen in relatively undeveloped HBN and NAWQA BASINS of the United States. Values are based on available data for water years 1990-95.



**Figure 5** – Flow-weighted concentrations and mean annual yields of total phosphorus in relatively undeveloped HBN and NAWQA basins of the United States. Values are based on available data for water years 1990-95.

# OUTCOMES OF PHOSPHORUS-BASED NUTRIENT MANAGEMENT IN THE EUCHA- SPAVINAW WATERSHED

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## **Outcomes of phosphorus-based nutrient management in the Eucha-Spavinaw Watershed**

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The role of phosphorus (P) in accelerating eutrophication of fresh waters is well documented (Carpenter et al. 1998), as are more recent findings that P can seasonally limit the productivity of coastal waters (Howarth et al. 2002). However, P is an essential dietary input for poultry production and is used as a fertilizer nutrient to achieve maximum pasture production in beef-cattle grazing systems, predominant in northwest Arkansas and northeast Oklahoma.

In many areas of the United States, regulatory and nonregulatory agencies have changed their strategic approach to nutrient management planning with respect to water quality impacts because it has become cheaper to control nutrient sources than treat the symptoms of nutrient enrichment. Such a strategy was put in place to target and remediate sources of P in the Eucha-Spavinaw Watershed (ESW) in northwest Arkansas and northeast Oklahoma, which collects and supplies water to the metropolitan area of Tulsa, Oklahoma.

In 2003, the City of Tulsa and Tulsa Metropolitan Utility Authority (Plaintiffs) agreed to a settlement with several poultry integrators (including Tyson Foods, Cargill, Cobb–Vantress, George’s, Peterson Farms, and Simmons Foods) and the City of Decatur, Arkansas (Defendants), wastewater treatment plant. The settlement addressed concerns that P in runoff from pastures fertilized with poultry litter and in wastewater discharge from Decatur accelerated algal growth, which caused subsequent taste and odor problems in drinking water. The settlement required nutrient management plans (NMPs) for poultry producers to determine land application rates of poultry litter based on the risk of P loss

from fields to streams. Use of a P Index developed for ESW, the Eucha-Spavinaw P Index (ESPI), was required. It was also stipulated that no more than 67% of the poultry litter produced in ESW could be land applied, and that no litter could be applied to fields with a soil test P (STP) concentration (as Mehlich-3 extractable soil P) greater than 300 mg kg<sup>-1</sup>.

Nutrient flows on a typical poultry production–beef-cattle grazing farm, prevalent in ESW, are presented in figure 1, illustrating the challenges facing nutrient budgeting of these integrated farming systems. In general, N and P inputs far exceed outputs at a farm level. Estimates of annual flows and balance of N and P for pathways shown in figure 1 are presented in table 1 for a representative poultry–beef operation in northwest Arkansas (West and Waller 2007). For this example, only 14% of the imported N and 12% of the imported P were exported in animal produce (table 1). Thirty-two percent of the N and 17% of P were recycled back to the pasture through ungrazed vegetation and cattle excreta. The remaining N and P (about 54% and 74%, respectively) were unaccounted for within the farm system. This scenario illustrates the potential for N and P to accumulate within poultry production–beef-grazing systems. While litter N can be used to maintain forage production, adoption of P-based NMPs, as in ESW, can limit on-farm use of litter as a source of N. Because of increasing fertilizer costs, the purchase of fertilizer as a replacement for litter N, P, and K is no longer an economically viable option for graziers.

This chapter documents the outcomes of legislated NMP in terms of litter management, soil P levels, land affected, and most critically the impacts on beef-cattle grazing in ESW. Information given in this paper is from NMPs written in ESW by the team of trained planners assigned to this watershed since the 2004 settlement.

**Table 1. Annual N and P balance and flow through components of a poultry production–beef grazing system in northwest Arkansas (adapted from West and Waller 2007).**

Farm component*	Nitrogen (kg ha <sup>-1</sup> yr <sup>-1</sup> )	Phosphorus (kg ha <sup>-1</sup> yr <sup>-1</sup> )
<b>Poultry N and P balance†</b>		
N & P import in feed	370	100
N & P export in poultry	40	10
N & P recovered in litter and applied to pastures	100	52
<b>Cattle / forage N and P balance‡</b>		
N & P uptake into top growth§	127	19
Forage N & P consumed by cattle at 0.7 grazing utilization	88	13
Ungrazed forage N & P returned to soil	38	6
Supplement N & P consumed by cattle	1	<1
N & P excreted by cattle on pasture	81	11
N & P exported in cattle live weight: weaned cows and cull cows	10	2
<b>Whole-farm N and P balance</b>		
Total N & P import in feed and supplement	371	101
Total N & P export in poultry and beef	50	12
Excess N & P (import – export)	321	89
N & P returned to pasture as ungrazed forage and cattle excreta	119	17
Unaccounted for N & P (e.g., litter, N volatilization)	202	72

\* 80 ha farm in forage (bermudagrass, tall fescue, white clover, and some annuals) assuming 5.8 Mg ha<sup>-1</sup> yr<sup>-1</sup> forage dry matter produced.

† 3 poultry houses with 5 broiler flocks per year, producing 1.6 Tg of bird live weight, assuming 3.8 Mg ha<sup>-1</sup> yr<sup>-1</sup> litter produced.

‡ 80 beef cows, 72 calves, 12 heifers, and 3 bulls. Farm is self-sufficient in feed production for the cattle except winter energy supplement for cows and heifers and mineral supplement. No hay is imported or exported, and no phosphatic fertilizer is imported.

§ Top-growth concentration is 2.20% N and 0.32% P.

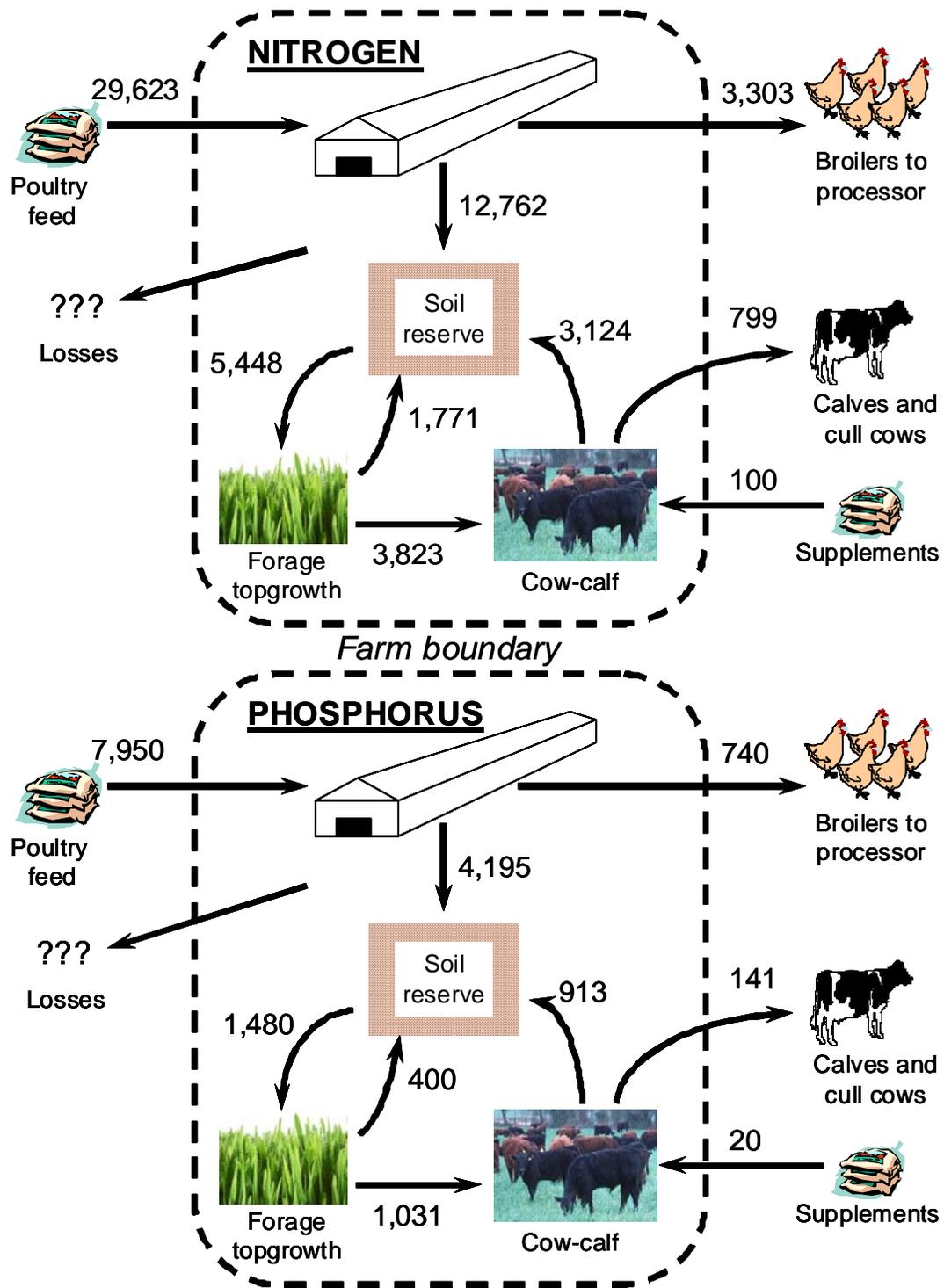
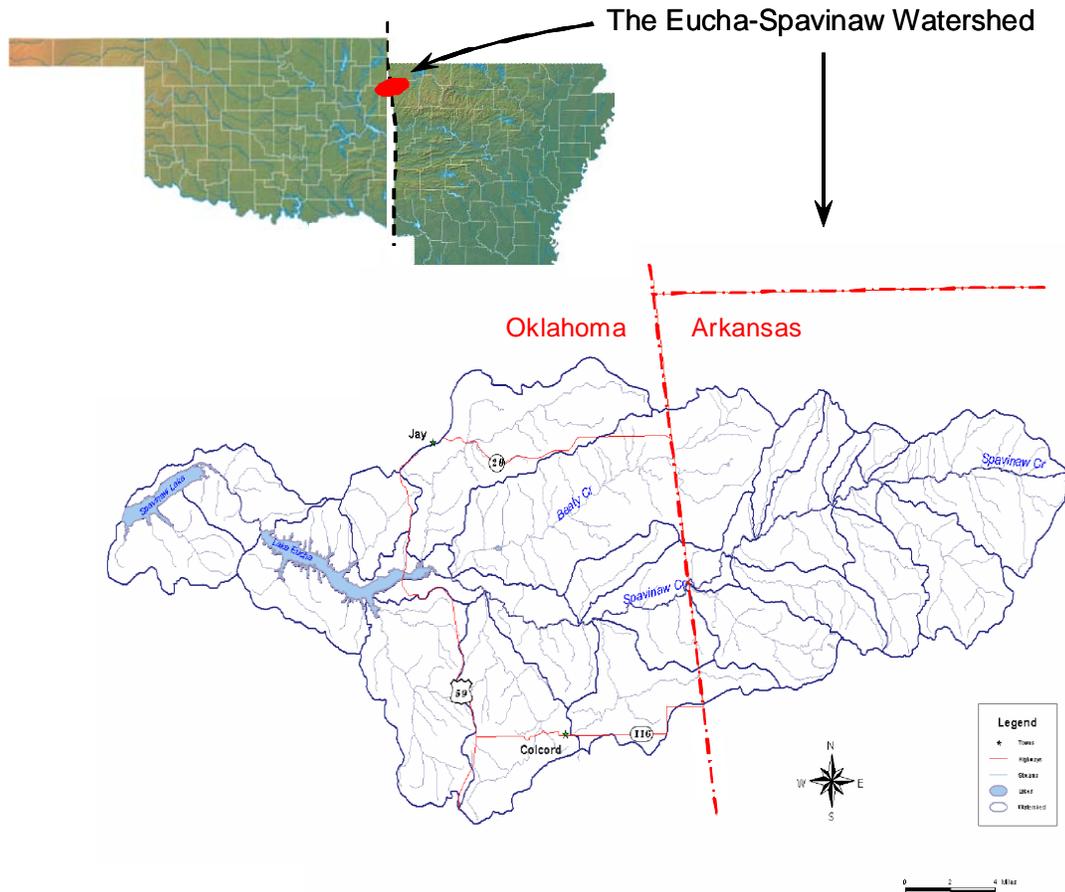


Figure 1. Farm-scale N and P budget for a theoretical 80 ha farm in northwest Arkansas with three broiler houses and 80 beef cows, 72 calves, 12 heifers, and 3 bulls. Values are total N and P in kg yr<sup>-1</sup> (adapted from West and Waller 2007).

**Experimental Design**

***Eucha-Spavinaw Watershed.*** The ESW is a 107,600 ha drainage basin in the southwest portion of the Ozark Plateau in northwest Arkansas and northeast Oklahoma (figure 2). The ESW drains into Lakes Eucha and Spavinaw, which serve as the municipal drinking water supply to the cities of Jay and Tulsa, Oklahoma, as well as some surrounding rural communities. Land use in ESW is mostly forest (51%) and pasture (43%), with lesser amounts of row crops and urban land use (table 2). The drainage area is densely populated with poultry–beef-cattle operations that use poultry litter as a fertilizer source for pastures dominated by bermudagrass (*Cynodon dactylon*) and tall fescue (*Lolium arundinaceum*). The area in which ESW is located is the top producing area for both poultry and beef cattle in Arkansas (USDA 2008).



**Figure 2. Eucha-Spavinaw Watershed.**

**Table 2. Land use in the Eucha-Spavinaw Watershed, based on 2004 information.**

Land use	Area (ha)	Percent
Forest	55,200	51.3%
Pasture	46,400	43.0%
Row crop	2,800	2.6%
Water	1,800	1.7%
Urban	1,400	1.3%
Total	107,600	

***Eucha-Spavinaw Phosphorus Index.*** The current version of ESPI used in NMP writing within the ESW is given in tables 3 and 4; this represents a nationally recognized approach to managing land application of P in terms of source and transport factors that influence environmental risk (Sharpley et al. 2003; DeLaune et al. 2007). Phosphorus source characteristics in ESPI are soil test P (STP), water-extractable P (WEP) (Self-Davis and Moore 2000) in applied litter, and an estimate of particulate P loss. Phosphorus transport characteristics were used to estimate the potential for P sources to be mobilized during rainfall and runoff. Surface runoff class for each site was a function of field slope and runoff curve number and reflected the potential for runoff to occur from a given site. Soils classified as frequently flooded had a much greater potential for P transport than occasionally and nonflooded soils. Greater loss ratings in ESPI were assigned to litter applied at times of the year when the occurrence of runoff was greatest. Finally, credit was given to reducing the potential for P loss when best management practices (BMPs) approved by the Natural Resources Conservation Service (NRCS) were implemented at a site. These BMPs included stream fencing, setback or buffer areas next to a stream where no litter was applied, and stream-side vegetative or riparian buffers, which have been shown to filter particulate P loss and decrease dissolved P loss in runoff entering a stream. Further rationale for including these factors and calculations in site risk assessment was given by DeLaune et al. (2007).

**Table 3. The Eucha-Spavinaw P Index, site characteristics, and calculation methodology.**

Characteristic	P loss category	Loss rating value
<b>P source characteristics</b>		
Soil test P	Continuous variable	0.0007 * STP <sup>†</sup> (lb ac <sup>-1</sup> )
Water-extractable manure P rate	Continuous variable	0.4 * WEP <sup>‡</sup> applied (lb ac <sup>-1</sup> )
Particulate P soil erosion factor	Continuous variable	RUSLE2 value * STP/667
<b>P source rating value = <math>\sum</math>source characteristics ratings</b>		
<b>P transport characteristics</b>		
Soil runoff class	Negligible	0.1
	Low	0.2
	Moderate	0.3
	High	0.5
	Very High	1.0
Flooding frequency	None	0
	Occasional	0.1
	Frequently	2.0
Application method	Incorporated	0.1
	Surface applied	0.2
	Surface applied on frozen ground or snow	0.5
	Application timing	July to October
Harvest management	April to June	0.4
	November to March	0.5
	Hayed only	0.1
	Hayed and grazed	0.2
	Grazed only	0.3
<b>P transport rating value = <math>\sum</math>transport characteristics ratings</b>		
<b>Other site characteristics</b>		
Best management practices	Approved BMPs	0.9
<b>ESPI site factor calculation</b>		
<b>ESPI = P source rating value * P transport rating value * BMP factor</b>		

<sup>†</sup> Mehlich-3 soil test P concentration for a 0 to 10 cm sample and a factor of 1.33 to convert from mg kg<sup>-1</sup> (as measured) to lbs acre<sup>-1</sup> (used by plan writers).

<sup>‡</sup> Water extractable P concentration of manure applied.

**Table 4. Eucha-Spavinaw P Index (ESPI) interpretations and nutrient application recommendations.**

ESPI scale	Site interpretations and recommendations
< 33	Low potential for P movement from site. Apply nutrients based on ESPI calculation. Caution against long-term buildup.
34 to 55	Medium potential for P movement from site. Evaluate the Index and determine any areas that could cause long-term concerns. Consider adding conservation practices or reduced P application to maintain the risk at 55 or less. Apply nutrients based on ESPI calculation.
56 to 100	High potential for P movement from site. Evaluate the Index and determine elevation cause. Add appropriate conservation practices and/or reduce P application. The immediate planning target is a PI value of 55 or less. If this cannot be achieved with realistic conservation practices and/or reduced P rates in the short term, then a progressive plan needs to be developed with a long-term goal of a PI less than 55. Apply nutrients to meet crop phosphorus needs according to NRCS Nutrient Management standard (590). Application rates based on phosphorus needs generally equate to <1 ton/ac. Since accurate, uniform applications at these low rates are rarely obtained, no litter application is recommended.
>100	Very High potential for P movement from site. No litter application. Add conservation practices to decrease this value below 100 in the short term and develop a progressive conservation plan that would reduce the PI to a lower risk category, with long-term goal of a PI less than 55.

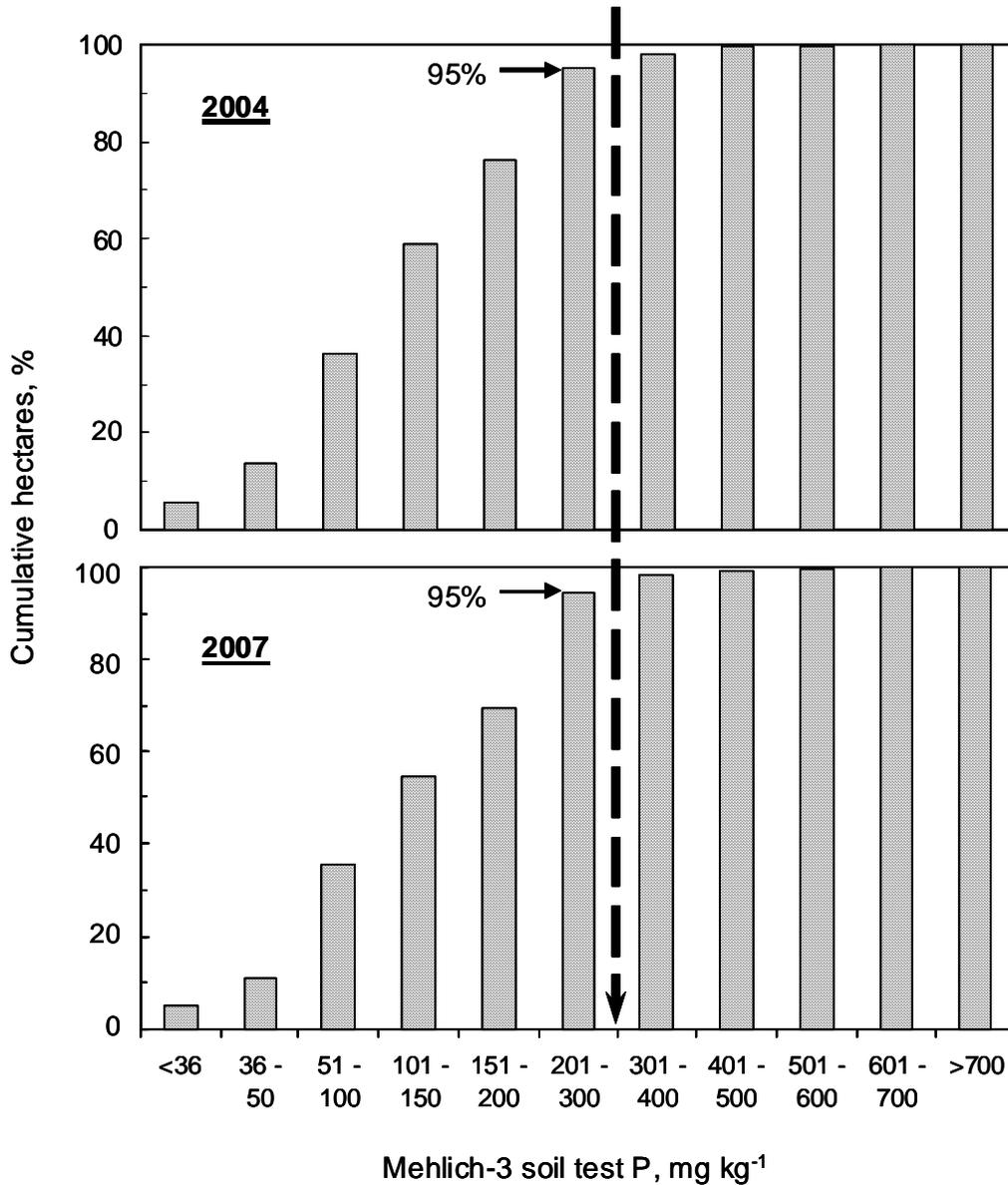
**Nutrient Management Planning.** Information used in this assessment was obtained from NMPs written between 2004 and 2007 in ESW as part of the settlement agreement. Available data included STP concentration (as Mehlich-3 P; 0 to 10 cm soil sampling depth), nutrient content of litter (total N, P, K, and WEP), number and area of fields for which a plan was written, timing and rate of litter application, and presence of NRCS-approved BMPs. These BMPs included riparian buffers (CP 390), stream bank protection (CP 395), and fencing (CP 382) (USDA NRCS 2003).

## Results and Discussion

**Poultry Litter Management.** There was no consistent change in STP since 2004, averaging 175 mg kg<sup>-1</sup> (table 5). While maximum STP concentration was >750 mg kg<sup>-1</sup> for each of the four years of study, 92% of the soils were below the 300 mg kg<sup>-1</sup> STP threshold in 2004, 86% in 2005, 89% in 2006, and 89% in 2007 (figure 3).

**Table 5. Annual mean, minimum, and maximum and 4-year mean soil test P, water-extractable P, and total P and mean total N and total K concentration in poultry litter sampled as part of nutrient management plan development in the Eucha-Spavinaw Watershed.**

Parameter	2004	2005	2006	2007	4-year mean
<b>Soil test P (mg kg<sup>-1</sup>)</b>					
Mean	165	186	178	170	175
Minimum	14	5	1	10	8
Maximum	893	972	811	766	861
<b>Poultry litter</b>					
<b>Water-extractable P (mg kg<sup>-1</sup>)</b>					
Mean	907	829	947	988	918
Minimum	116	238	300	191	211
Maximum	2,188	1,532	1,842	1,906	1,867
<b>Total P (mg kg<sup>-1</sup>)</b>					
Mean	15,960	14,460	14,540	15,450	15,100
Minimum	8,000	6,200	7,200	7,300	7,170
Maximum	25,330	20,700	25,600	22,400	23,510
<b>Total N (mg kg<sup>-1</sup>)</b>	29,530	30,440	32,910	28,860	30,440
<b>Total K (mg kg<sup>-1</sup>)</b>	22,880	23,910	26,110	25,450	24,590



**Figure 3. Cumulative hectares within the Eucha-Spavinaw Watershed with soil samples testing below 300 mg kg<sup>-1</sup> Mehlich-3 soil test P from nutrient management plans written in 2004 and 2007.**

Nutrient content of poultry litter was fairly consistent among years, averaging 30.4 g N kg<sup>-1</sup>, 15.1 g P kg<sup>-1</sup>, and 24.6 g K kg<sup>-1</sup> (table 5). Mean annual WEP concentration of litter, which was used in ESPI as an estimate of the potential for P to be released from litter to rainfall-runoff water, ranged from 829 to 988 mg kg<sup>-1</sup> and was an average of 6.0% of total P (table 5). Poultry litter WEP was fairly constant from year to year, averaging 918 mg kg<sup>-1</sup> from 2004 to 2007. However, there was a nine-fold variation between the four-year mean minimum and maximum values (table 5). This shows how important it was to measure WEP for consideration in ESPI rather than using a book value of 500 mg kg<sup>-1</sup> prior to 2004.

Since 2004, ESPI-based plan writing has continued to have a direct impact on nutrient management and has decreased land application of poultry litter. The number of fields and land area for which NMPs were written in ESW are given in table 6. In 2007, NMPs were written for 839 fields, totaling approximately 6,650 ha, with an average recommended litter application rate of 2.6 Mg ha<sup>-1</sup> yr<sup>-1</sup> (table 6). These application rates are 40% to 60% less than historic recommendations of county conservation districts in the Arkansas portion of the watershed, which were 4.5 Mg ha<sup>-1</sup> yr<sup>-1</sup> for cool-season grasses and 6.7 Mg ha<sup>-1</sup> yr<sup>-1</sup> for warm-season grasses. Each year since 2004, average poultry application rate decreased, and in 2007 it was 2.6 Mg ha<sup>-1</sup> yr<sup>-1</sup>. This represented a 20% decline in poultry litter application each year from 2004 to 2007.

**Table 6. Number of fields for which a plan was written, acres planned, number of fields receiving litter, area receiving litter, and litter application rates recommended by Eucha-Spavinaw P Index in the Eucha-Spavinaw Watershed.**

Parameter	2004	2005	2006	2007
Number of fields	970	860	993	839
Hectares planned	8016	6999	8023	6655
Number of fields receiving litter	902	738	797	696
Hectares receiving litter	7642	6280	7243	6274
Percent of watershed receiving litter	7	6	7	6
Percent of planned area receiving litter	95	90	90	94
<b>Litter application (Mg ha<sup>-1</sup>)</b>				
Mean	3.34	3.18	2.91	2.62
Minimum	0	0	0	0
Maximum	9.52	6.16	6.72	5.82

Based on data collected by the planning team, the percentage of fields receiving poultry litter declined from 93% in 2004 to 83% in 2007, which amounted to only 6% to 7% of the whole ESW area that received poultry litter each year since 2004 (table 6). The lack of change in STP values since 2004, even though litter application rates decreased by about 50%, was, therefore, not unexpected. Research has shown that STP levels increase much more rapidly with added P than the rate of decline with forage uptake and harvest (McCollum 1991; Sharpley et al. 2007).

Approximately 82 Gg of poultry litter is produced within ESW annually. Export of litter from ESW was 69%, 75%, 74%, and 78% in 2004, 2005, 2006, and 2007, respectively (table 7). Thus, ESPI-based NMPs exceeded the guidelines (i.e., at least 33% of the litter produced be exported out of ESW) set forth in the settlement agreement each year since its enactment.

**Table 7. Impact / cost of N, P, and K removed in poultry litter in terms of replacement fertilizer N, P, and K values in the Eucha-Spavinaw Watershed.**

	2004			2005			2006			2007		
	N	P	K	N	P	K	N	P	K	N	P	K
Litter applied (Mg)	25,640			20,760			20,940			17,980		
Litter removed (Mg)	55,990			60,870			60,690			63,650		
Average litter total N, P, and K (mg kg <sup>-1</sup> )	29,530	15,960	22,800	30,440	15,620	23,910	32,910	14,540	26,110	28,860	15,670	25,450
Nutrients exported in litter (Mg)	1,650	900	1,280	1,850	950	1,460	2,000	880	1,590	1,840	1,000	1,620
Fertilizer cost (\$ Mg <sup>-1</sup> ) <sup>†</sup>	304	293	200	366	330	270	399	357	301	499	577	388
Fertilizer nutrient value (\$ Mg <sup>-1</sup> )	662	637	333	796	717	450	868	776	502	1,086	1,254	647
Litter nutrient value (\$ Mg litter <sup>-1</sup> )	20	10	8	24	11	11	29	11	13	31	20	17
<b>Total N, P, and K value (\$ Mg litter<sup>-1</sup>)</b>	<b>38</b>			<b>46</b>			<b>53</b>			<b>68</b>		
ESW replacement cost (\$1,000) <sup>‡</sup>	1,094	570	425	681	655		1,733	685	795	1,995	1,233	1,048
<b>Total ESW cost (\$)</b>	<b>2,088,150</b>			<b>2,810,927</b>			<b>3,213,210</b>			<b>4,292,742</b>		

<sup>†</sup> Based on prices in April of each year for N as urea (46% N), P as triple superphosphate (46% P), and K as potash (60% K). Data from USDA Economic Research Service, <http://www.ers.usda.gov/Data/FertilizerUse>.

<sup>‡</sup> Total cost to poultry growers in the Eucha-Spavinaw Watershed.

**Economic Impacts on Beef-Cattle Graziers.** Using information from the NMPs, estimates were obtained for nutrient content of poultry litter from each farm, average annual cost of mineral fertilizer, and economic impact of the NMP process on ESW farmers (table 7). The amount of N, P, and K exported in litter was calculated as the product of litter exported and nutrient concentration of litter. During this period, fertilizer prices increased dramatically. Based on elemental analysis, N from urea increased from \$662 to \$1086 Mg<sup>-1</sup>, triple superphosphate increased from \$637 to \$1254 Mg<sup>-1</sup>, and K as potash increased from \$333 to \$647 Mg<sup>-1</sup> (table 7) (USDA ERS 2008). This translated to an increase in the nutrient value of litter based on fertilizer replacement cost, which in 2007 was \$31 Mg<sup>-1</sup> for N, \$20 Mg<sup>-1</sup> for P, and \$17 Mg<sup>-1</sup> for K. The nutrient value of litter exported from ESW amounted to \$68 Mg<sup>-1</sup> in 2007 (table 7). With continued increase in fertilizer prices, the value of exported litter rose to \$134 Mg<sup>-1</sup> in 2008. As the farmer would receive only \$6 to \$9 Mg<sup>-1</sup> for litter, due to high transportation costs, income from the sale of litter was minimal compared to the cost of buying replacement fertilizer N, assuming soil P and K were sufficiently high to warrant no P or K application.

For a bermudagrass pasture, a poultry litter application of 6.7 Mg ha<sup>-1</sup> could be recommended. However, with the average 2007 litter application rate of 2.6 Mg ha<sup>-1</sup> in ESW, a farmer would have to spend \$128 ha<sup>-1</sup> on replacement fertilizer N to maintain yields. Based on ESW as a whole, the value of nutrients exported in litter in 2007 was \$1,995,000 for N, \$1,250,000 for P, and \$1,048,000 for K—a total of \$4,292,742. The economic impact of replacing nutrients exported in litter to beef-cattle grazing farmers is clear.

### Management Implications

Nutrient management planning in ESW since the settlement agreement has led to an overall reduction in poultry litter application rates, and twice as much litter being exported as applied in the watershed. As poultry litter has been an inexpensive source of N (and to a lesser extent P and K) to maximize forage production and quality for beef-

cattle graziers, changes in litter management have impacted these farmers most. Thus, the NMP process must go beyond addressing poultry litter application rates and environmental risk assessment by including an educational effort to help farmers develop sustainable whole-farm operations. Some management practices that can contribute to the economic and environmental sustainability of beef-cattle grazing operations include incorporation of N<sub>2</sub>-fixing legumes into pastures; rotational grazing; exclusion of livestock from streams, forage harvest, and feed management; forage species diversification; and introduction of tall fescue containing a nontoxic endophyte.

**Legumes.** Established stands of legumes (e.g., white clover [*Trifolium repens* L.]) can fix 90 to 280 kg N ha<sup>-1</sup> yr<sup>-1</sup> in perennial grass pastures, with values increasing as percentage legume increases (Mallarino et al. 1990a; West and Mallarino 1996). A portion of the N fixed by legumes is transferred to associated grass via decomposition of nodules, roots, leaves, and stems and excreted forage consumed by cattle. Mallarino et al. (1990b) determined that an average of 41 kg ha<sup>-1</sup> yr<sup>-1</sup> of fixed N was transferred from white clover and recovered in tall fescue forage using <sup>15</sup>N-tracer technique. However, successful use of legumes as an alternative N source depends on fine-tuned management practices, such as maintaining favorable soil pH, replenishment of the soil seed bank to promote continual recruitment of new legume seedlings, preventing overgrazing to maintain legume plant vigor and N<sub>2</sub> fixation rate, and avoiding insufficient grazing of the grass component to prevent excessive shading of the legumes by grass.

**Rotational Grazing.** Rotational grazing can more uniformly redistribute excreted N and P within pastures, decreasing the potential for accumulation and subsequent loss in frequented (e.g., camping) sites, such as at water and shade. In fact, rotational grazing consistently increases pasture carrying capacity and animal weight gain over continuous grazing. For instance, Aiken (1998) reported a 39% increase in carrying capacity and 44% increase in weight gain ha<sup>-1</sup> with steers grazing wheat (*Triticum aestivum* L.) and annual ryegrass (*Lolium multiflorum* Lam.) during spring in an 11-paddock rotation. Hoveland et al. (1997) observed a 37% increase in weight gain ha<sup>-1</sup> in rotational over continuous stocking with tall fescue–bermudagrass, which was explained entirely by an increase in carrying capacity.

**Livestock Exclusion from Streams.** Livestock that defecate and urinate in and near streams can potentially contribute significant amounts of N and P over time. By observing four pastures where cattle had access to streams over four intervals during the spring and summer of 2003 in the Cannonsville Watershed in south central, New York, James et al. (2007) were able to estimate fecal P contributions to streams. On average, approximately 30% of all fecal deposits expected from a herd were observed to fall on land within 130 feet of a stream, and 7% fell directly into streams. Approximated to all grazed pastures in the watershed, cattle excreta contributed 12% of the agriculturally-derived P loading (Scott et al. 1998). While some programs may subsidize streambank fencing, farmer participation is mixed. These programs often include stipulations concerning reimbursement, maintenance, and upkeep that are simply too restrictive and time-consuming to farmers. In addition, riparian exclusion may result in various secondary effects that are not subsidized, such as the loss of productive pasture land. Because riparian areas serve as watering sources for cattle as well as shade, alternative amenities away from the stream or controlled access should be considered.

**Harvest and Feed Management.** Another challenge facing those farming high-P soils in watersheds such as ESW is to draw down soil P to levels considered low risk for P loss in runoff. As grazing beef excrete >90% of the P they consume, forage management may shift from all-grazing to harvesting and removing some or all the herbage as hay or silage. For example, Coblenz et al. (2004) reported 45 kg N ha<sup>-1</sup> yr<sup>-1</sup> was removed by bermudagrass that received 112 kg N ha<sup>-1</sup> yr<sup>-1</sup> as fertilizer in western Arkansas. Mehlich-3 extractable soil P declined 48 mg kg<sup>-1</sup> during two years. Forage harvested from high-P sites can be fed back to animals in identifiable low-P, low-runoff risk areas on the same farm; however, that does not mitigate the farm-scale P accumulation problem. Export of the harvested forage from the watershed as a cash hay crop to buyers demanding feed of high nutritional quality, such as dairy and horse producers, offers the best opportunity to draw down soil P to sustainable levels while making a profit.

**Forage Species Diversification.** Diversifying the type of forage on a farm can more thoroughly exploit changing growing conditions throughout the year to maximize nutrient uptake and recycling. For instance, bermudagrass has a five- to seven-month production lapse during which temperature is too cold for growth (West and Waller 2007). Annual grasses and legumes can be autumn-planted and grazed during the winter and early spring and/or allowed to accumulate growth in spring for a harvest of hay or silage. Winter crops would take up N and P during a time of year when nutrients are most subject to leaching and runoff losses.

**Nontoxic Endophyte-Free Tall Fescue.** Tall fescue is the predominant perennial forage grass in ESW and the surrounding region, owing to its high yield and adaptation to widely variable soil and climatic conditions and grazing management systems (West and Waller 2007). However, infection of tall fescue by its wild fungal endophyte (*Neotyphodium coenophialum*) generally reduces animal productivity and health (Nihsen et al. 2004). Endophyte toxins exacerbate heat stress in cattle during hot, humid conditions, causing animals to seek shade or stand in ponds for relief; they also reduce blood flow to body extremities in cold weather. Endophyte-free cultivars of tall fescue, which lack such toxins, do not persist well under the combined stresses of drought and heavy grazing pressure. New cultivars contain endophytes specifically selected for lack of ergot alkaloid production, but they retain the benefits of drought and grazing tolerance for host grass persistence. Parish et al. (2003) reported that steers grazing tall fescue with a nontoxic endophyte spent less time idling and standing, consumed less water, and consumed more forage than steers grazing toxic fescue, indicating the potential for better redistribution of excreted nutrients when using nontoxic endophytes. Steer-calf weaning weight increased 15% when cow-calf pairs grazed tall fescue infected with a nontoxic endophyte compared with grazing on wild-type toxic endophyte. Greater live-weight gain may increase farm revenues, while minimizing environmental impacts.

## Conclusions

Even when large amounts (>70%) of poultry litter are exported out of ESW and BMPs are implemented, this will not translate into an immediate decrease in P inputs into Lakes Eucha and Spavinaw because of elevated P storage in soils and river sediments. This stored P is expected to be released to river water for a period of time (i.e., years). Thus, it is critical to acknowledge that a lack of significant decrease in P concentrations

in Lakes Eucha and Spavinaw does not mean that improved nutrient management planning, lower litter applications, and adopted BMPs have not been successful in decreasing P loss from pastures in ESW.

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# Arkansas Phosphorus Index

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## Introduction

The Arkansas Phosphorus Index (API) is used to assess the risk of phosphorus (P) runoff from pastures and hayland as part of farm nutrient management plan (NMP) development. Nutrient management plans are required by farmers in nutrient surplus areas of Arkansas (see Fact Sheet FSA9529) who apply P with manure or biosolids. As such, it is basically used to determine maximum application rates of P on pastures, as a function of source potential (i.e., soil and manure management), transport potential (i.e., risk of runoff and erosion, field slope and proximity to streams), presence of best management practices (BMPs) and an acceptable level of risk. This publication details the structure, use and interpretation of the recently revised API, which from January 2010 is used in preparing nutrient management plans in Arkansas. Development of the API was a collaborative group effort involving many stakeholders within Arkansas who are listed at the end of this publication.

## Structure of the Phosphorus Index

The API is multiplicative in nature and assigns a risk value for P loss in runoff as follows:

$$\text{P Index} = \text{P Source Potential} * \text{P Transport Potential} * \text{BMPs Multiplier}$$

Seven site characteristics are included in the API which are grouped

into either P Source or P Transport Potential categories. Phosphorus Source Potential characteristics are (1) soil test P and (2) soluble P application rate, while the P Transport Potential characteristics are (3) soil erosion, (4) soil runoff class, (5) flooding frequency, (6) application method and (7) timing of P application.

In addition to management practices that influence site characteristics, there are nine BMPs that can be considered to reduce P runoff risk. The landowner has the option to implement one or a combination of diversions, terraces, ponds, filter strips, grassed waterways, paddock fencing, riparian forest buffers, riparian herbaceous buffers and field borders to meet his or her conditions and preferences.

The P Source Potential, P Transport Potential and BMP Multiplier are determined independently, as described below, before determining the overall API.

## P Source Potential

The estimated P Source Potential is calculated as follows:

$$\text{P Source Potential} = \text{WEP}_{\text{coef}} * (\text{WEP}_{\text{applied}} + \text{MNRL}_{\text{coef}} * (\text{TP}_{\text{applied}} - \text{WEP}_{\text{applied}})) + \text{STP}_{\text{coef}} * \text{STP}$$

**STP:** Soil test P (lbs/acre) is determined by the standard Mehlich-3 extraction method for a 0-4 inch soil sample (see Fact Sheet FSA1035 for proper soil sampling procedures). This

is the method used by the University of Arkansas Soil Laboratory. To obtain STP input value in lbs P/acre, the laboratory results in parts per million (ppm) should be multiplied by 1.33.

**WEP<sub>applied</sub>:** Water extractable P (lbs WEP/acre) is the amount of water soluble P applied with manure or biosolids. The University of Arkansas Diagnostics Laboratory follows national standard procedures to estimate WEP. It is determined by multiplying WEP<sub>applied</sub> (lbs/ton of manure) by the manure application rate (tons/acre).

**TP<sub>applied</sub>:** Total amount of P applied (lbs P/acre) with manure or biosolids. The University of Arkansas Diagnostics Laboratory follows national standard procedures to estimate total P. It is determined by multiplying TP<sub>applied</sub> (lbs/ton of manure) by the manure application rate (tons/acre).

**MNRL:** There is a continued but slow release of P from manure or biosolid after land application which can contribute additional P in runoff. To account for this, a mineralization factor (MNRL) of 0.05 (5% of non-WEP total P) for untreated material and 0.005 (0.5% of non-WEP total P) for alum-treated materials is included in the P Source Potential calculation.

The lower mineralization factor for alum-treated material reflects the fact that aluminum (Al) from added alum binds with P in a mineral rather than organic form. Thus, there is a lower potential for organic P mineralization in alum-treated material. Liquid manures treated with aluminum chloride to reduce WEP would also use the 0.005 mineralization factor. In order for biosolids to be considered “alum-treated,” they must have an Al:P mole ratio of 0.1 or greater (i.e., at least one molecule of Al to every molecule of P).

**WEP<sub>coef</sub> and STP<sub>coef</sub>:** These P source coefficients were determined from runoff P load data collected during rainfall simulation studies using various poultry litters, swine slurries and biosolids (Table 1). WEP<sub>coef</sub> varies for the different source materials to be land applied, while STP<sub>coef</sub> is always 0.0018.

Management history of the manure determines whether a liquid or dry manure WEP<sub>coef</sub> should be used. If water has been used in the handling and treatment process, such as for swine manure that has been flushed from the house into a holding pond, the liquid manure WEP<sub>coef</sub> should be used. If water has not been used, such as for poultry housed on bedding, the dry manure WEP<sub>coef</sub> should be used.

**Table 1. P source coefficients**

P Source Potential = $WEP_{coef} * (WEP_{applied} + MNRL_{coef} * (TP_{applied} - WEP_{applied})) + STP_{coef} * STP$			
API variable <sup>†</sup>	WEP <sub>coef</sub>	MNRL <sub>coef</sub>	STP <sub>coef</sub>
Dry litter, not treated	0.095	0.05	0.0018
Dry litter, treated <sup>¶</sup>	0.095	0.005	0.0018
Liquid manure, not treated	0.031	0.05	0.0018
Liquid manure, treated	0.031	0.005	0.0018
Biosolid cake	0.058	0.05	0.0018
Biosolid cake, treated <sup>§</sup>	0.058	0.005	0.0018
Liquid biosolid	0.029	0.05	0.0018
Liquid biosolid, treated	0.029	0.005	0.0018

† Units for both WEP<sub>applied</sub> and STP are lbs P/acre.

¶ Treated dry and liquid manures refers to treatment with aluminum compounds to reduce soluble P concentrations in the litter or manure.

§ Treated biosolids have an aluminum to P (Al:P) mole ratio of 1.0 or greater.

## P Transport Potential

Five factors influencing P transport are considered in estimating P Transport Potential: soil erosion, soil runoff class, flooding frequency, method of application and timing of application (Table 2). Each factor is divided into classes with each class associated with a specific loss rating value.

P Transport Potential is the sum of all the loss rating values as follows:

$$\text{P Transport Potential} = \text{soil erosion} + \text{runoff class} + \text{flooding frequency} + \text{application method} + \text{application timing}$$

**Soil Erosion:** Soil erosion is to be estimated by RUSLE2, a computerized method used by USDA Natural Resources Conservation Service (NRCS) to estimate soil loss in tons/ac/year in the API. Well-managed pasture systems would be expected to have negligible annual erosion; hence, this value is typically near zero.

**Soil Runoff Class:** Soil runoff class is determined from slope gradient and runoff curve number of a given soil (Tables 3 and 4). While slope will vary across a field, typical field slope can be roughly estimated from NRCS soil classification/survey information (available at <http://soildatamart.nrcs.usda.gov> and <http://websoilsurvey.nrcs.usda.gov>), with site visits

providing the opportunity to refine the estimate. The runoff curve number is a factor of pasture management and soil hydrologic group (Table 3). This is based on runoff predicted from a 40-acre field for a one-year, 24-hour storm event (i.e., in units of cubic feet per second – cfs). The soil runoff classes are Negligible (0.2-0.4 cfs/ac/in), Very Low (0.5-0.6 cfs/ac/in), Low (0.7-0.8 cfs/ac/in), Moderate (0.9-1.0 cfs/ac/in), High (1.1-1.2 cfs/ac/in) and Very High (1.3-1.4 cfs/ac/in).

**Pasture Management and Runoff Curve Numbers:** In the API, pasture management is classified as continuously grazed, rotationally grazed or hayed only (Table 4). Continuously grazed pastures are also broken down between those that have greater than or less than 0.75 animal units/acre; where an animal unit is defined as 1,000 lbs of live animal weight. The effect of cattle grazing has an important bearing on site hydrology and runoff potential. A pasture under continuous grazing would be expected to have a higher risk for P runoff than a pasture with rotational grazing. This is due to compaction and additional P inputs from cattle.

The soil hydrologic group for the predominant soil for the field can be found in the NRCS soil classification/survey information (available at <http://soildatamart.nrcs.usda.gov> and <http://websoilsurvey.nrcs.usda.gov>).

**Table 2. Phosphorus transport potential characteristics and calculations**

Site Characteristic	Description					Loss Rating Value
Soil erosion (tons/ac/yr)	<1	1 to 2	2 to 3	3 to 5	>5	
Loss rating value	0	0.1	0.2	0.4	1	LRV
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High
Loss rating value	0.1	0.15	0.2	0.5	1.0	1.5
Flooding frequency	None to very rare	Rare	Occasional	Frequent		
Loss rating value	0	0.2	0.5	2.0		LRV
Application method	Incorporated	Surface applied		Surface applied on frozen ground or snow		
Loss rating value	0.1	0.2		0.5		LRV
Application timing	July-Oct	March-June		Nov-Feb		
Loss rating value	0.1	0.25		0.6		LRV

**Table 3. Runoff class based on site slope and curve number**

		Runoff Curve Number <sup>†</sup>						
		<60	60-65	66-70	71-75	76-80	81-85	>85
Slope %	<1	N	N	N	N	VL	VL	VL
	1	N	N	VL	VL	VL	L	L
	2	N	VL	VL	VL	L	L	M
	3	N	VL	VL	L	L	M	M
	4	N	VL	L	L	M	M	M
	5	N	VL	L	L	M	M	H
	6	N	VL	L	M	M	H	H
	7	N	L	L	M	M	H	H
	8	N	L	L	M	M	H	VH
	9	N	L	L	M	H	H	VH
	10	N	L	M	M	H	H	VH
	11	N	L	M	M	H	H	VH
	12	N	L	M	M	H	VH	VH
	13	N	L	M	M	H	VH	VH
	14	N	L	M	H	H	VH	VH
	15	N	L	M	H	H	VH	VH
	>15	N	L	M	H	H	VH	VH

<sup>†</sup>Runoff curve numbers for pasture and its management are given in Table 4.

**Table 4. Influence of grazing management on runoff curve numbers used in the API**

Pasture Use	Soil Hydrologic Group			
	A	B	C	D
Continuously grazed > 0.75 An. Units/ac	68	79	86	89
Continuously grazed < 0.75 An. Units/ac	49	69	79	84
Rotational Grazing	39	61	74	80
Hayland	30	58	71	78

**Flooding Frequency:** Flooding frequency includes four categories: none to very rare, rare, occasional and frequent, and for any given site can be found through NRCS soil classification/survey information (available at <http://soildatamart.nrcs.usda.gov> and <http://websoilsurvey.nrcs.usda.gov>).

**Application Method:** Application methods are grouped into three areas: incorporated, surface applied or surface applied on frozen or snow-covered ground. The associated loss rating values of 0.1, 0.2 and 0.5 reflect the estimated risk of P transport during seasonal rainfall events.

**Application Timing:** The effect of application timing on P runoff potential is categorized into three periods of equal length (July-Oct, March-June and Nov-Feb), which are associated with loss rating factors 0.1, 0.25 and 0.60, respectively. These times were chosen after evaluating historical rainfall and stream flow data.

### Best Management Practices (BMPs) Multiplier

In addition to the management practices considered in the Source and Transport Potential factors, there are nine BMPs that can be considered for implementation to decrease the risk of P runoff. The credited effectiveness in decreasing P runoff and associated Conservation Practice Standards for these BMPs are shown in Table 5. The method to estimate the effectiveness of the implemented BMPs in reducing P transport in runoff is:

$$\text{BMPs Multiplier} = (1 - \text{Effectiveness}_1) * (1 - \text{Effectiveness}_2) * \dots * (1 - \text{Effectiveness}_9)$$

The effectiveness values are the BMP credits given in Table 5 expressed in a fractional format. That is, 20% would be expressed as 0.20. If a BMP is not implemented, it is assigned an effectiveness of 0. As a consequence, if no BMPs are implemented, the BMP multiplier will be equal to 1.0. If BMPs are used, then the BMP multiplier will have a value of less than 1.

**Table 5. Credit given in the revised API for various BMPs whose implementation meet NRCS Conservation Practice Standards**

(see <http://www.nrcs.usda.gov/technical/Standards/nhcp.html>)

Best Management Practice	CPS#	Credit
Diversion	362	5%
Terrace	600	10%
Pond	378	20%
Fenced pond		30%
Filter strip	393	20%
Fenced filter strip		30%
Grassed waterway	412	10%
Fencing	382	30%
Riparian forest buffer	391	20%
Fenced riparian forest buffer		35%
Riparian herbaceous cover	390	20%
Fenced riparian herbaceous cover		30%
Field borders	386	10%

The effectiveness rating given for a pond will depend on how much of the field drains into the pond. Nutrient management plan writers must make a professional judgment on percentage of field that drains into pond and the assigned effectiveness adjusted by that percentage. Determination of the percentage of the field draining to the pond should be based on topographic maps and site visits.

There are three additional potential adjustments regarding BMPs. If a pond is fenced, then the assigned effectiveness is increased from 20% to 30%. If a riparian forest buffer is fenced, then an effectiveness of 35% should be assigned for the combination. If fencing is used in conjunction with filter strips or riparian herbaceous buffers, an effectiveness of 30% should be assigned for the combination.

## Risk Interpretation

Based on the API site rating, fields are assigned a P Index risk class of low, medium, high or very high based on the resulting numeric value. Each class is associated with interpretations and recommendations as shown in Table 6. Recommendations range from cautions regarding buildup of soil P levels for the low risk class, to no additional P applications until soil P levels and P Index values are reduced for the very high class.

It should be noted that the recommendations are not expressed in nitrogen (N) or P-based application rates, as P application rates are inputs for the calculation of P Index values. While the API does not address environmental concerns associated with N applications, application rates should never exceed the crops' N requirement. In practice, the P Index value specified in the plan determines the maximum P application for the life of the plan. Application rates below those used to estimate the P runoff risk will result in a lower risk, assuming all other factors remain the same.

## Background Information and Reading

Arkansas Natural Resources Commission Title 20. 2010. *Rules governing the Arkansas Nutrient Management Planner certification program*. The Revised Arkansas Phosphorus Index by Moore, P.A., Jr., A. Sharpley, W. Delp, B. Haggard, T. Daniel, K. VanDevender, A. Baber and M. Daniel. <http://www.anrc.arkansas.gov/Title%2020%2012-10-09.pdf>.

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**Table 6. Interpretation and recommendations for the revised Arkansas Phosphorus Index**

P Index Value	Site Interpretations and Recommendations
LOW	Caution against long-term buildup of P in the soil.
MEDIUM	Evaluate the Index and determine any field areas that could cause long-term concerns. Consider adding BMPs.
HIGH	Evaluate the Index and determine elevation cause. Add appropriate BMPs and/or reduce P application. The immediate planning target is an API value in the Medium class or lower. If this cannot be achieved with realistic BMPs and/or reduced P rates in the short-term, then a conservation plan needs to be developed with a long-term goal of an API value in the Medium class or lower.
VERY HIGH	No P application. Add BMPs to decrease this value below the Very High class in the short-term and develop a conservation plan that would reduce the API value to a lower risk category, with a long-term goal of an API in the Medium class or lower.

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# Soil Phosphorus: Management and Recommendations

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## Phosphorus – Necessary for Plant and Animal Growth

Phosphorus (P) is a naturally occurring element that can be found in all living organisms, as well as in water and soils. It is an essential component of many physiological processes related to proper energy utilization in both plants and animals. Phosphorus can be added to the environment by man's activities as point source discharges or as non-point source runoff. Typical sources include industrial and municipal wastewater point source discharge or runoff from agricultural and urban areas. This publication addresses management issues and recommendations arising from application of P, mainly as manures to agricultural lands.

Plants derive P from soil; livestock, in turn, derive part of their P needs from plant materials. However, much of the naturally occurring P in grains is in a form that is indigestible to the animal. Therefore, inorganic P sources are added to animal diets to ensure adequate nutrition and sound bone development and reproduction. As a result, much of the dietary P passes through the animal (70 percent) and is excreted in animal manure. Applying animal manure as a fertilizer to crop and grazing land can utilize this excreted P.

**Plants, like animals, need a certain amount of P for healthy growth.**

Plants uptake P from soil as dissolved orthophosphate. However, native soil P levels are often low enough to limit crop production. Both inorganic P fertilizers (treated rock phosphates) and organic P sources (animal manures) are equally adept at supplying the orthophosphate ion and correcting P deficiencies in soil. Although it varies, typically 30 to 50 percent of the P in animal manure is in an organic form, which must be converted to plant-available inorganic forms via soil biological activity, a process known as mineralization. The net effect of this mineralization is that P derived from animal manure can act more like a slow-release fertilizer than commercial inorganic fertilizers, in which the P is formulated to be more soluble and readily available to plants.

**Not all the P applied to soil is taken up by plants – some is fixed; and not all the P fed to animals is absorbed – some is excreted.**

## Understanding Soil Test Numbers

The University of Arkansas' P fertilizer recommendations for pastures and crops are based on soil testing where samples are analyzed to determine the current levels of P available to the plant. Research-based recommendations are then made on the amount of additional P needed to achieve yield goals.

When discussing P, it is important to make the distinction between

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elemental P and phosphate ( $P_2O_5$ ). Soil test results are usually reported as elemental P, while commercial fertilizers are reported as  $P_2O_5$ , where 2.29 pounds of  $P_2O_5$  is the equivalent of 1 pound of P. For example, 100 lbs of  $P_2O_5$  is equivalent to 44 lbs P.

Soil test phosphorus (STP) is an indicator of how much P is expected to be available for plant use. If STP values are to be compared, the laboratory test method for extracting P and how the number is reported (parts per million – ppm or lbs/acre) must be known. Different testing laboratories can use different methods for extracting P, producing different test results that are difficult to compare even for the same sample. The University of Arkansas Soil Testing Laboratory uses the Mehlich-3 extraction method, with results reported in ppm and lbs/acre. The lbs/acre units on the soil test report assumes a 6-inch sample depth representing 2,000,000 lbs of soil, which results in lbs/acre values being two times greater than ppm. Finally, Mehlich-3 is one of the most common STP methods used on acidic soils (i.e., noncalcareous soils) in the U.S.

**Soil test P estimates how much P is available in a soil for plant use.**

To convert an STP value reported as ppm to lbs/acre, the depth of soil sample taken is needed. The conversion from ppm to lbs/acre, as used in the Arkansas P Index, assumes that a 4-inch deep layer of soil (furrow slice) covering 1 acre weighs 1,300,000 lbs. A 4-inch soil sample depth is recommended for pastures in Arkansas. To convert soil test results from ppm to lbs/acre for a 4-inch soil sample, multiply the value in ppm by 1.3. For example, an STP value of 100 ppm is the same as 130 lbs/acre.

**Applying manure can increase soil fertility and productivity by adding nutrients and organic matter, which increase ground cover and reduce surface runoff.**

## The Phosphorus Concern

Commercial fertilizers are commonly applied to pastures and croplands in a mixture of nitrogen (N), P and potassium (K) that is balanced to meet the nutrient needs of the desired crop. However, nutrients in livestock manure are not balanced with respect to crop requirements.

Table 1 reveals that there is about two to four times more N than elemental P for various manures. However, Table 2 indicates that typical forage crops require about six to ten times as much N as P. As indicated by these two tables, using animal manures to supply a crop's N requirement tends to result in applying more P than the plant needs.

Growers with confined livestock and poultry operations import feed onto the farm. This feed contains P at nationally recommended dietary levels for healthy animals to maintain bone structure strength, reproduction, etc. However, as only about 30 percent of that P is absorbed by the animal, most of the dietary P passes through the animal and is excreted in manure. In turn, the manure is spread on fields to take advantage of its nutrient value and organic matter. This practice has increased the overall fertility and productivity of soils by providing needed nutrients and organic matter which can increase ground cover and improve water infiltration and holding capacity. In turn, this decreases runoff and erosion.

**EXAMPLE SCENARIO**  
**Comparing N- vs. P-Based Litter Applications**

This example is for a broiler farm, consisting of four houses, that places 20,000 four-pound birds per house and averages five flocks per year. The litter produced will be applied to produce 4 tons of fescue per acre.

**Assumptions**

- Litter is produced at a rate of 1 ton per 1,000 birds per flock.
- The litter contains 60 lbs N/ton and 55 lbs  $P_2O_5$ /ton.
- The fescue produced will contain 36 lbs N/ton and 15 lbs  $P_2O_5$ /ton.
- 25% of the N is lost during litter application to volatilization.
- No other mineralization, denitrification or leaching losses for N or P are considered.

**Litter Nutrient Information**

- 400 tons litter/year
- 18,000 lbs N available/year
- 22,000 lbs  $P_2O_5$  available/year

**Fescue Nutrient Information**

- 4 tons fescue/acre
- 144 lbs N required/acre
- 60 lbs  $P_2O_5$  required/acre

**Application Comparisons**

<b>N Based</b>	<b>P Based</b>
• 125 acres required	• 393 acres required
• 3.2 tons litter/acre	• 1 ton litter/acre
• 144 lbs N applied/acre	• 46 lbs N applied/acre
• 176 lbs $P_2O_5$ applied/acre	• 55 lbs $P_2O_5$ applied/acre
• N needs met	• 98 lbs N deficit/acre
• 116 lbs $P_2O_5$ surplus/acre	• P needs met

**Comment**

For the N-based application, a  $P_2O_5$  surplus of 116 lbs/acre does not imply that the STP will increase by 116 lbs/acre. Due to soil chemical reactions, significant amounts of the surplus P will become bound in soil in forms unavailable for plant use, which are not estimated by soil test procedures. For this reason, a 116 lbs/acre surplus of  $P_2O_5$  will increase the STP level by less than 14 lbs P/acre; from about 6 to 13 lbs P/acre depending on soil properties.

**TABLE 1. Typical Nutrient Values for Manure Samples Collected by Arkansas Producers**

Type	N	P <sub>2</sub> O <sub>5</sub> (P) <sup>†</sup>	K <sub>2</sub> O (K) <sup>†</sup>	N/P
<b>Broiler litter (n = 522)<sup>‡</sup></b>				
Mean	61.60	65.5 (28.6)	59.8 (49.4)	2.2
Minimum	20.60	24.7 (10.8)	25.4 (21.0)	
Maximum	88.20	116.8 (51.0)	89.8 (74.2)	
<b>Dairy manure (= 142)<sup>¶</sup></b>				
Mean	11.57	6.8 (3.0)	10.4 (8.6)	3.9
Minimum	1.01	0.2 (0.1)	0.4 (0.4)	
Maximum	41.67	34.3 (15.0)	53.1 (43.9)	
<b>Swine slurry (n = 535)<sup>¶</sup></b>				
Mean	9.99	9.8 (4.3)	8.0 (6.6)	2.3
Minimum	0.17	0.01 (0.006)	0.1 (0.1)	
Maximum	97.33	256.0 (111.8)	79.5 (65.7)	

<sup>†</sup> To convert from P<sub>2</sub>O<sub>5</sub> to elemental P, divide by 2.29, and from K<sub>2</sub>O to elemental K, divide by 1.21.

<sup>‡</sup> These values (lb/ton) are derived from poultry litter samples submitted from the Eucha-Spavinaw Watershed to the University of Arkansas Agricultural Diagnostics Laboratory between 2005 and 2009.

<sup>¶</sup> These values (lb/1,000 gal) are derived from manure samples collected by producers and sent to the University of Arkansas Agricultural Diagnostics Laboratory between 2007 and 2009.

**TABLE 2. Nutrients Removed Per Ton of Forage Dry Matter for Samples Submitted to the Fayetteville Agricultural Diagnostic Laboratory (University of Arkansas, Division of Agriculture) and Identified as Hay**

Forage Type	No. of Observations	N	P <sub>2</sub> O <sub>5</sub> (P) <sup>†</sup>	K <sub>2</sub> O (K) <sup>‡</sup>	N/P
----- lbs removed / ton forage -----					
Alfalfa	378	62.6	14.0 (6.1)	51.4 (42.5)	10.3
Bahiagrass	369	31.4	9.8 (4.3)	31.9 (26.4)	7.3
Bermudagrass	6,676	42.0	13.7 (6.0)	48.0 (39.7)	7.0
Clover	31	45.4	11.9 (5.2)	45.4 (37.5)	8.7
Fescue	1,532	36.2	14.7 (6.4)	49.0 (40.5)	5.7
Legume/grass	268	40.6	13.7 (6.0)	46.8 (38.7)	6.8
Ryegrass	366	37.2	13.7 (6.0)	46.6 (38.5)	6.2
Sudangrass	773	36.4	13.7 (6.0)	47.2 (39.0)	6.1
Wheat	127	36.2	18.5 (8.1)	55.2 (45.6)	4.5

<sup>†</sup> To convert from P<sub>2</sub>O<sub>5</sub> to elemental P, divide by 2.29.

<sup>‡</sup> To convert from K<sub>2</sub>O to elemental K, divide by 1.21.

<sup>¶</sup> N from N fixation not N fertilizer.

Data from the UACES "Feed Analysis Program" database as determined on Jan. 5, 2010. Available at <http://feedanalysis.uaex.edu/>.

Litter and manure were historically applied to meet the N requirements of forages or crops and to offset the use of costly mineral N fertilizers. However, this approach applied two to four times more P than was needed by the plant (Tables 1 and 2). Repeated application of manure based on plant N needs results in the accumulation of P in the soil, primarily in surface layers. In some cases, years of repeated applications have increased STP above optimum levels for production [36 to 50 ppm P (47 to 65 lbs P/acre)], particularly for pastures not cut for hay.

**Soil is not an infinite sink for P.**

In the past, this STP buildup has not been perceived as significant cause for concern. For instance, even at high levels, P is usually not detrimental to plant growth. Furthermore, it was understood by the national scientific community that P was tightly bound to soil in relatively stable forms. It was further thought that significant movement of this P off fields only occurred if soil moved by erosion. Finally, N management had been a priority to address concerns about elevated nitrate concentrations in groundwater.

**The repeated application of manure at rates meeting plant N needs will increase soil test P levels.**

A large amount of research between 1985 and 2000, showed that as STP increased, especially in the top 2 to 4 inches of soil, so did the concentration of soluble P in runoff (Figure 1). While conservation programs and improved pasture management and productivity were decreasing total P losses, research found that more of the P that was moving was in a soluble form, which was immediately available for algal uptake. This exacerbated the frequency and occurrence of nuisance algae blooms in freshwater lakes and reservoirs. In most cases, biological productivity (or eutrophication) is accelerated by P inputs because N and carbon can freely exchange between air and water and some blue-green algae can fix atmospheric N.

**Research shows as soil test P increases, so does the concentration of P in runoff.**

## How Much Soil Test Phosphorus Is Needed?

Arkansas scientists agree that there is no agronomic reason or need for STP levels to be greater than about 50 ppm P (Mehlich-3 extraction; or 65 lbs P/acre for a 4-inch soil sample). Typical forage crops

will annually remove from 4 to 8 pounds of elemental P per ton of production. As an example, bermuda-grass removes about 14 P<sub>2</sub>O<sub>5</sub> lbs/ton or 84 lbs P<sub>2</sub>O<sub>5</sub> for a 6-ton/acre crop annually.

It must also be emphasized that P contained in plant material is recycled to the soil unless it is removed, either by crop or forage harvesting, soil erosion or runoff. On grazing land, most P is recycled to the soil in manure, with only a small portion (<30 percent) of ingested P removed from the land with the animal.

**The measurement of soil test P is an important management and educational tool. Testing every year to every other year facilitates tracking soil test P buildup/reduction trends over time.**

## How Much Soil Test Phosphorus Is Too Much?

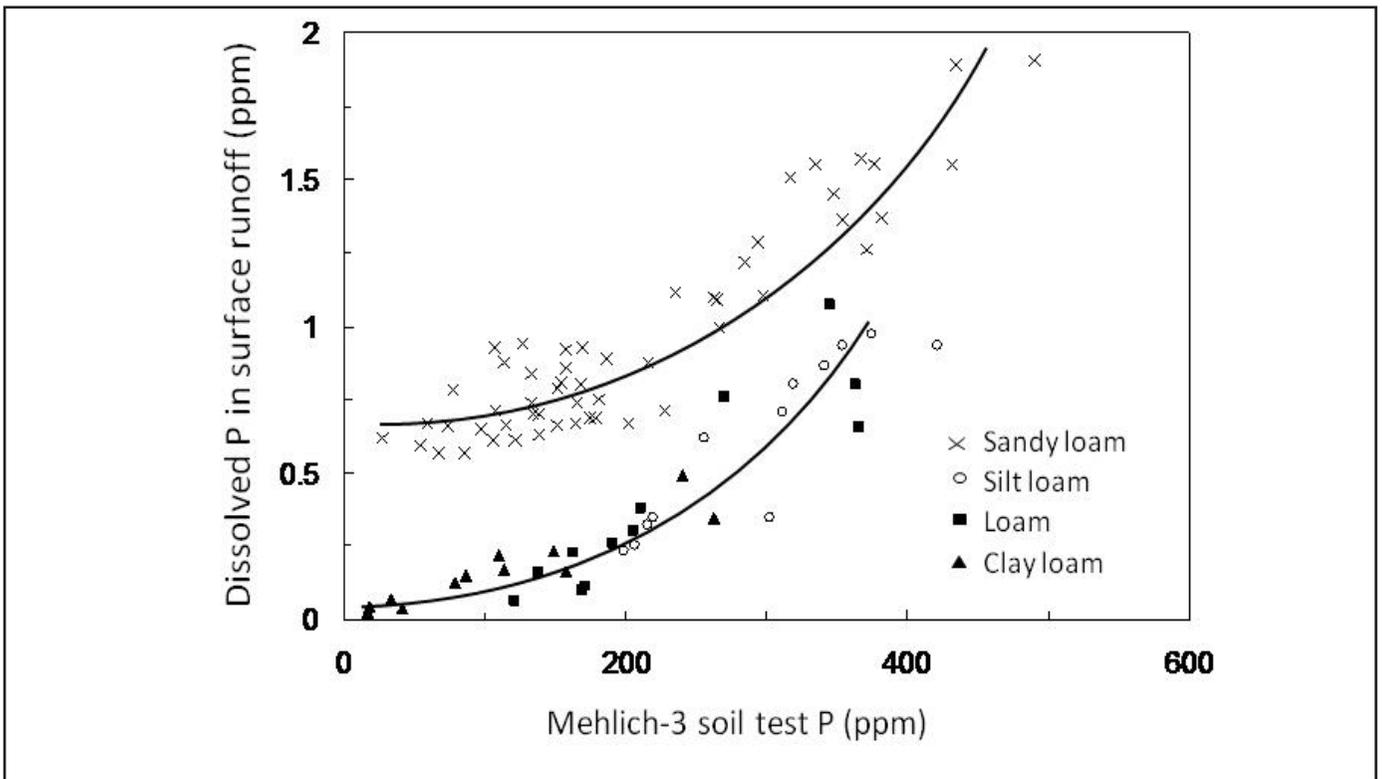
With the move from agronomic to environmental concerns with P, soil P testing has been used to indicate when P enrichment of runoff may become unacceptable. A common approach has been to use agronomic soil P standards, following the rationale that soil P in excess of crop requirements is vulnerable to removal by surface runoff or leaching. As agronomic standards already exist for STP, this approach required little investment in research and development and could be readily implemented. However, care must be taken in interpreting STP values for environmental purposes (Figure 2).

Interpretations given on soil test reports (i.e., low, medium, optimum and above optimum) are based on the expected crop yield response to P and not on soil P release to surface or subsurface runoff. Some have tried to simply extend crop response levels and say that STP above the level where no crop response is expected is in excess of crop needs and, therefore, is cause for concern (Figure 2). Although research has shown agricultural soil P tests can estimate a soil's potential to enrich runoff with P, this relationship is neither direct nor quantitative. It is of critical importance to remember that soil P is only one of several sources (rate, timing and type of manure or fertilizer P applied) and transport factors (runoff, erosion and proximity of a field to a stream) that influence the potential for P transport, which are site specific. Because of this, the P Index was developed and is now widely used to assess the risk of P loss in runoff from a given site (see fact sheet *FSA9531, Arkansas Phosphorus Index*).

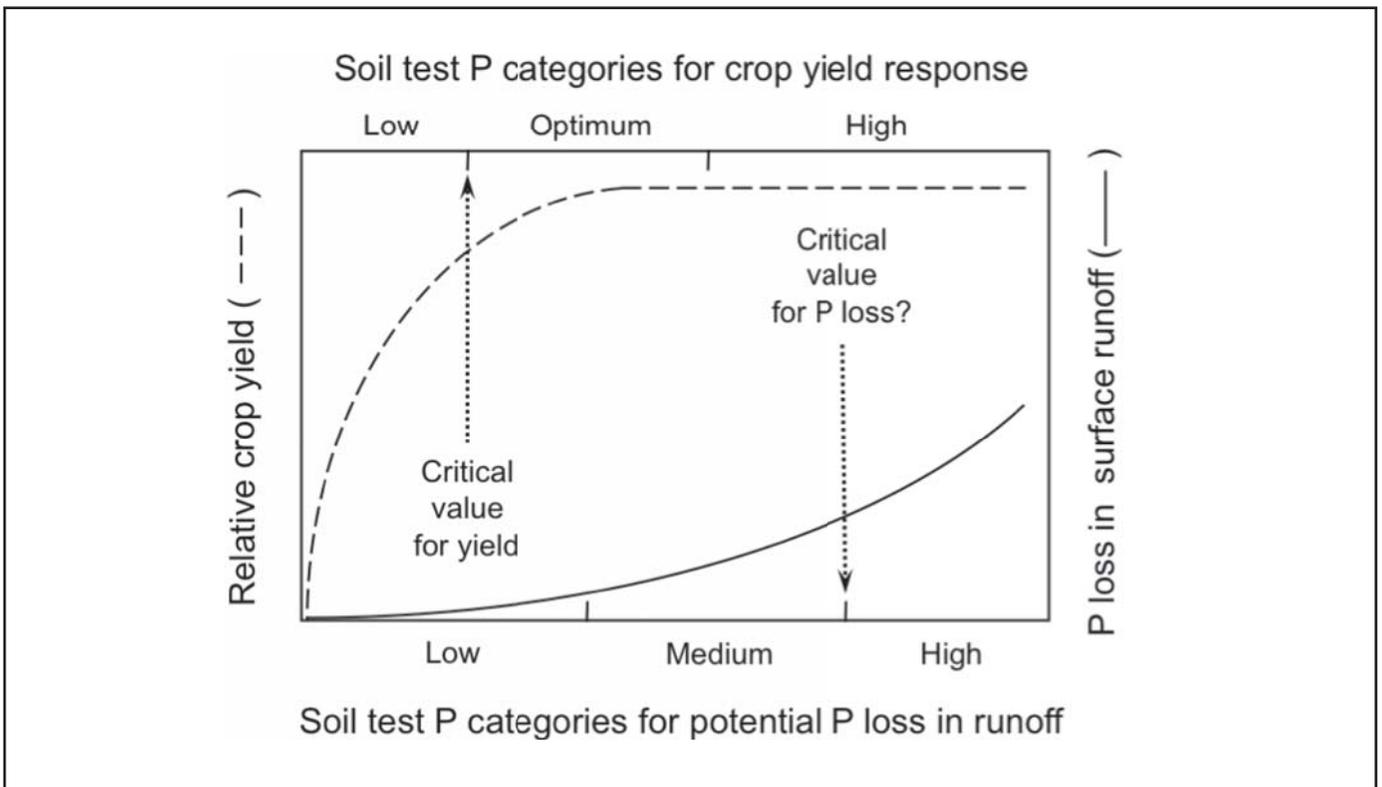
**There are several Best Management Practices that can decrease the risk of P loss in runoff from fields.**

**FIGURE 1**  
**Relationship Between Mehlich-3 Extractable Soil P and Dissolved Reactive P (DRP) in Runoff**  
**(based on STP levels in the top 1 inch of soil)**

Adapted from Pote et al., 1996, and Sharpley et al., 2001



**FIGURE 2**  
**As Soil P Increases So Does Crop Yield and the Potential for P Loss in Surface Runoff**



## Recommendations and Concerns

- If applying animal manures to pasture or cropland, it is highly recommended to voluntarily obtain a nutrient management plan written by a state-certified plan writer or from NRCS that utilizes the P-Index approach, which determines the relative risk of P-loss and makes site-specific recommendations related to:
  - Maximum allowable manure application rate for individual fields;
  - Appropriate “Best Management Practices” that can reduce the transport potential of P from a given field;
  - Appropriate “set back” distances from critical water features.
- Current scientific evidence is limited on how much P can be tolerated for all fields in all situations. However, growers with management alternatives for litter or manure should consider reducing P applications to fields with high STP. It is known that high P fields can require as much as 15 to 20 years of continuous crop harvesting, with no added P during that time to reduce high STP levels. Therefore, it is to the landowner’s advantage not to let STP build to high levels if he/she has alternatives for management.
- Litter and manure management applications should be based on the risk of P loss, of which STP is one of many factors controlling the loss. This is a requirement of managing P applications in nutrient surplus areas of Arkansas (see Fact Sheets *FSA9528, What Is Water Quality?*, and *FSA9529, Nutrient Analysis of Poultry Litter*).
- Growers should be encouraged to make commercial fertilizer applications formulated with N, K, and lime to meet the forage needs of fields where animal manure is no longer applied. Otherwise, decreased fertility can result in a loss of forage cover and increase the potential for runoff and erosion.
- Proper soil sampling techniques are critical to the accurate characterization of STP in pastureland. Samples should be collected from a minimum of 12 to 15 locations within a field in a zigzag

pattern across the field. These samples should be mixed together and a composite sample taken from the mixture. This provides the most representative sample possible. Also, care should be taken to collect a sample approximately 4 inches in depth. Producers are encouraged to contact their local county extension office for sampling instructions prior to sampling.

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# Using the 2010 Arkansas Phosphorus Index



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# Using the 2010 Arkansas Phosphorus Index

## Introduction

On January 1, 2010, the Arkansas Natural Resources Commission (ANRC) adopted a revised Arkansas P Index (API). ANRC requires the use of the API to prepare nutrient management plans in those watersheds which Title XXII designates as Nutrient Surplus Areas. The USDA Natural Resources Conservation Service (NRCS) has also adopted the API as part of the 590 nutrient management planning conservation practice standard. As nutrient management plans (NMPs) are required by several regulations pertaining to the application of manure, participation in certain cost-share programs and many integrator contracts, most land application of manure is usually associated with the API and a nutrient management plan.

The API assesses the risk of phosphorus (P) loss in runoff from pastures and hayland as a function of source potential (i.e., P from the soil and manure application), transport potential (i.e., risk P movement offsite as affected by runoff and erosion, field slope, grazing intensity and proximity to streams) and any additional best management practices (BMPs) implemented between the application site and potential receiving waters. As a result, for a specific set of field conditions, the API associates a P runoff risk value to a specific manure or biosolids application rate. The classification of this value into a risk range determines if the application is environmentally acceptable. If acceptable, the nutrient management plan specifies this application rate as the maximum rate for the combination of P source and field in question. During the implementation of a nutrient management plan, application rates up to the specified maximum can be applied. Lower rates are generally considered to be associated with lower environmental P runoff risk and therefore also acceptable. This publication describes the API and how to interpret the assigned risk and provides example calculations.

## The Phosphorus Index

The API addresses seven site characteristics which are grouped into either Source or Transport Factors. The P Source Factors are (1) soil test P and (2) soluble P application rate. The P Transport Factors include

(3) soil erosion, (4) soil runoff class, (5) flooding frequency, (6) application method and (7) timing of P application. In addition to management practices that influence site characteristics, there are nine additional BMPs that can be considered to reduce P runoff risk. The landowner has the option to implement a combination of diversions, terraces, ponds, filter strips, grassed waterways, paddock fencing, riparian forest buffers, riparian herbaceous buffers and field borders to meet his or her conditions and preferences.

The API is calculated as:

$$\text{P Index} = [(\text{P Source Potential} * \text{P Transport Potential} * \text{BMPs Multiplier}) / 1.8] * 100 \quad [\text{Eq. 1}]$$

The product of the P Source Potential, P Transport Potential and BMPs Multiplier is divided by 1.8 and then multiplied by 100 to express the risk value on a 100-point scale to facilitate interpretation. Prior to calculating the overall P Index value, each of its components must be calculated separately as indicated below.

## Calculating the P Source Potential

As previously indicated, the P Source Potential considers both the soil and the material applied as potential P sources (equation 2).

$$\text{P Source Potential} = \{\text{WEP}_{\text{coef}} * [\text{WEP} + \text{MNRL}_{\text{coef}} * (\text{TP} - \text{WEP})]\} + \{\text{STP}_{\text{coef}} * \text{STP}\} \quad [\text{Eq. 2}]$$

STP is soil test P (lbs/acre) as determined by the Mehlich-3 extraction method for a 0-4 inch soil sample (see FSA1035, *Soil Testing for Manure Management*, and FSA2121, *Test Your Soil for Plant Food and Lime Needs*, for proper soil sampling procedures). Input values of STP in lbs P/acre are determined by multiplying soil test report values in parts per million (ppm) by 1.33 for a standard 4-inch soil sample.

WEP is water extractable P applied (lbs WEP/acre) as manure or biosolids. This value is calculated as the WEP concentration of the material being applied times the amount of material being applied. For example, broiler litter with a WEP concentration of 5 lbs/ton applied at a rate of 1.5 tons/acre would result in 7.5 lbs/acre WEP application.

**TP** is the total amount of P applied (lbs P/acre) as manure or biosolids. This value is calculated as the TP concentration of the material being applied times the amount of material being applied. For example, broiler litter with a total P concentration of 25 lbs P/ton applied at a rate of 1.5 tons/acre would result in 37.5 lbs P/acre of total P application. Multiplying 37.5 by 2.29 results in 86 lbs P<sub>2</sub>O<sub>5</sub> /acre total P application.

**MNRL<sub>coef</sub>** is a factor accounting for the continued but slow release of P from manure or biosolid after land application, which can contribute additional P in runoff. MNRL is 0.05 (5% of non-WEP total P) for untreated material and 0.005 (0.5% of non-WEP total P) for alum-treated materials. The intention of treating with alum (aluminum sulfate) is to bind up the soluble P in the litter or manure and therefore reduce the P runoff risk.

**WEP<sub>coef</sub>** is a research-derived multiplier that correlates to the potential for land-applied materials to release P to runoff; it is 0.095 for poultry litter, 0.031 for liquid manure, 0.058 for biosolid cake and 0.029 for liquid biosolids.

**STP<sub>coef</sub>** is a research-derived multiplier of 0.0018, which describes the fraction of STP that will likely result in runoff P.

## Calculating the P Transport Potential

The P Transport Potential is calculated as the sum of the loss rating value for soil erosion, soil runoff class, flooding frequency, application method and application timing. Each of these factors is divided into subclasses where each class is associated with a loss rating value (Table 1). When calculating the P Transport Potential, each site is

evaluated in terms of the various factors and the appropriate loss rating values assigned, then summed to estimate the total P Transport Potential. Larger P Transport Potential values indicate greater P runoff risk than lower values.

**Soil Erosion** as estimated by RUSLE2. Well-managed pasture systems would be expected to have erosion rates less than one ton/acre/year, hence the loss rating value for erosion is typically zero.

**Soil Runoff Class** is determined from the Runoff Curve Number and Soil Runoff Class tables (Tables 2 and 3). To use these tables, the planned Pasture Management, Soil Hydrologic Group and representative Soil Slope are needed. This information is determined from a combination of NRCS soil classification and survey information (available at <http://soildatamart.nrcs.usda.gov> and <http://websoilsurvey.nrcs.usda.gov>), landowner interviews and site visits. In practice, the planned Pasture Management and Soil Hydrologic Group provide the Runoff Curve Number from Table 2. The Runoff Curve Number and Soil Slope provide the Soil Runoff Class from Table 3. The Soil Runoff Class provides the Soil Runoff Class loss rating value from Table 1.

**Flooding Frequency** falls into four categories: none to very rare, rare, occasional and frequent as classified by NRCS soil classification/survey information (available at <http://soildatamart.nrcs.usda.gov> and <http://websoilsurvey.nrcs.usda.gov>). Flooding frequency is used as a surrogate for proximity of a field to a stream and assumes that the potential for runoff from a field to enter a stream increases as its flooding frequency increases.

**Table 1. P Transport Potential Loss Rating Values**

Factor	Rating					
Soil erosion (tons/acre/year)	<1	1 to 2	2 to 3	3 to 5	>5	
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1.0</b>	
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>
Flooding frequency	None to very rare		Rare	Occasional	Frequent	
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>	
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>	
Application timing	July-Oct.		March-June		Nov.-Feb.	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>	
<b>P Transport Potential = (soil erosion + runoff class + flooding frequency + application method + application timing)</b>						

**Table 2. Runoff Curve Number**

Pasture Management	Soil Hydrologic Group			
	A	B	C	D
Continuously grazed > 0.75 Animal Units/Acre	68	79	86	89
Continuously grazed < 0.75 Animal Units/Acre	49	69	79	84
Rotational Grazing	39	61	74	80
Hayland	30	58	71	78

**Table 3. Soil Runoff Class**

		Runoff Curve Number						
		<60	60-65	66-70	71-75	76-80	81-85	>85
Slope %	<1	N	N	N	N	VL	VL	VL
	1	N	N	VL	VL	VL	L	L
	2	N	VL	VL	VL	L	L	M
	3	N	VL	VL	L	L	M	M
	4	N	VL	L	L	M	M	H
	5	N	VL	L	L	M	M	H
	6	N	VL	L	M	M	H	H
	7	N	L	L	M	M	H	H
	8	N	L	L	M	M	H	VH
	9	N	L	L	M	H	H	VH
	10	N	L	M	M	H	H	VH
	11	N	L	M	M	H	H	VH
	12	N	L	M	M	H	VH	VH
	13	N	L	M	M	H	VH	VH
	14	N	L	M	H	H	VH	VH
	15	N	L	M	H	H	VH	VH
>15	N	L	M	H	H	VH	VH	

N = Negligible, VL = V. Low, L = Low, M = Moderate, H = High, VH = V. High

**Application Method** describes how manure or biosolids are land-applied with the choices of incorporated, surface applied or surface applied to frozen or snow-covered ground. It should be noted that surface application to frozen or snow-covered

ground may not be an option, depending on which regulations may apply.

**Application Timing** is categorized into July-Oct, March-June and Nov-Feb, as a function of the propensity for rainfall and runoff to occur based on historical rainfall and stream flow data.

## Calculating the Best Management Practices (BMPs) Multiplier

The presence of NRCS Conservation Practices or BMPs can decrease P runoff with varying degrees of effectiveness (Table 4). The multiplier associated with each BMP is calculated as one minus the effectiveness of the BMP implemented. The multiplier for all the BMPs implemented is the product of the multiplier for each BMP (Equation 3).

$$\text{BMPs Multiplier} = (1 - \text{Effectiveness 1}) * (1 - \text{Effectiveness 2}) * \dots * (1 - \text{Effectiveness n}) \quad [\text{Eq. 3}]$$

Effectiveness rating values from Table 4 are expressed as values between 0 and 1. Multiplier values will be between 0 and 1. If no additional BMPs are implemented, the BMPs Multiplier value will be 1.

If only a portion of the field drains to a particular BMP, the multiplier for that BMP should be reduced to reflect the fraction of the field that drains to it.

**Table 4. Approved BMPs for Use in the Arkansas Phosphorus Index**

Best Management Practice	CPS†	Effectiveness
Diversion	362	5%
Fencing	382	30%
Field borders	386	10%
Filter strip	393	20%
Fenced filter strip		30%
Grassed waterway	412	10%
Pond‡	378	20%
Fenced pond		30%
Riparian forest buffer	391	20%
Fenced riparian forest buffer		35%
Riparian herbaceous cover	390	20%
Fenced riparian herbaceous cover		30%
Terrace	600	10%

† CPS is the NRCS Conservation Practice Standard; see <http://www.nrcs.usda.gov/technical/Standards/nhcp.html>

‡ The effectiveness rating for any given pond will depend on how much of field drains into the pond. Nutrient management plan writers must make a professional judgment on percentage of a field that drains into pond based on topographic maps and site visits. The assigned effectiveness is adjusted by that percentage.

Professional judgment based on available maps and site visits should normally be sufficient to guide decisions regarding the modification of the multiplier.

## Risk Interpretation

After a P Index value is determined from Equation 1, fields are assigned a P Index risk class of low, medium, high or very high based on the normalized risk value (Table 5). Each class is associated with interpretations and recommendations. Recommendations range from cautions regarding buildup of STP levels for the low risk class to no additional P applications until the API rating is reduced from the very high class. While the API does not address environmental concerns associated with N applications, application rates should never exceed the crops' N requirement after N storage and application losses are considered. Although most nutrient management plans will be written for a five-year period, plans for fields receiving biosolids (sewage sludge) will only be valid for one year.

**Table 5. Interpretation and Recommendations for the Arkansas P Index**

P Index Value	Site Interpretations and Recommendations
Low < 33	Caution against long-term buildup of P in the soil.
Medium 33-66	Evaluate the Index and determine any field areas that could cause long-term concerns. Consider adding BMPs.
High 67-100	Reduce litter application rate and re-run PI until the P index is in the Medium range.
Very High > 100	No P application. Add BMPs to decrease this value below the Very High class in the short term and develop a conservation plan that would reduce the API value to a lower risk category, with a long-term goal of a value in the Medium class or lower.

## Using the Index

Several scenarios are presented below to demonstrate how the API works and how BMPs can reduce the risk of P loss as a function of the API. Obviously, these scenarios do not cover all eventualities but are meant to show the flexibility of management options resulting from an API assessment. Further, the concepts of a split-litter application (spring and fall) and manure-nutrient banking are presented. For Scenarios 2 to 5, the source and transport variables changing from the previous scenario are in red type for ease of comparison.

**Scenario 1** – In this scenario, STP is 100 lbs/acre, litter is surfaced applied at 1.5 tons/acre in September, litter WEP is 5 lbs P/ton, litter total P is 25 lbs P/acre, soil erosion is negligible, runoff class is negligible (Soil Hydrologic Group C, Rotational Grazing, RCN 74, Slope <1%), no flooding occurs and there are no BMPs in place.

**Scenario 2** – In this scenario, **STP is 500 lbs/acre**, litter is surface applied at 1.5 tons/acre in **April**, litter WEP is 5 lbs P/ton, litter total P is 25 lbs/ton, soil erosion is negligible, runoff class is **moderate** (Soil Hydrologic Group C, Rotational Grazing, RCN 74, Slope 6%), no flooding occurs and there are no BMPs.

**Scenario 3** – In this scenario, STP is 500 lbs/acre, litter is surface applied at 1.5 tons/acre in April, litter WEP is 5 lbs P/ton, litter total P is 25 lbs/ton, soil erosion is negligible, runoff class is moderate (Soil Hydrologic Group C, Rotational Grazing, RCN 74, Slope 6%), no flooding occurs, **there is a riparian herbaceous buffer and 50% of the field's runoff enters a pond.**

**Scenario 4** – In this scenario, STP is 500 lbs/acre, litter is surface applied at 1.5 tons/acre in April, litter WEP is 5 lbs P/ton, litter total P is 25 lbs P/ton, soil erosion is negligible, runoff class is **high** (Soil Hydrologic Group C, RCN 86 **continuous grazing at >0.75 animal units/acre**, Slope 6%), no flooding occurs and **there is a fenced riparian herbaceous buffer.**

**Scenario 5** – Split application of litter: For split applications the API is calculated three times to estimate the P runoff risk associated with soil only (WEP = 0, TP = 0, Application Timing same as higher risk application timing window), first litter application only (STP = 0) and second litter application only (STP = 0). The three values are then summed to estimate the total P runoff risk.

In this scenario, STP is **50 lbs/acre**, litter is surface applied at 1.5 tons/acre in April and again in September, litter WEP is 5 lbs P/ton, litter total P is 25 lbs P/ton, soil erosion is **negligible**, runoff class is negligible (Soil Hydrologic Group C, Rotational Grazing, RCN 74, Slope <1%), no flooding occurs and there is a fenced riparian herbaceous buffer.

**Scenario 6** – Manure Nutrient Banking – When the P Index value is classified as high or lower and the application rate used to calculate this value is no more than 1 ton/acre, or 300 gallons/acre, manure banking can be considered. Manure banking is typically applying twice the volume of manure every other year. In the off-year(s), no application of P is made. The intent is to allow farm management options that include practical nutrient applications with acceptable uniformity, while addressing water quality concerns.

## Scenario 1

Characteristic	Description					Rating
<b>P Source Potential</b>						
$P \text{ Source Potential} = \{WEP_{\text{coef}} * [(WEP + MNRL_{\text{coef}} * (TP - WEP))]\} + \{STP_{\text{coef}} * STP\}$						
STP = 100 lbs/acre	WEP = 5 lbs/ton * 1.5 tons/acre = 7.5 lbs WEP/acre			TP = 25 lbs/ton * 1.5 tons/acre = 37.5 lbs TP/acre		
$P \text{ Source Potential} = \{0.095 * [7.5 + 0.05 * (37.5 - 7.5)]\} + \{0.0018 * 100\}$						<b>1.04</b>
<b>P Transport Potential</b>						
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5	
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>
Flooding frequency	None to very rare		Rare	Occasional	Frequent	
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>	
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>	
Application timing	July-Oct.		March-June		Nov.-Feb.	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>	
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>0.4</b>
<b>BMPs Multiplier</b>						
$BMPs \text{ Multiplier} = (1 - Effectiveness \ 1) * (1 - Effectiveness \ 2) * \dots * (1 - Effectiveness \ n)$						
$BMPs \text{ Multiplier} = (1 - 0.0)$						<b>1.0</b>
$P \text{ Index} = [(P \text{ Source Potential} * P \text{ Transport Potential} * BMPs \text{ Multiplier}) / 1.8] * 100$						
$P \text{ Index} = [(1.04 * 0.4 * 1.0) / 1.8] * 100$						<b>23</b> <b>(Low)</b>

## Scenario 2

Characteristic	Description					Rating
<b>P Source Potential</b>						
$P \text{ Source Potential} = \{WEP_{\text{coef}} * [(WEP + MNRL_{\text{coef}} * (TP - WEP))]\} + \{STP_{\text{coef}} * STP\}$						
STP = 500 lbs P/acre	WEP = 5 lbs/ton * 1.5 tons/acre = 7.5 lbs WEP/acre			TP = 25 lbs/ton * 1.5 tons/acre = 37.5 lbs TP/acre		
$P \text{ Source Potential} = \{0.095 * [7.5 + 0.05 * (37.5 - 7.5)]\} + \{0.0018 * 500\}$						<b>1.76</b>
<b>P Transport Potential</b>						
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5	
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>
Flooding frequency	None to very rare		Rare	Occasional	Frequent	
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>	
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>	
Application timing	July-Oct.		March-June		Nov.-Feb.	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>	
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>0.95</b>
<b>BMPs Multiplier</b>						
$BMPs \text{ Multiplier} = (1 - Effectiveness \ 1) * (1 - Effectiveness \ 2) * \dots * (1 - Effectiveness \ n)$						
$BMPs \text{ Multiplier} = (1 - 0.0)$						<b>1.0</b>
$P \text{ Index} = [(P \text{ Source Potential} * P \text{ Transport Potential} * BMPs \text{ Multiplier}) / 1.8] * 100$						
$P \text{ Index} = [(1.76 * 0.95 * 1.0) / 1.8] * 100$						<b>93</b> <b>(High)</b>

Scenario 3

Characteristic	Description					Rating
<b>P Source Potential</b>						
$P \text{ Source Potential} = \{WEP_{\text{coef}} * [WEP + MNRL_{\text{coef}} * (TP - WEP)]\} + \{STP_{\text{coef}} * STP\}$						
STP = 500 lbs P/acre	WEP = 5 lbs/ton * 1.5 tons/acre = 7.5 lbs WEP/acre			TP = 25 lbs/ton * 1.5 tons/acre = 37.5 lbs TP /acre		
$P \text{ Source Potential} = \{0.095 * [7.5 + 0.05 * (37.5 - 7.5)]\} + \{0.0018 * 500\}$						<b>1.76</b>
<b>P Transport Potential</b>						
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5	
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>0.5</b>
Flooding frequency	None to very rare		Rare	Occasional	Frequent	
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>	
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>	
Application timing	July-Oct.		March-June		Nov.-Feb.	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>	
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>0.95</b>
<b>BMPs Multiplier</b>						
$BMPs \text{ Multiplier} = (1 - \text{Effectiveness } 1) * (1 - \text{Effectiveness } 2) * \dots * (1 - \text{Effectiveness } n)$						
$BMPs \text{ Multiplier} = (1 - 2.0) * (1 - 0.20 * 0.5)$						<b>0.72</b>
$P \text{ Index} = [(P \text{ Source Potential} * P \text{ Transport Potential} * BMPs \text{ Multiplier}) / 1.8] * 100$						
$P \text{ Index} = [(1.76 * 0.95 * 0.72) / 1.8] * 100$						<b>67 (High)</b>

Scenario 4

Characteristic	Description					Rating
<b>P Source Potential</b>						
$P \text{ Source Potential} = \{WEP_{\text{coef}} * [WEP + MNRL_{\text{coef}} * (TP - WEP)]\} + \{STP_{\text{coef}} * STP\}$						
STP = 500 lbs P/acre	WEP = 5 lbs/ton * 1.5 tons/acre = 7.5 lbs WEP/acre			TP = 25 lbs/ton * 1.5 tons/acre = 37.5 lbs TP /acre		
$P \text{ Source Potential} = \{0.095 * [7.5 + 0.05 * (37.5 - 7.5)]\} + \{0.0018 * 500\}$						<b>1.76</b>
<b>P Transport Potential</b>						
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5	
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.0</b>
Flooding frequency	None to very rare		Rare	Occasional	Frequent	
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>	
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>	
Application timing	July-Oct.		March-June		Nov.-Feb.	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>	
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>1.45</b>
<b>BMPs Multiplier</b>						
$BMPs \text{ Multiplier} = (1 - \text{Effectiveness } 1) * (1 - \text{Effectiveness } 2) * \dots * (1 - \text{Effectiveness } n)$						
$BMPs \text{ Multiplier} = (1 - 0.7)$						<b>0.7</b>
$P \text{ Index} = [(P \text{ Source Potential} * P \text{ Transport Potential} * BMPs \text{ Multiplier}) / 1.8] * 100$						
$P \text{ Index} = [(1.76 * 1.45 * 0.7) / 1.8] * 100$						<b>99 (High)</b>

Scenario 5 – Part A. Soil Only Sub API

Characteristic	Description						Rating
<b>P Source Potential</b>							
P Source Potential = {WEP <sub>coef</sub> * [WEP + MNRL <sub>coef</sub> * (TP – WEP)]} + {STP <sub>coef</sub> * STP}							
STP = 50 lbs/acre	WEP = 0 lbs/acre			TP = 0 lbs/acre			
P Source Potential = {0.095 * [0 + 0.05 * (0 – 0)]} + {0.0018 * 50}						<b>0.09</b>	
<b>P Transport Potential</b>							
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5		
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>	
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High	
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>	
Flooding frequency	None to very rare		Rare	Occasional	Frequent		
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>		
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>		
Application timing	July-Oct.		March-June		Nov.-Feb.		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>		
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>0.55</b>	
<b>BMPs Multiplier</b>							
BMPs Multiplier = (1 – Effectiveness 1) * (1 – Effectiveness 2) * ... * (1 – Effectiveness n)							
BMPs Multiplier = (1 – 0.3)						<b>0.7</b>	
P Index = [(P Source Potential * P Transport Potential * BMPs Multiplier) / 1.8] * 100							
P Index = [(0.09 * 0.55 * 0.7) / 1.8] * 100						<b>2 (Low)</b>	

Scenario 5 – Part B. April Application Only Sub API

Characteristic	Description						Rating
<b>P Source Potential</b>							
P Source Potential = {WEP <sub>coef</sub> * [WEP + MNRL <sub>coef</sub> * (TP – WEP)]} + {STP <sub>coef</sub> * STP}							
STP = 0 lbs/acre	WEP = 5 lbs/ton * 1.5 tons/acre = 7.5 lbs WEP/acre			TP = 25 lbs/ton * 1.5 tons/acre = 37.5 lbs TP /acre			
P Source Potential = {0.095 * [7.5 + 0.05 * (37.5 – 7.5)]} + {0.0018 * 0}						<b>0.86</b>	
<b>P Transport Potential</b>							
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5		
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>	
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High	
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>	
Flooding frequency	None to very rare		Rare	Occasional	Frequent		
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>		
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>		
Application timing	July-Oct.		March-June		Nov.-Feb.		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>		
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>0.55</b>	
<b>BMPs Multiplier</b>							
BMPs Multiplier = (1 – Effectiveness 1) * (1 – Effectiveness 2) * ... * (1 – Effectiveness n)							
BMPs Multiplier = (1 – 0.3)						<b>0.7</b>	
P Index = [(P Source Potential * P Transport Potential * BMPs Multiplier) / 1.8] * 100							
P Index = [(0.86 * 0.55 * 0.7) / 1.8] * 100						<b>18 (Low)</b>	

## Scenario 5 – Part C. September Application Only Sub API

Characteristic	Description					Rating
<b>P Source Potential</b>						
$P \text{ Source Potential} = \{WEP_{\text{coef}} * [WEP + MNRL_{\text{coef}} * (TP - WEP)]\} + \{STP_{\text{coef}} * STP\}$						
STP = 0 lbs/acre	WEP = 5 lbs/ton * 1.5 tons/acre = 7.5 lbs WEP/acre			TP = 25 lbs/ton * 1.5 tons/acre = 37.5 lbs TP /acre		
$P \text{ Source Potential} = \{0.095 * [7.5 + 0.05 * (37.5 - 7.5)]\} + \{0.0018 * 0\}$						<b>0.86</b>
<b>P Transport Potential</b>						
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5	
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>
Flooding frequency	None to very rare		Rare	Occasional	Frequent	
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>	
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>	
Application timing	July-Oct.		March-June		Nov.-Feb.	
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>	
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>0.4</b>
<b>BMPs Multiplier</b>						
$BMPs \text{ Multiplier} = (1 - Effectiveness \ 1) * (1 - Effectiveness \ 2) * \dots * (1 - Effectiveness \ n)$						
$BMPs \text{ Multiplier} = (1 - 0.3)$						<b>0.7</b>
$P \text{ Index} = [(P \text{ Source Potential} * P \text{ Transport Potential} * BMPs \text{ Multiplier}) / 1.8] * 100$						
$P \text{ Index} = [(0.86 * 0.4 * 0.7) / 1.8] * 100$						<b>13 (Low)</b>

### Example 5. Calculating Total PI From Sub APIs A, B, C

	P Index Rating
Part A, Soil Only Sub PI	2 (Low)
Part B, April Application Only Sub PI	18 (Low)
Part C, September Application Only Sub PI	13 (Low)
<b>Total P Index Rating</b>	<b>33 (Medium)</b>

If banking is used, the application must occur in July, August, September or October. In all cases when an application is made, the agronomic N rate for year of application should not be exceeded. The average P Index value for the application and non-application years should be classified as low or medium.

In this scenario, STP is 500 lbs/acre. Initially the litter was to be surface applied at 1 ton/acre in September; litter WEP is 5 lbs P/ton, litter total P is 25 lbs P/ton, soil erosion is negligible, runoff class is moderate (Soil Hydrologic Group C, Rotational Grazing, RCN 74, Slope 6%), no flooding occurs and there is a riparian herbaceous buffer. The decision was made to apply 2 tons/acre every other year.

## Summary

These scenarios demonstrate how the API functions. For example, with an increase in STP from 100 to 500 lbs P/acre with 1.5 tons litter applied in April rather than September, and with all other factors remaining the same, there is an increase in site risk from Low to High (i.e., Scenarios 1 and 2, respectively). However, having a herbaceous buffer in place and where half the field drains into a pond reduces the site risk from High to Medium (Scenarios 2 and 3, respectively). If that same field is continuously grazed with more than 0.75 AU/acre, the potential for runoff from that field increases to such an extent that the site risk value is elevated from Medium to High (i.e., Scenarios 3 and 4, respectively).

The benefit of a split application and manure-banking in certain cases is demonstrated in Scenarios 5 and 6, respectively. However, it must be recognized that the continual, long-term application of P above crop P removal rates will eventually elevate STP levels to an extent that alternatives to application may be needed. This is an integral part of the API and nutrient management planning process in general to educate farmers and applicators to the various options available to manage manures in ways that maintain pasture productivity and protect natural resources.

**Scenario 6 – Part A. Initial 1 ton/acre API**

Characteristic	Description						Rating
<b>P Source Potential</b>							
$P \text{ Source Potential} = \{WEP_{coef} * [WEP + MNRL_{coef} * (TP - WEP)]\} + \{STP_{coef} * STP\}$							
STP = 500 lbs/acre	WEP = 5 lbs/ton * 1 ton/acre = 5 lbs WEP/acre			TP = 25 lbs/ton * 1 ton/acre = 25 lbs TP/acre			
$P \text{ Source Potential} = \{0.095 * [5 + 0.05 * (25 - 5)]\} + \{0.0018 * 500\}$						<b>1.47</b>	
<b>P Transport Potential</b>							
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5		
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>	
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High	
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>	
Flooding frequency	None to very rare		Rare	Occasional	Frequent		
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>		
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>		
Application timing	July-Oct.		March-June		Nov.-Feb.		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>		
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>0.8</b>	
<b>BMPs Multiplier</b>							
$BMPs \text{ Multiplier} = (1 - Effectiveness 1) * (1 - Effectiveness 2) * \dots * (1 - Effectiveness n)$							
$BMPs \text{ Multiplier} = (1 - 0.2)$						<b>0.8</b>	
$P \text{ Index} = [(P \text{ Source Potential} * P \text{ Transport Potential} * BMPs \text{ Multiplier}) / 1.8] * 100$							
$P \text{ Index} = [(1.47 * 0.8 * 0.8) / 1.8] * 100$						<b>52</b> <b>(Medium)</b>	

**Scenario 6 – Part B. 2 tons/acre API**

Characteristic	Description						Rating
<b>P Source Potential</b>							
$P \text{ Source Potential} = \{WEP_{coef} * [WEP + MNRL_{coef} * (TP - WEP)]\} + \{STP_{coef} * STP\}$							
STP = 500 lbs/acre	WEP = 5 lbs/ton * 2 tons/acre = 10 lbs WEP/acre			TP = 25 lbs/ton * 2 tons/acre = 50 lbs TP /acre			
$P \text{ Source Potential} = \{0.095 * [10 + 0.05 * (50 - 10)]\} + \{0.0018 * 500\}$						<b>2.04</b>	
<b>P Transport Potential</b>							
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5		
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>	<b>0</b>	
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High	
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>	
Flooding frequency	None to very rare		Rare	Occasional	Frequent		
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>		
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>		
Application timing	July-Oct.		March-June		Nov.-Feb.		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>		
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)						<b>0.8</b>	
<b>BMPs Multiplier</b>							
$BMPs \text{ Multiplier} = (1 - Effectiveness 1) * (1 - Effectiveness 2) * \dots * (1 - Effectiveness n)$							
$BMPs \text{ Multiplier} = (1 - 0.2)$						<b>0.8</b>	
$P \text{ Index} = [(P \text{ Source Potential} * P \text{ Transport Potential} * BMPs \text{ Multiplier}) / 1.8] * 100$							
$P \text{ Index} = [(2.04 * 0.8 * 0.8) / 1.8] * 100$						<b>73</b> <b>(High)</b>	

Scenario 6 – Part C. 0 ton/acre API

Characteristic	Description						Rating
<b>P Source Potential</b>							
$P \text{ Source Potential} = \{WEP_{\text{coef}} * [WEP + MNRL_{\text{coef}} * (TP - WEP)]\} + \{STP_{\text{coef}} * STP\}$							
STP = 500 lbs/acre	WEP = 0 lbs/acre			TP = 0 lbs/acre			
$P \text{ Source Potential} = \{0.095 * [0 + 0.05 * (0 - 0)]\} + \{0.0018 * 500\}$							<b>0.9</b>
<b>P Transport Potential</b>							
Soil erosion (tons/acre/yr)	< 1	1 to 2	2 to 3	3 to 5	> 5		
<b>Loss rating value</b>	<b>0</b>	<b>0.1</b>	<b>0.2</b>	<b>0.4</b>	<b>1</b>		<b>0</b>
Soil runoff class	Negligible	V. Low	Low	Moderate	High	V. High	
<b>Loss rating value</b>	<b>0.1</b>	<b>0.15</b>	<b>0.2</b>	<b>0.5</b>	<b>1.0</b>	<b>1.5</b>	<b>0.5</b>
Flooding frequency	None to very rare		Rare	Occasional	Frequent		
<b>Loss rating value</b>	<b>0</b>		<b>0.2</b>	<b>0.5</b>	<b>2.0</b>		<b>0</b>
Application method	Incorporated		Surface applied		Surface applied on frozen ground or snow		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.2</b>		<b>0.5</b>		<b>0.2</b>
Application timing	July-Oct.		March-June		Nov.-Feb.		
<b>Loss rating value</b>	<b>0.1</b>		<b>0.25</b>		<b>0.6</b>		<b>0.1</b>
P Transport = (soil erosion + runoff class + flooding frequency + application method + application timing)							<b>0.8</b>
<b>BMPs Multiplier</b>							
$BMPs \text{ Multiplier} = (1 - Effectiveness \ 1) * (1 - Effectiveness \ 2) * \dots * (1 - Effectiveness \ n)$							
$BMPs \text{ Multiplier} = (1 - 0.2)$							<b>0.8</b>
$P \text{ Index} = [(P \text{ Source Potential} * P \text{ Transport Potential} * BMPs \text{ Multiplier}) / 1.8] * 100$							
$P \text{ Index} = [(0.9 * 0.8 * 0.8) / 1.8] * 100$							<b>32 (Medium)</b>

Example 6. Calculating Total PI From Sub APIs A, B, C

	P Index Rating
Part A, Initial 1 ton/acre API	52 (Medium)
Part B, Application Year, 2 tons/acre API	73 (High)
Part C, Non-Application Year, 0 ton/acre API	32 (Medium)
Average of Application and Non-Application Years	53 (Medium)

- Collect or direct water for water-spreading or water-harvesting systems.
- Increase or decrease the drainage area above ponds.
- Protect terrace systems by diverting water from the top terrace where topography, land use or land ownership prevents terracing the land above.
- Divert water away from active gullies or critically eroding areas.

## BMP Descriptions

### Diversion (Code 362)

A diversion is a channel constructed across the slope, generally with a supporting ridge on the lower side, in order to:

- Break up and intercept concentrated flows on long slopes, on undulating land surfaces and on land generally considered too flat or irregular for terracing.
- Divert water away from farmsteads, manure storage systems and other improvements.



- Supplement water management on conservation cropping or strip cropping systems.

This applies to all cropland and other land uses where surface runoff water control and/or management are needed.

## Fencing (Code 382)

Fencing is a constructed barrier to livestock, wildlife or people. This practice may be applied on any area where livestock and/or wildlife control is needed. Fences are not needed where natural barriers will serve the purpose. The practice may be applied as part of a management plan to facilitate application of conservation practices that treat soil, water, air and plant animal resource concerns.



## Field Border (Code 386)

A field border is a strip of permanent vegetation established at the edge or around the perimeter of a field to:

- Reduce erosion and nutrients in runoff.
- Provide wildlife food and cover.



- Increase carbon storage.

This practice is applied around the perimeter of fields. Its use can support or connect other buffer practices within and between fields.

## Filter Strip (Code 393)

A filter strip is a strip or area of herbaceous vegetation to:

- Reduce erosion and nutrients in runoff.



- Reduce dissolved nutrient loadings in runoff.
- Reduce suspended solids and associated nutrients in irrigation tailwater.

## Grassed Waterway (Code 412)

A grassed waterway is a shaped or graded channel that is established with suitable vegetation to:

- Carry runoff water at a nonerosive velocity from terraces, diversions or other water concentrations without causing erosion or flooding.
- Reduce gully erosion.
- Protect/improve water quality.



Grassed waterways are used in areas where added water conveyance capacity and vegetative protection are needed to control erosion resulting from concentrated runoff.

## Pond (Code 378)

A pond is a water impoundment made by constructing a dam or an embankment or by



excavating a pit or dugout. In this standard, ponds constructed by the first method are referred to as embankment ponds, and those constructed by the second method are referred to as excavated ponds. Ponds constructed by both the excavation and the embankment methods are classified as embankment ponds if the depth of water impounded against the embankment at spillway elevation is three feet or more. Ponds are designed to:

- Provide a trap for erosion and associated nutrient runoff.
- Provide water for livestock, fish and wildlife, recreation, fire control, crop and orchard spraying and other related uses.

## Riparian Forest Buffer (Code 391)

A riparian forest buffer is an area of trees and shrubs located adjacent to streams, lakes, ponds or wetlands. Riparian forest buffers of sufficient width intercept sediment and nutrients in surface runoff and reduce nutrients in shallow subsurface water flow.

Woody vegetation in buffers provides food and cover for wildlife, helps lower water temperatures by shading the stream or waterbody and slows out-of-bank flood flows. In addition, the vegetation closest to the stream or waterbody provides litter fall and large wood important to fish and other aquatic organisms as a nutrient source and structural components to increase channel roughness and habitat complexity. Also, the woody roots increase the resistance of

streambanks to erosion caused by high water flows or waves. Some tree and shrub species in a riparian forest buffer can be managed for timber, wood fiber and horticultural products.



## Riparian Herbaceous Cover (Code 390)

Riparian herbaceous covers are grasses, sedges, rushes, ferns, legumes and forbs tolerant of intermittent flooding or saturated soils, established or managed as the dominant vegetation in the transitional zone between upland and aquatic habitats.



This practice may be applied as part of a conservation management system to accomplish one or more of the following purposes:

- Provide or improve food and cover for fish, wildlife and livestock.
- Improve and maintain water quality.
- Establish and maintain habitat corridors.
- Increase water storage on floodplains.
- Reduce erosion and associated nutrient runoff and improve stability to stream banks.
- Increase net carbon storage in the biomass and soil.
- Enhance pollen, nectar and nesting habitat for pollinators.
- Restore, improve or maintain the desired plant communities.
- Dissipate stream energy and trap sediment and associated nutrients.
- Enhance stream bank protection as part of stream bank soil bioengineering practices.

Conditions where riparian herbaceous buffers apply are:

- Areas adjacent to perennial and intermittent watercourses or waterbodies where the natural plant community is dominated by herbaceous vegetation that is tolerant of periodic flooding or saturated soils. For seasonal or ephemeral watercourses and waterbodies, this zone extends to the center of the channel or basin.
- Where channel and stream bank stability is adequate to support this practice.

- Where the riparian area has been altered and the potential natural plant community has changed.

## Terrace (Code 600)

A terrace is an earthen embankment, a channel or a combination ridge and channel constructed across the slope to:

- Reduce slope length.
- Reduce erosion.



- Reduce sediment and associated nutrients in runoff water.
- Improve water quality.
- Intercept and conduct surface runoff at a nonerosive velocity to a stable outlet.
- Retain runoff for moisture conservation.
- Prevent gully development.
- Reduce flooding.

## Arkansas Phosphorus Index Advisory Panel

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