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Nutrient Concentrations at Baseflow Conditions in the Upper White River Basin, Southwest Missouri and Northwest Arkansas

Gopala G. Borchelt

NUTRIENT CONCENTRATIONS AT BASEFLOW CONDITIONS IN THE UPPER WHITE RIVER BASIN, SOUTHWEST MISSOURI AND NORTHWEST ARKANSAS

A Thesis

Presented to

The Graduate College of

Missouri State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science, Geospatial Science

By

Gopala G. Borchelt

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NUTRIENT CONCENTRATIONS AT BASEFLOW CONDITIONS IN THE UPPER WHITE RIVER BASIN, SOUTHWEST MISSOURI AND NORTHWEST ARKANSAS

Geography, Geology, and Planning

Missouri State University, December 2007

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ABSTRACT:

The Upper White River Basin (UWRB) is becoming increasingly vulnerable to water quality degradation from urban/population growth and increased agricultural production. This study examines the relationships among nutrient levels, water chemistry and watershed characteristics of 19 watersheds in the UWRB. Water samples were collected during baseflow conditions each month for one year at USGS continuous-flow gage stations. Watershed characteristics evaluated were land use, geology, drainage area, flow discharge, and wastewater treatment plant discharge (WTP). Measured chemical water quality indicators include total nitrogen (TN), total phosphorus (TP), specific conductivity, turbidity, pH and dissolved oxygen. Rapidly expanding urban areas are associated with relatively high nutrient concentrations at baseflow such as found in the James River Basin, where mean levels range from 0.9 to 11.7 mg/L for TN and 18 to 175 µg/L for TP. Nutrient concentrations have a strong positive correlation to specific WTP discharge (gal/day/km^2). Non-point source-affected watersheds with no or only slight WTP inputs show a negative relationship between percent forest cover and nutrient concentrations. Higher nutrient concentrations are found in watersheds with less than 50% forest in non-point source watersheds, although these nutrient levels remain below the James River recommended Total Maximum Daily Load (< 75 µg/L TP and < 1.5 mg/L TN). Agricultural watersheds (>50% ag land) in karst limestone plain areas also show elevated nutrient concentrations ranging from 0.4 to 5.2 mg/L for TN and 9 to 103 µg/L for TP.

KEYWORDS: Nutrients; water quality; Ozarks; non-point; land use; watershed; karst; loading; WTP effluent; correlation; spatial trends; drainage area; carbonate bedrock

This abstract is approved as to form and content

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Robert T. Pavlowsky, Ph.D.
Chairperson, Advisory Committee
Missouri State University

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Approved:

Robert T. Pavlowsky Ph.D., Chair

Doug Gouzie Ph.D.

Richard N. Biagioni, Ph.D.

Frank Einhellig Ph.D., Graduate College Dean

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CHAPTER 1: INTRODUCTION

Runoff from urban land use, agricultural land use and discharge from wastewater treatment plants cause excessive nutrient loading of many lakes, streams and aquifer systems in the United States (Edwards et. al. 1996; Jordan et. al. 1997; Petersen et. al. 1998; Turner and Rabalais 2003; Dupré and Robertson 2004). Sources of nutrients include wastewater treatment plant (WTP) effluent, industrial wastewater, urban run-off, soil erosion, septic tank effluent, run-off from confined animal feeding operations and run-off from agricultural fields (Petersen et. al. 1998). Excessive nutrient loading causes eutrophication of lakes and streams through overproduction of algae. Increased nutrient and algae concentration can lead to other water quality problems. Decaying algae decreases dissolved oxygen in the water and may cause streams to become unable to support fish and other aquatic life (Turner and Rabalais 2003; Lunetta et. al. 2005; Thorp et. al. 2005). Ammonia, a form of nitrogen, is also released from decaying algae and, in excessive amounts, causes tissue damage to fish (USEPA 1999; McNair and Fraser 2003).

Suspended algae, soil erosion and other contaminants add turbidity to water which then captures more solar radiation and increases water temperature. Aquatic organisms that have adapted to clear cool springs and rivers may not be able to survive when oxygen levels are depleted, temperature is increased and water chemistry is altered. Only tolerant species will thrive in streams disturbed by excessive nutrient loading, causing a reduction in aquatic biodiversity (Turner and Rabalais 2003). In general, the public's perception of water quality is based on water clarity. Clarity may be measured by the ability to clearly see the stream or lake bottom through the water column. Unsightly masses of suspended

or attached algae in a eutrophic stream may emit an unpleasant odor from decaying vegetation and have greenish or brownish tint making them unattractive for recreational use. The large densities of algae in drinking water sources increases removal costs for consumption and may cause water to acquire an undesirable odor and taste (Peterson 1998). With increased human population/development and it's associated excessive nutrient loading, eutrophication from excessive algal growth is becoming a major water quality problem throughout worldwide water resources (USEPA 1999; Schueler and Holland 2000; Turner and Rabalais 2003; McNair and Chow-Fraser 2003).

This study focuses on determining the levels and distribution of nutrient concentrations in surface water throughout the Upper White River Basin (UWRB) watershed. This watershed drains approximately 15,636 square kilometers in southwest Missouri and northwest Arkansas, part of the Ozarks Plateau physiographic region (MORAP, 2004). The basin is a major drainage system in the Ozarks region and is characteristic of rivers draining other karst areas with its many deep valleys, broad hilltops and highly weathered limestone bluffs and bedrock formations. Weathered karst geology is highly porous containing many caves, sinks, and subterranean channels which convent flow directly from surface run-off into ground water stores through a system of highly dynamic hydrological networks (Langer, 2002; Matějíček et al., 2003). The "Swiss cheese-like" structure of the karst terrain was formed when rainwater and surface run-off eroded the carbonate rock over millions of years and dissolved channels in the primarily limestone and dolomite formations. This formed conduits deep into the layers of bedrock creating complex subterranean water networks (Langer 2002).

Surface released contaminants can move down through sinkholes and karst fractures quickly entering groundwater and reemerging at spring outlets. The karst geological structure of the Ozarks and the UWRB therefore makes this region extremely vulnerable to infiltration of contaminants associated with surface run-off (MODNR 2001; USEPA 2004). The UWRB watershed has one of the fastest growing populations in the nation, having increased by 30% in the last decade (MODOC, 2001). There are concerns over the effects of urban and suburban development on the water quality in the UWRB since water quality has long been central to this region's economy and natural attractions. The four major impoundments, Beaver, Table Rock, Taneycomo, and Bull Shoals Lakes draw millions of tourists and visitors to the UWRB while dams produce electricity and provide a drinking water supply. The UWRB is also one of the best fishing destinations in the nation with many species of bass, crappie, catfish, trout and sunfish (MODOC 2001).

Scenic landscapes, lakes and the many clear, spring-fed streams have made the UWRB a popular family vacation and retirement destination. A consequence of the region's natural attraction has been its rapidly increasing population, rural development and expansion of metropolitan areas including Springfield, Nixa, Ozark, Branson, Eureka Springs, and Fayetteville. Also increasing is the associated pollution from human activities such as lawn fertilizer, construction erosion, pet wastes, septic seepage and impervious run-off (Meals and Budd, 1998). In addition to urban growth, agriculture production has increased in the UWRB (MODNR, 2001; USEPA, 2004). Nutrient sources from agriculture including wastewater run-off from confined animal feeding operations and poultry litter fertilizer on pastures and direct deposition of animal manure

into streams and rivers. The Ozarks region has become the second largest poultry producer in the U.S. generating over one billion birds per year (USDA (a), 2004). This industry provides an inexpensive, abundant source of fertilizer from poultry litter. Nutrient-rich litter is spread on pastures to enhance the production capacity of relatively poor Ozarks soils (Edwards et. al., 1996). Increased pasture production has expanded cattle production in the basin. Missouri ranks 6th in U. S. cattle production and second for its number of small (100 animals or less) farm beef/cow operations. Greene, Lawrence and Barry counties in the UWRB are among the top ten beef cow counties in Missouri (Olson et. al. 2004). Arkansas ranks second behind the state of Georgia for poultry broiler production with much of this occurring in northwest Arkansas, the UWRB (USDA (b) 2004). Overuse of abundant manure fertilizers is affecting streams in the UWRB, especially those with large areas of pastures and in the poultry producing counties of northwest Arkansas (Edwards et. al. 1996).

Previous water quality studies on the UWRB have generally been limited to a single sub-watershed or stream such as the James River, Kings River, or other tributary in the UWRB and have not provided data on basin-wide nutrient status. This project seeks to provide a basin-wide analysis of nutrient concentrations through sampling during baseflow conditions in the UWRB. Nutrient results of this analysis will be compared to land use and other variables to obtain a better understanding of how watershed characteristics are related to water quality and nutrients. This information will provide a baseline for further, in-depth investigations and support water quality management programs in the Upper White River Basin.

Research Questions

This study begins to fill gaps in the knowledge about nutrient levels occurring in streams during baseflow conditions in the UWRB. There are three main questions that this study seeks to address:

1) What are the baseflow nutrient levels in watersheds throughout the UWRB? Base-flow is the low-flow, non-flooded state of the stream where changes in stream chemistry and dissolved compounds are related primarily to ground water sources, point source inputs and residual non-point source contributions. Water quality variations at baseflow tend to be gradual, thus allowing for comparable sampling.

2) How does water quality compare between the different sample watersheds? Nutrient concentrations are controlled by many factors including point-source discharge, land use, stream size and geology (Fitzpatrick et. al. 1998; Lent et al. 1998; Binkley et al. 2004). This study investigates the role of these factors in influencing nutrient concentrations throughout the UWRB.

3) How do varying physical watershed characteristics and chemical water properties correlate with nutrient concentrations? Watershed characteristics such as the percentage of different land use types and predominant geological formations were examined to discover any relationships between these characteristics and water nutrient concentrations. Water chemistry including pH, DO, specific conductance, temperature and turbidity are compared to nutrient concentrations to examine their relationships.

Purpose and Objectives

This study evaluated nutrient concentrations in watersheds of the UWRB and examined effects of drainage basin characteristics on these concentrations. The status of nutrients in the UWRB and the various roles of land use, geology and other watershed factors influencing nutrient concentrations must be understood in order to implement effective water quality management programs. The primary objectives of this thesis research are:

1. Quantify baseflow concentrations of Total Nitrogen (TN), Total Phosphorus (TP) and water chemistry of 19 sample watersheds in the UWRB.

No previous studies have sought to determine nutrient concentrations throughout the UWRB during baseflow conditions. There have been projects that have focused on one or a few sub-watersheds in the UWRB such as the James or the Kings River watersheds, but these have not provided data on the nutrient status throughout the Basin.

2. Develop a Geographic Information System (GIS) with land use, geology, wastewater treatment plants, hydrology and other spatial data for the UWRB.

Currently most spatial data is divided by political boundaries including state, county and regional boundaries. The UWRB watershed lays roughly half in the state of Arkansas and half in Missouri. This study uses GIS and spatial data to piece together a single dataset that spans both Missouri and Arkansas sides of the Basin.

3. Examine relationships between water quality and drainage basin characteristics in the 19 sample watersheds of the UWRB.

Correlation between drainage basin and chemical factors within a watershed and the nutrient concentrations sampled in the watershed may provide data to aid management efforts to reduce nutrient contribution from land use practices associated with high nutrient levels.

Hypotheses

From previous studies and reasoning, this study suggests the following three hypotheses:

1) Nutrient trends among watersheds are dominated by point-sources such as WTP effluent due to baseflow sampling conditions.
2) It will be difficult to distinguish between point-source effects and land use effects on nutrient loading for watersheds receiving WTP effluent since these basins also contain a higher percentage of urban land use.
3) Non-point source dominated watersheds will have less correlation among water quality variables than those affected by point-sources since point-source influenced watershed have common factors (wastewater effluent) influencing water chemistry.

Nutrient concentrations are expected to show a relationship to land use/land cover types within the drainage area. Urban or agricultural areas are expected to have higher nutrient concentrations than rural and forested watersheds due to TN being very mobile in the environment and TP being associated with soil disturbance on the landscape. However, since water sampling for this project was conducted at baseflow conditions, it is probable

that the influence of run-off from non-point sources will be lessened while the effects of point-sources actively discharging into streams will have a greater measurable impact on the watersheds receiving these discharges (Petersen et. al. 1998; Baginska et al. 2003). Streams receiving high volumes of wastewater treatment plant effluent will have higher concentrations of nutrients than streams that do not have major sources of effluent. These streams will also have a larger percentage of urban/developed land use. This may present a problem when interpreting the relationships between land use and water quality. Watersheds with major effluent sources are more likely to be located in areas of higher urban land use. High nutrient concentrations from base-flow sampling in these watersheds may appear to be related with the high urban and agricultural land use but may be the result of the large point-source discharge. On the other hand, some point sources may be located in watersheds that have little urban or agricultural land use and may therefore deviate from the expected low nutrient concentrations.

Non-point watersheds may exhibit less correlation among water quality indicators due to variations in landscape, hydrology and watershed influences. In watersheds containing large areas of urban development and agriculture, water quality may be highly variable due to flashy hydrology in these impervious or less pervious watersheds. At baseflow conditions the stream may be still be affected by nutrients moving through the system from the previous storm event. In the non-point source dominated watersheds, there is less expected variability in discharge making the water quality variables more constant within a particular non-point sample watershed. Each stream has a different shape, drainage area, land use and other factors that influence water chemistry which may cause non-point watersheds to exhibit less common water quality characteristics.

Background

Many research projects have studied the effects of land use, watershed physiography and hydrology on water quality in streams (Stark et al. 1999; Turner and Rabalais 2003; Matějíček et al. 2003). This section discusses previous studies that examined watershed factors associated with increased nutrient concentrations. Studies that deal with spatial information such as drainage area and variations in water chemistry through a watershed have often found geographical Information Systems (GIS) to be a useful tool to enhance understanding of these spatial relationships.

It is well known that forms of nitrogen and phosphorus occur naturally in streams and vary from one geographical region to another (Clark et al. 2000; Binkley et al. 2004). Natural sources include soil erosion, wildlife fecal matter and decomposition of organic material such as fallen leaves (Benfield 1996; USEPA 1999; Clark et al. 2000; Binkley et al. 2004). Nitrogen and phosphorus are major plant nutrients essential for growth of biofilms and aquatic vegetation and form the basis of aquatic food chains (Benfield et. al. 1996; Graca et. al. 2001). Natural concentrations of nitrogen in undisturbed forested streams are low due to a high removal rate by vegetation and lack of excessive inputs. Naturally occurring nitrogen typically averages 0.68 mg/L for combined nitrate, dissolved organic nitrogen and ammonium. Phosphorus levels are also low in forest streams and are generally less than 30 µg/L for combined inorganic and dissolved organic phosphorus. Variations in nutrient levels for undisturbed streams are associated with ecological region, atmospheric deposition, vegetative species and other inherent watershed characteristics such as geology, geography and land cover (Binkley et. al. 2004).

Excessive nutrient loading in streams occurs in association with large areas of urban and agricultural development (Jordan et. al. 1997; Meals and Budd 1998). Nutrient loading may be caused by point-sources such as WTP effluent which is a result of the human fecal matter that contains nutrients as byproducts of the digestive process. Towns with municipal infrastructure usually have WTP which is often a major source of nutrient loading. Another nutrient contributor is non-point source pollution (NSP) (Jordan et. al. 1997; USEPA 1999; Miller 2006). NSP is cause by run-off and leaching of broad areas of urban and agricultural land including fertilized fields, construction sites and impervious surface (Miller et al. 1997; Brezonik and Stadelmann 2002). Fertilizers containing high amounts of N and P can be washed off of agricultural fields and into streams by precipitation. Manure fertilizer is often applied at rates that exceed plant phosphorus requirements in order to increase nitrogen application to crops which need 10 parts nitrogen to 1 part phosphorus or to dispose of manure (Mallarino et al. 2004). Excess nutrients leach into nearby groundwater and streams.

Studies have found that nutrients in agricultural watersheds may be measurably lower during summer than in winter due to plant assimilation, aquatic uptake and less run-off from precipitation (Boyd 1996; Winter and Dillon 2005). Better practices on quantity and timing of fertilization and alternative waste disposal methods can help protect water quality (Edwards et al. 1996). These practices include maintenance of vegetative buffers around streams which can dramatically decrease nutrient loading from fertilization (Winter and Dillon 2005). Vegetative buffers can assimilate a large amount of nutrient-rich run-off from agriculture fields or from urban storm water run-off before it reaches surface waters in addition to stabilizing stream banks against erosion.

Impervious surfaces including roads, parking lots, building tops, and some lawns and sidewalks collect nutrients and other contaminants from vehicles, yard waste, soil erosion, fertilizer and animal waste. All of this non-point source contamination is washed by precipitation run-off into nearby streams which makes towns and urban areas one of the largest contributors to nutrient pollution. Another NSP is on-site septic tanks. Septic tanks are often used as a means of wastewater treatment in rural areas that do not have municipal sewers. Wastewater treatment depends on the ability of soil to absorb effluent. Large numbers of septic systems in shallow soil with poor absorption can release nutrient pollution into the watershed (Aley and Thompson 2002; Wernick et. al. 1998). Point source pollution is addressed by the National Pollution Discharge Elimination System (NPDES), established in section 402 of the Clean Water Act (CWA), through use of permits and limitations. Under the NPDES program, permits are required for discharge of pollutants from most point sources (USEPA 1999). Point sources are arguably easier to control due to their being easily identifiable and monitored at an end-of-pipe location. Tools for controlling non-point source pollution can also be found under the CWA in section 319. This section provides assistance to states, local governments, environmental organizations and educational institutions along with many other programs for addressing a wide variety of non-point source water quality issues (USEPA 2007).

Geology and Land Use. Geology plays a significant role in how anthropogenic activities affect nutrient loading in streams. The nature of the geological formations and structure underlying a watershed influence nutrient mobility, filtration and transport (Jordan et al. 1997; Panfil and Jacobson 2001; Vesper and White 2003). In regions with karst geology the effects of human disturbance may not only influence watersheds

draining the pollution source, but also the surrounding watersheds. Shallow karst aquifer systems act as sinks for nutrients and then redistribute them into surrounding watershed basins through springs and cave systems (Wernick et. al. 1998; Meals and Bud 1998; Dupré and Robertson 2004). According to a study by Miller et al. (1997) karst watersheds containing agricultural land use can have higher total nitrogen (TN) concentrations than watersheds without karst terrain but also containing agricultural fields. The highly weathered, fractured bedrock of the karst region does not provide adequate filtration of nitrogen which leaches into streams and quickly effects the water quality in these regions. The U. S. Geological Survey's assessment of water quality in the Ozarks found that nitrogen concentrations were high in streams draining urban areas with WTP effluent (Peterson 1998). Wastewater treatment plants are located in urban areas so the high nutrient concentrations may actually be caused as much by the land use in these karst watersheds.

Total phosphorus (TP) levels have often been correlated to the proportion of agricultural land-use in a watershed regardless of geology type (Jordan et al. 1997). This is due to phosphorus transport being closely related to sediment transport. Row-crop cultivation on floodplains, removal of riparian vegetation and excessive grazing are all practices that increase the sediment delivery to streams as well as loading of phosphorus attached to this sediment. Soil absorbency and landscape topography can influence nutrient loading as well. In the sub-basins of the Quabbin Reservoir, Massachusetts, waters sampled in low-lying wetlands contained higher levels of TP, while streams with elevated, well-drained soils contained higher amounts of TN (Lent et al. 1998). The mobility of nitrogen allows it to leach through the soil into groundwater or streams, while

in low-lying, lentic systems, such as wetlands, nitrogen is easily converted to gas or used by aquatic plants (Lent et al. 1998). Nitrogen therefore may not remain in stagnant water bodies for long while phosphorus may concentrate in sediment and become re-suspended in the water (Lent et al. 1998; Turner and Rabalais 2003). Due to the known impacts of land use upon nutrient concentrations, especially in karst systems, land use planning for conservation is important to water quality protection.

GIS in Water Quality Studies. Geographic Information Systems (GIS) is an important tool that is used to describe the spatial distribution and variation of watershed features essential to water quality studies. GIS has been used by planners, decision-makers at all levels of government, researchers, developers and the general community for water quality protection efforts. Developing regions of the nation have found this data management tool extremely valuable for precise analysis and effective distribution of spatial data (USEPA 2004). A recent study by the USEPA utilized GIS and a combination of existing water quality data from USGS stations, land use data and knowledge of the relationships between water quality and land use to develop a model of watershed vulnerability throughout the UWRB (Lopez et. al. 2006). The USEPA study was the first broad-scale model of water quality vulnerability by distribution of potential water quality drivers including development and forest areas. This GIS database allowed the USEPA study to produce prediction maps of sub-watersheds that were likely to be vulnerable to water quality degradation. A GIS database was used in a study by Greene and Cruise (1995) to quantify the volume of run-off from a given storm event in an urbanized watershed near Baton Rouge, Louisiana. Surface data on slope, land use, impervious and pervious areas and soils were compiled into a GIS database and used to

model storm run-off in the watershed. Huang et. al. (2003) also used GIS-based modeling of the Malian River Basin, China to analyze hydrological processes and run-off impacts on erosion. Watershed information including land use, stream discharge, numbers of septic systems precipitation and point-source discharge has been often used in GIS models to estimate non-point nutrient loads to watersheds (Meals and Bud 1998; Stark et. al. 1999). GIS databases facilitate the organization and study of interrelationships between watershed data and water quality variables through an integrated approach that is well suited to the complex nature of watershed processes. However, Lent et al. (1998) and Brezonik (2002) suggest that for large drainage basins effective water quality analysis may require division of the large watershed into numerous smaller watersheds. Lent et. al. (1998) reasoned that hydrologic and geologic components may differ considerably from one region of a large watershed to another and may confound application of a single model or management strategy.

Benefits of this Study

This study includes the entire Upper White River Basin of southwest Missouri and northwest Arkansas in an evaluation of basin-wide nutrient status. This study is intended to be a baseline analysis that will provide a snap-shot view of the status of nutrients at baseflow conditions in the UWRB watershed. The advantage to the baseflow sampling done in this study is that water quality characteristics can more accurately be compared among watersheds. The USEPA study on the UWRB watersheds produced a prediction model of sub-watershed vulnerability (Lopez, 2006). This study further examines the water quality status of the UWRB watersheds through regular sampling and comparison of relatively undisturbed watersheds to the more urbanized and populated watersheds. Basin-wide nutrient analysis can help set a baseline for further monitoring and future studies. Results of this analysis will provide data to help guide monitoring and watershed protection efforts for the UWRB. As population in this watershed continues to increase, adding to the demands on its water resources, knowledge of the factors that control nutrient loading as well as the affects of land use practices on water quality is essential to aid in water quality conservation practices and management strategies.

CHAPTER 2: STUDY AREA

The Upper White River Basin watershed drains a large portion of the Ozarks plateau in southwest Missouri and northwest Arkansas encompassing portions of 9 Arkansas counties and 10 Missouri counties. The UWRB consists of three 8-digit hydrologic unit codes (HUC): Beaver Lake watershed (11010001), James River watershed (11010002) and Bull Shoals Lake watershed (11010003) (Figure 2.1). This chapter describes the size, location, climate, hydrology, geology, and land uses throughout the UWRB. The 19 watersheds selected in this study are located at existing USGS stations throughout the basin (Table 2.1).

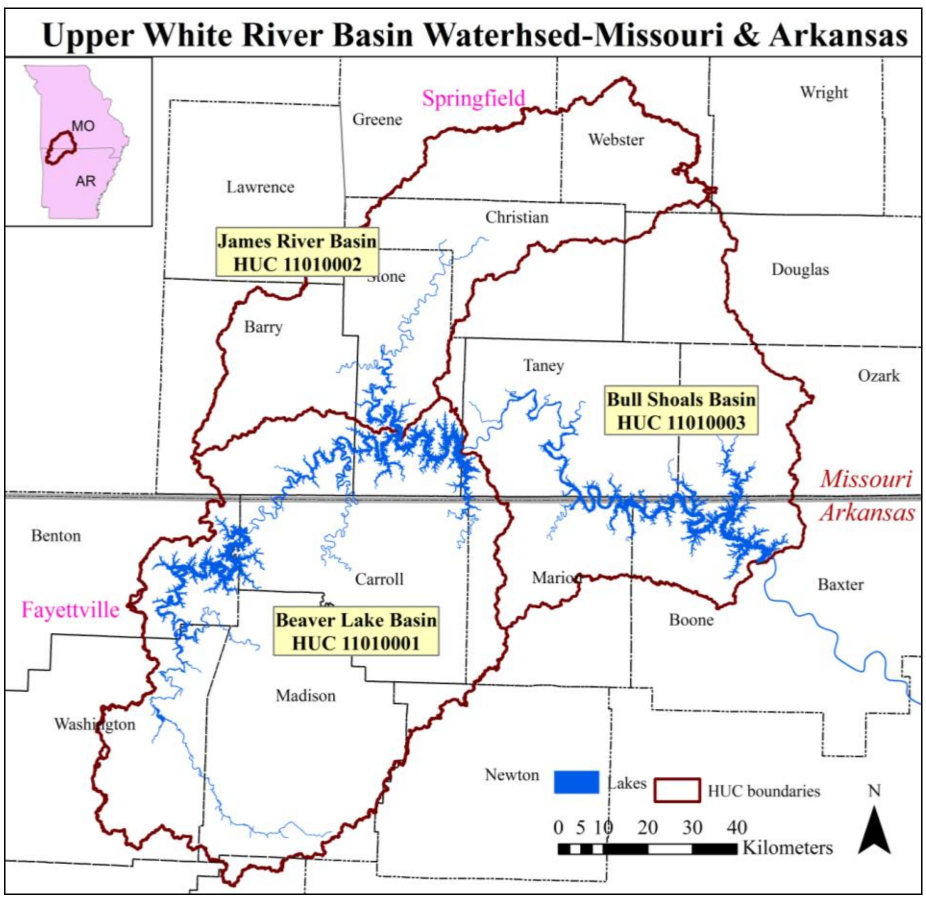


Figure 2.1: UWRB reference map: Location of the UWRB in Missouri and Arkansas

Table 2.1: USGS gages: hydrologic unit, site number, name and sample site label of each USGS gage used as a sampling site in this study (USGS 2005)

8 digit HUC number	USGS site number	USGS gage name	1st year In operation	Site name for this study
11010002	7052000	Wilson Creek at Springfield, MO	1933	WC-Springfield (1)
11010002	7052100	Wilson Creek near Springfield, MO	1972	WC-above SWTP (2)
11010002	7052152	Wilson Creek Below Springfield, MO	1967	WC-at SWTP (3)
11010002	7052250	James River near Boaz, MO	1972	JR-Boaz (4)
11010002	7052345	Finley Creek below Riverdale, MO	2002	Finley R (5)
11010002	7052500	James River at Galena, MO	1922	JR-Galena (6)
10010001	7053400	Table Rock Lake near Branson, MO	1974	WR-below TR Dam (7)
11010003	7053810	Bull Creek near Walnut Shade, MO	1995	Bull Ck (8)
11010003	7054080	Beaver Creek at Bradleyville, MO	1994	Beaver Ck (9)
11010002	7050700	James River near Springfield, MO	1956	JR-above Springfield (10)
11010002	7050690	Pearson Creek near Springfield, MO	1999	Pearson Ck (11)
11010001	7053207	Long Creek at Denver	1996	Long Ck (12)
11010001	7053250	Yocum Creek near Oak Grove, AR	1993	Yocum Ck (13)
11010001	7050500	Kings River near Berryville, AR	1939	Kings R (14)
11010001	7049000	War Eagle Creek near Hindsville, AR	1952	War Eagle Ck (15)
11010001	7048800	Richland Creek at Goshen, AR	1999	Richland Ck (16)
11010001	7048600	White River near Fayetteville, AR	1974	White R-Fayetteville (17)
11010001	7048550	West Fork White River E Fayetteville, AR	2001	West Fork White (18)
11010003	7054410	Bear Creek near Omaha, AR	1994	Bear Ck (19)

The UWRB drains a large portion of the Ozarks ecoregion that encompasses over 15,636 km^2 (6,037 square miles or 3,863,844 acres) (MORAP 2004). Ten Missouri counties including Barry, Christian, Douglas, Greene, Lawrence, Ozark, Stone, Taney, Webster and Wright and nine Arkansas counties including Baxter, Benton, Boone, Carroll, Franklin, Madison, Marion, Newton, and Washington are included in the UWRB (Figure 2.1). Major population centers include Springfield, Fayetteville, Springdale, Ozark, Nixa, Branson, and Berryville. From 1990 to 2005 the population of most Southwest Missouri counties increased by 30% to 60% while average population growth for the entire state during this time was 13% (U.S. Census 2006).

Besides the main town centers, a large portion of the population growth and development is taking place in rural areas around the lakes and scenic waterways in the basin as inhabitants seek these areas to build retirement and recreation homes. Much of this new population is moving into rural developments that use on-site septic systems to treat wastewater. Many of these systems fail to adequately treat the wastewater due to lack of filtering soils or lack of maintenance by property owners. Failing septic systems are considered a non-point source of nutrients and can add significant nutrient contamination to surface and ground water (Wernick et. al. 1998).

Originating from the western end of the Boston Mountain uplands in northwestern Arkansas, the White River forms a 6^{th} order stream as it flows north toward Missouri into Beaver Lake. The river eventually becomes an 8^{th} order stream and enters Table Rock, Taneycomo and Bull Shoals Lake systems. These lakes provide water and electric power to the region’s population. The UWRB is home to many sports fish species. These include smallmouth bass, largemouth bass, spotted bass, white crappie, Ozark bass, channel catfish, brown trout and rainbow trout (MODOC 2001). The abundance of many of these species has given the watershed a reputation as one of the best fishing regions in the country. The dams have also provided ideal locations for cold-water fisheries which thrive in the cool water emanating from below the dams. Among some of the endangered aquatic species in this watershed are Ozark cavefish, checkered madtom, Ozark shiner, several species of darters, the Salem Cave crayfish and the Meek’s crayfish (MODOC 2001).

Geology

Geology in the UWRB is typical of the Ozarks characterized by karst features such as sinkholes, caves, bedrock fractures and loosing streams. This allows direct linkage from surface waters to groundwater without filtration (Langer 2002). Karst terrain is formed over time by the erosion and weathering of limestone and dolomite bedrock as slightly acidic rainwater creates channels, caverns and sinkholes into this material. The weathered carbonate rock forms residual soils containing resistant cherts and clay. Erosion of the residual soil accounts for the tumbled gravels found in streambeds of the region. The headwaters of the White River are composed of coarser stones and boulders of limestone and sandstone in confined valleys where many riverbanks in northwestern Arkansas are composed of layers of shale, a feature of the Boston Mountain uplands. Figure 2.2 shows the predominantly carbonate geology of the UWRB with large areas of shale in the southern headwaters region of the White River.

The landscape, topography and soils in the basin are typical of the Ozarks. Slopes can be 5 to 90 degrees and tend to be steeper in areas close to creeks or water bodies where bedrock bluffs are exposed. Soils on the broad ridge tops are relatively deep with thin silt-loams over clayey residuum on limestone, shale and sandstone bedrock. Soils often contain a moderate amount of cherty rock fragments and support a variety of oak and hickory trees. Soils on slopes are thin and poor, supporting mainly smaller oaks, smoke-bush and cedar. Creek-bottom soils are gravelly in the upper reaches and become deeper silt loams in the lower reaches of streams. These areas contain sycamore, willow and other bottom-land vegetation. The majority of the streams in the basin are characterized by a shallow bottom composed of bedrock rock and gravel.

Climate

The climate of the UWRB is temperate with mild winters and warm summers. The thirty-year mean temperature for the region is approximately 14 Cº. Average seasonal temperatures in the study area rangees from 13 to 18 Cº in the spring, 24 to 26 Cº in the summer, 13 to 16 Cº in the fall and 5 to 18 Cº in the winter (NOAA 2006). The northern section of the UWRB receives an average annual precipitation of 107 centimeters while the southern areas of the basin receive 120 centimeters per year. Rainfall throughout the region averages 109 centimeters (43 inches) per year (MODOC 2001).The majority of precipitation occurs from March to June (NOAA 2006).

Hydrology

Originating in the Boston Mountain uplands of Arkansas, the White River flows approximately 3,000 kilometers as it makes its way north into Missouri and south again to the Bull Shoals reservoir in Arkansas. At its origin, the White River is at an elevation of approximately 675 meters and by the time it flows over Bull Shoals dam its elevation has dropped to 160 meters (NED 1999). The UWRB contains 18 major tributaries with approximately 7,300 kilometers of flowing streams and many ephemeral streams where most or all flow drops below the surface into underground channels during dry periods (USGS 1993). Table 2.2 shows the sampling sites and their drainage area size. Figure 2.3 shows the locations of the sites along the major tributaries of the White River in both Missouri and Arkansas.

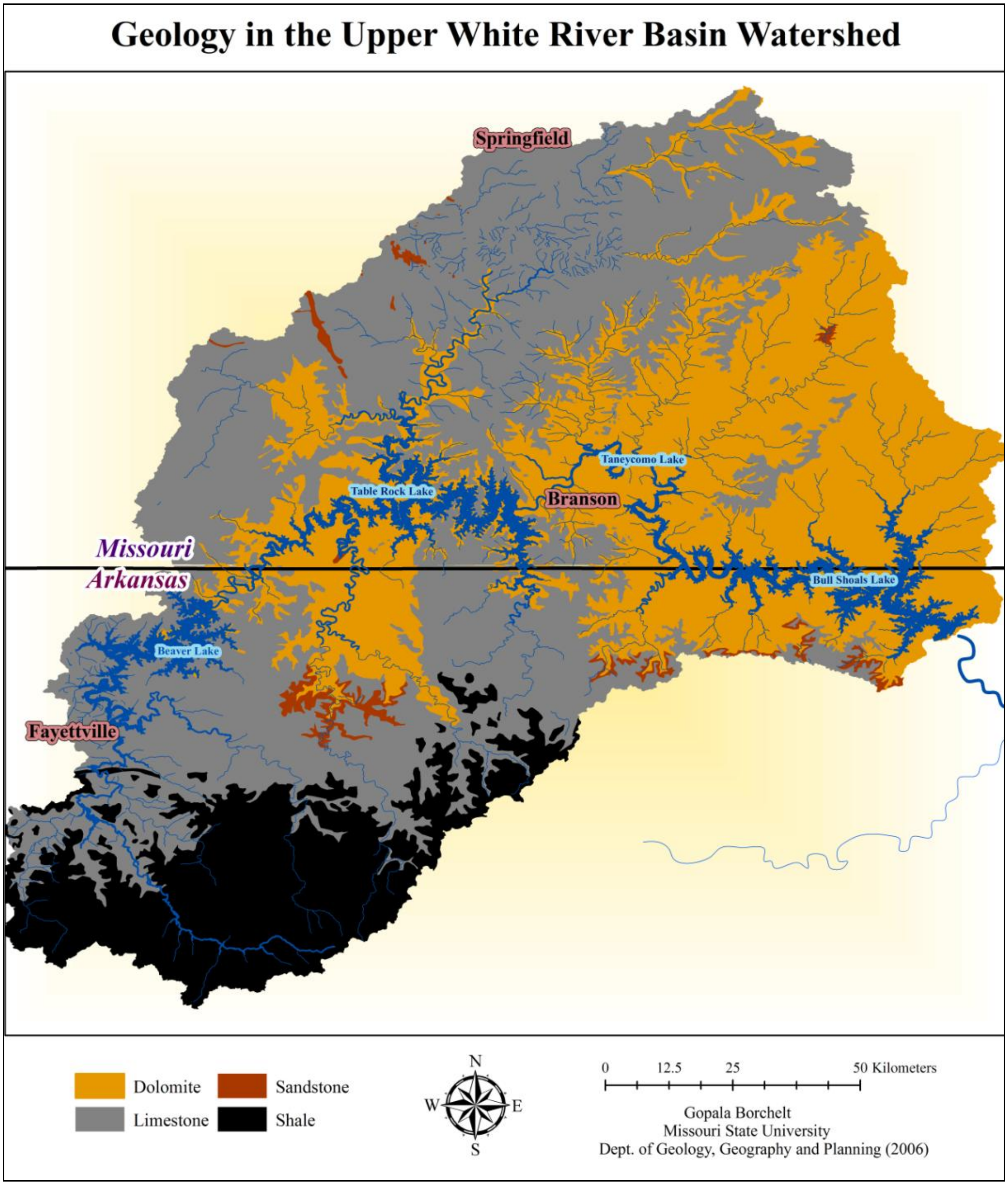


Figure 2.2: Surficial Bedrock map. General bedrock types in the Upper White River Basin (Arkansas Archaeological Survey 1989; MODNR 1979)

Table 2.2: Sampling sites: Site labels, elevation, drainage area size and location of each USGS gage/sampling site used in this study

Sampling Sites	Elevation (m)	Drainage area (km²)	County	State
WC-Springfield (1)	366	51	Greene	MO
WC-above SWTP (2)	350	92	Greene	MO
WC-at SWTP (3)	344	132	Greene	MO
JR-Boaz (4)	316	1199	Christian	MO
Finley R (5)	347	665	Christian	MO
JR-Galena (6)	281	2567	Stone	MO
WR-below TR Dam (7)	212	10394	Taney	MO
Bull Ck (8)	217	503	Taney	MO
Beaver Ck (9)	245	771	Taney	MO
JR-above Springfield (10)	348	633	Greene	MO
Pearson Ck (11)	366	56	Greene	MO
Long Ck (12)	305	265	Carroll	AR
Yocum Ck (13)	305	117	Carroll	AR
Kings R (14)	294	1374	Carroll	AR
War Eagle Ck (15)	356	685	Madison	AR
Richland Ck (16)	351	361	Washington	AR
White R-Fayetteville (17)	347	1039	Washington	AR
West Fork White (18)	351	325	Washington	AR
Bear Ck (19)	305	344	Marion	AR

Land Use

The majority of the land within the UWRB is privately owned. There are also several thousand acres of National Forest including portions of Mark Twain National Forest and Ozark National Forest. Land use includes urban development, poultry production, agricultural pasture, crops and forest (Figure 2.4). Agriculture, including pasture and confined animal feeding operations, make up a large portion of the UWRB watershed and its economy. Farming in the UWRB includes beef and dairy cattle pastures, hog and poultry production, fruit crops, corn, and feed and forage crops. Urban areas in the UWRB are largely centered on Springfield, Springdale, Fayetteville and Branson. Springdale and Fayetteville largely drain into the Elk and Spring Rivers to the west of the UWRB.

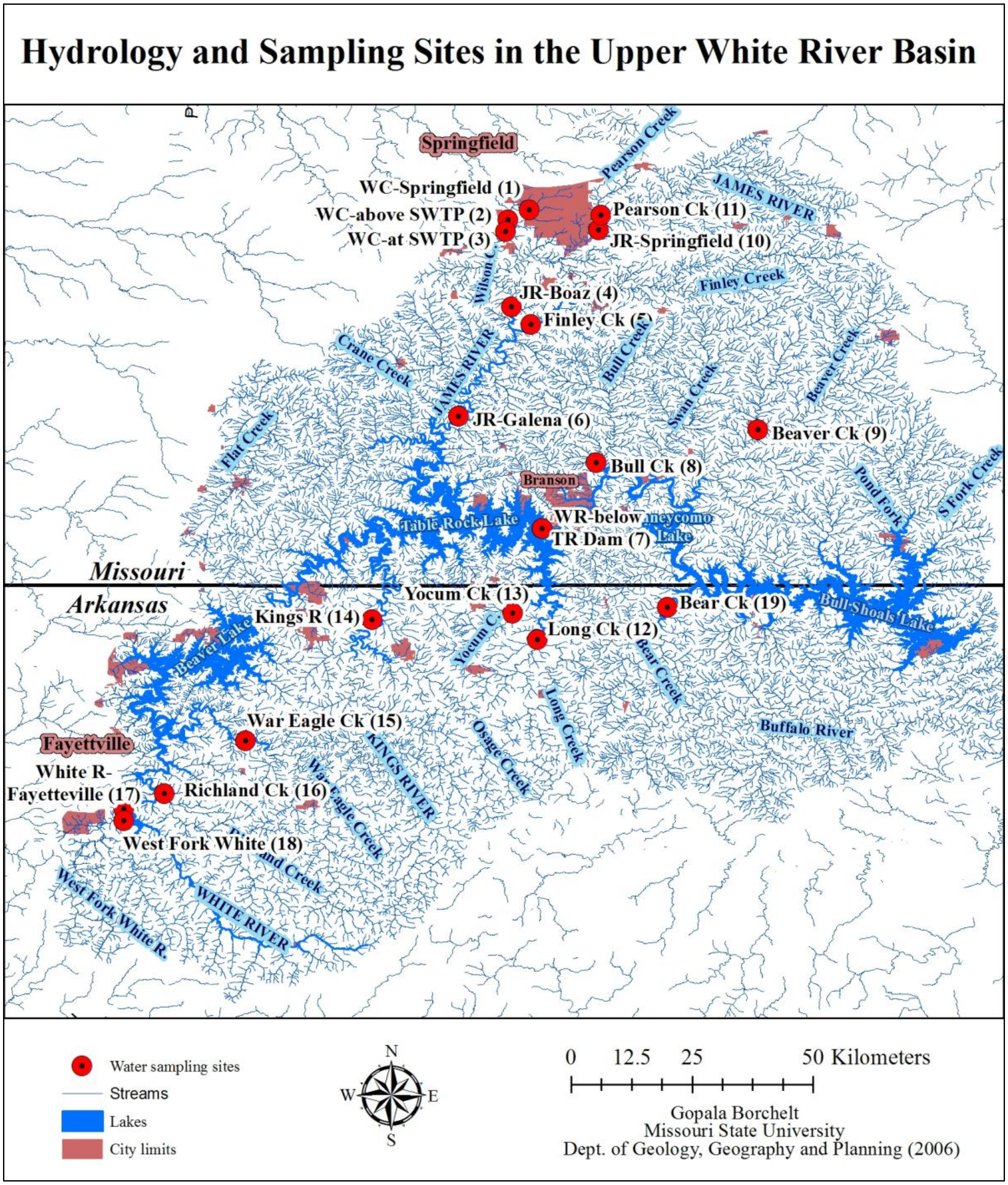


Figure 2.3: Hydrology and sample site map. Sampling sites, streams and lakes in the UWRB watershed, Missouri and Arkansas

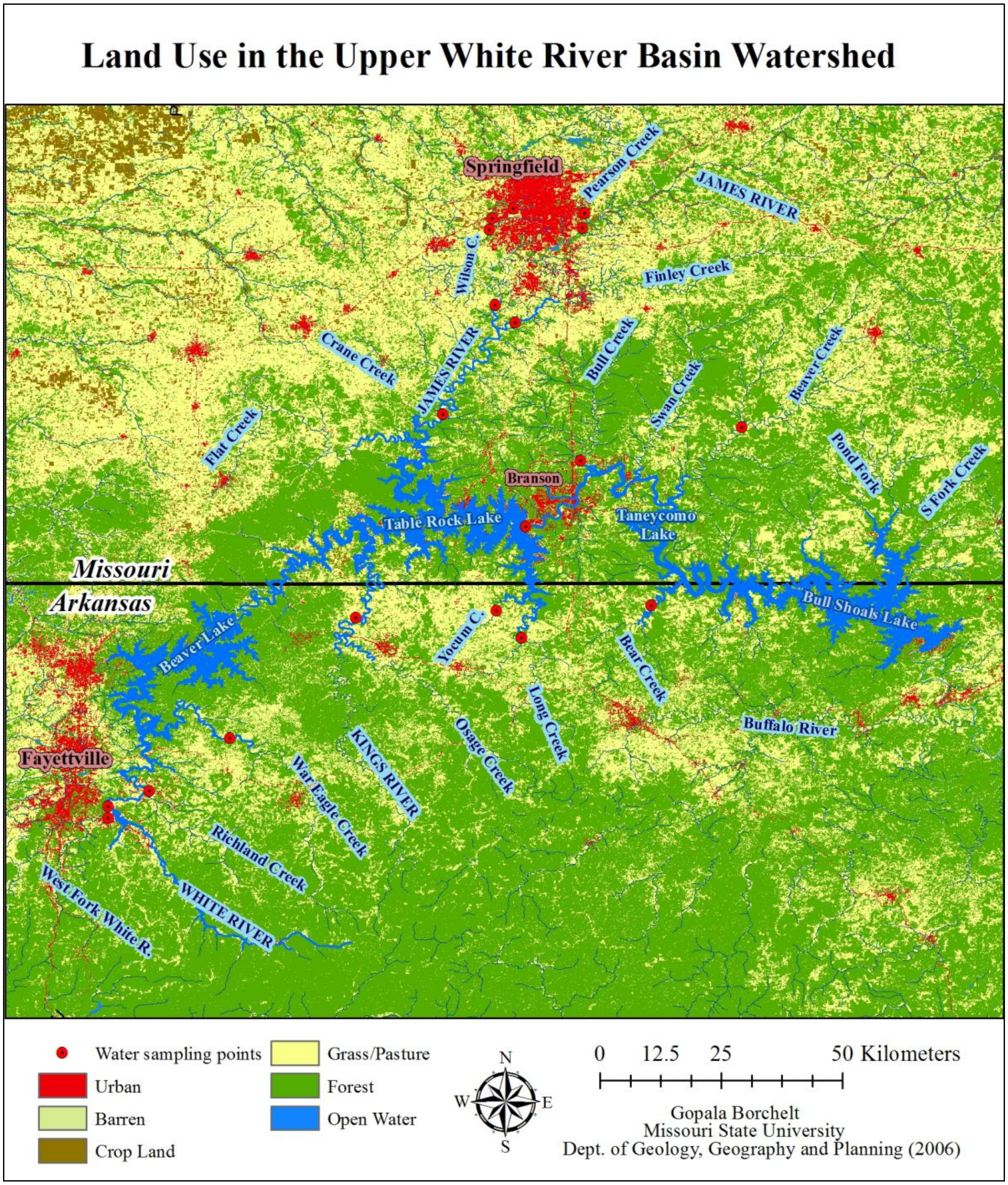


Figure 2.4: Land use classification map. Land use in the Upper White River Basin

Individual Sampling Sites

James River Basin Watershed (HUC 11010002). Three sampling locations are in the Wilson Creek watershed which drains the Springfield, MO area. WC-Springfield (1), WC-above SWTP (2) and WC-at SWTP (3) are located at USGS gages 07052000, 07052100 and 07052152 and are dominated by urban land use (Figure 2.5). Agricultural land use in these watersheds increases outside of the city limits in surrounding rural areas. However, population growth around Springfield is transforming much of the farmland into residential subdivisions and urban industrial areas to meet the housing and shopping needs of the expanding city. The WC-Springfield (1) sample site is located beneath the bridge at Scenic Ave. (Figure 2.6). The drainage area of this site is the smallest of all the sites sampled in this study with approximately 52 km^2 (MORAP 2004).

WC-Springfield (1) sampling site was always very slow-moving at base-flow conditions during the sampling period. This reach was approximately 25 meters across at bank-full level with some areas of bank erosion and incision. The channel at this site showed evidence of human disturbance from trash dumping, construction materials dumping and flood control structures such as boulders and concrete. Gravely substrate was mixed with pieces of concrete and large cobbles that had been torn from widening banks during rain events. There was also a large amount of woody debris and plastic trash in the streambed and on trees farther up on the banks, indicating flash flooding and rapidly receding storm waters characteristic of this highly impervious watershed. Downstream of WC-Springfield (1) at County Road 156 is the location of sample site WC-above SWTP (2) (Figure 2.7). This site encompasses the watershed of WC-Springfield (1) at 92 km^2.

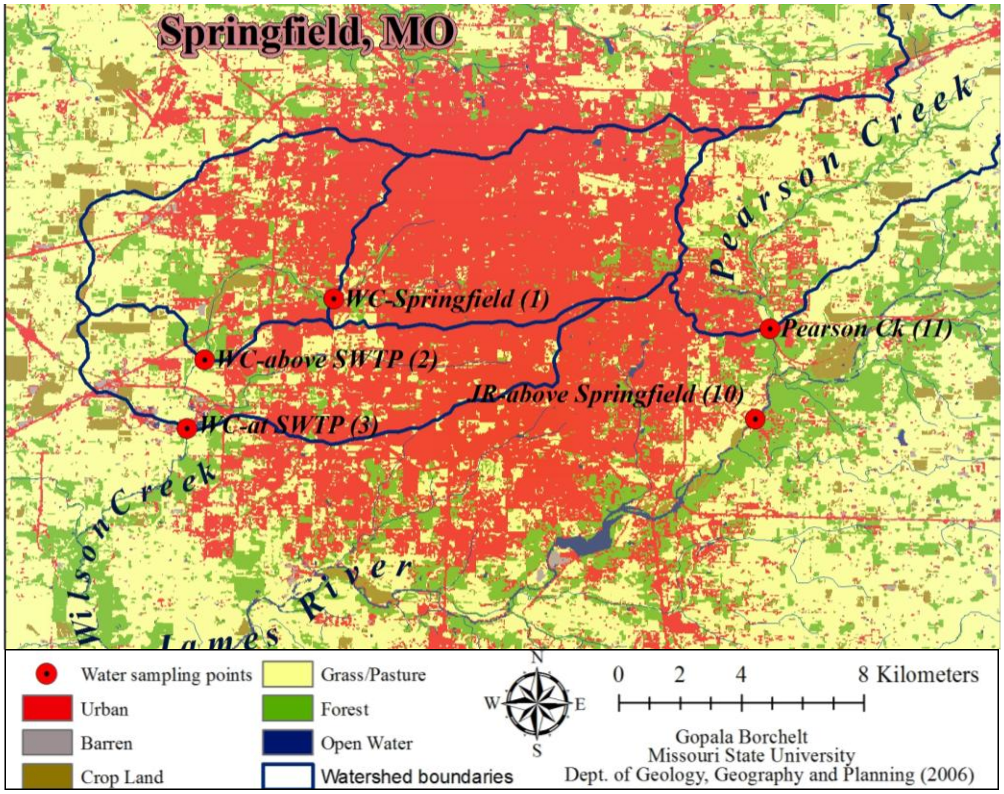


Figure 2.5: Springfield urban map. Extent of urban land use in Wilson Creek and Pearson Creek basins

Figure 2.6: WC-Springfield (1). Scenic Ave. Springfield, MO (November 12, 2005)

There are pastures on both sides of this reach and cattle use the stream as a drinking source. Cattle have also caused loss of vegetation on the banks which show evidence of severe scouring and soil erosion. Baseflow discharge during the sampling period was very low and completely swallowed up just below the USGS gage where fractured bedrock allowed stream flow to enter below the surface of the streambed in a feature known as a swallow hole or karst fracture. The stream was completely dry during the September 2005 sampling run when there had been no rain in this region for over a month. Due to the extremely flashy hydrology of Wilson Creek, large tree trunks move down the channel during storm events and can be seen clogging the channel (Figure 2.7).

Located downstream of the WC-Springfield (1) and WC-above SWTP (2) is WC-at SWTP (3) near Brookline, Missouri. This drainage basin is 132 km^2 but the sample site receives most of its baseflow discharge from the Springfield Southwest Wastewater Treatment Plant, an average of 39 million gallons of effluent per day (SWTP 2006). Stream levels are therefore relatively constant at base-flow conditions. Water samples were taken on the downstream side of the Farm Road 168 Bridge (Figure 2.8). Again, there was evidence of very high water levels during storm events. Large woody debris, trash, tires and other objects were scattered on the banks as high up as the aging stone wall supporting the bridge. Gravel substrate was clean indicating that there is not a large community of attached algae in this reach which is severely affected by flashy storm events as run-off from urban areas upstream flushes quickly downstream.

Figure 2.7: WC-above SWTP (2). Site at County Road 156 near Springfield, Missouri (February 5, 2006)

Figure 2.8: WC-at SWTP (3). Site off West Farm Road 168 (November 12, 2005)

James River-Boaz (4) is located a USGS gage number 07052250 and drains nearly 1,200 km^2 of area including Wilson Creek, Pearson Creek and the upper James River watersheds. This watershed receives effluent from the Springfield WTP and from Nixa and Rogersville WTPs. This sample site is surrounded by farmland made up of cattle pastures. There are also many construction projects ongoing in the Boaz area where more homes and subdivisions are being built to accommodate the growing population of Springfield. Figure 2.9 shows the shallow, wide channel of the James Rive at Boaz. Substrate in this reach is made up of small to mid-sized gravel which provide attachment surface for the prolific growth of algae in the sun-lit, high-nutrient water. Sycamore trees lean into the open space of the river as soil is scoured out of the banks, removing support at the root zone.

Figure 2.9: James R-Boaz (4). Photo was taken looking upstream from the bridge at West Big Bend Road (November 12, 2005)

Finley Ck (5) at the Riverdale Road Bridge (USGS gage 07052345) has a drainage area of 665 km² (Figure 2.10). It is dominated by agricultural land use, mainly cattle pastures, and also has some urban area and forest land. Geology is similar to the James River watershed, made up of predominantly carbonate bedrock with varying soils from clayey in the uplands to gravel and organic soils in the bottomland areas. This watershed is affected by the 5 wastewater treatment facilities located near the towns of Nixa, Ozark, Sparta, Fordland and Seymour. The nearest of these municipal facilities is located 7 km upstream of the sampling point. Combined discharge is 1.5 million gallons of effluent per day. As with many of the cattle operation near streams in rural areas Finley Creek is used as a water source for livestock which are allowed access to the stream. This site also had signs of illegal dumping of appliances, tires and deceased animals.

Figure 2.10: Finley Ck (5). Site at Riverdale Road Bridge (February 12, 2006)

James River-Galena (6) sampling site is at USGS gage 07052500 and is the largest of the watersheds in this study. It encompasses Wilson Creek, Finley Creek, Pearson Creek and the upper and middle James River watershed. This basin is over 2,560 km^2 and approximately 1/3 forest area with much of the remaining areas made up of grassland/pastures and urban areas. James R-Galena receives the wastewater effluent from Springfield, Nixa, Ozark, Rogersville, Crane, Seymour, Fordland, Hurley, Sparta and Cleaver as well as the Galena WTP just upstream of the sample site. Figure 2.11 shows the accumulation of algae in the slower moving portions of the river. Attached algae as well as floating algal masses were abundant during the sampling period and during all seasons. Figure 2.12 shows the same location as that in Figure 2.11 later in the winter season of the sampling year. Attached algae on the streambed also covered the majority of the base-flow channel in late winter and early spring months (Figure 2.13).

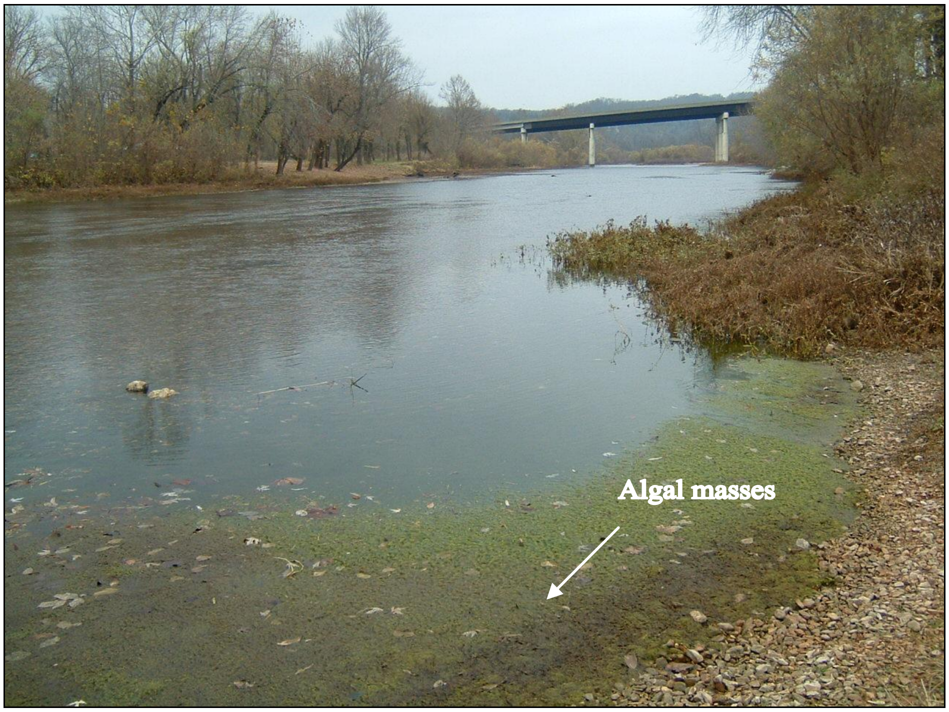


Figure 2.11: Algae in the James River. Galena, Missouri (November 12, 2005)

Figure 2.12: Floating algae in the James River. Galena, Missouri (February 5, 2006)

Figure 2.13: Attached algae: James River-Galena (6), Missouri (February 5, 2006)

James R-above Springfield (10) is located in the upper reach of the river just above the USGS gage 07050700 near East Kinser Road (Figure 2.14). This watershed drains the headwaters of the James River and Pearson Creek watershed covering 633 km^2. Land use includes pastures, forest and developing urban areas, particularly near Springfield. The expanding cities threaten this watershed with more non-point sources of nutrient pollution from urban growth. Stream flow at the JR-above Springfield (10), is slow-moving at baseflow due to low gradient. Yard wastes, grass clippings, pet litter, trash, animal carcasses and fish cleaning wastes are thrown into the river all along this reach creating an undesirable odor and reduced aesthetic value of the river at this site.

Figure 2.14: James R-above Springfield (10) (November 12, 2005)

Pearson Creek is also heavily impacted by construction and development on the northeast side of Springfield (Figure 2.11). The drainage area is nearly 57 km^2 and has a large amount of urban impervious area especially in the southwest area of the watershed in Springfield. Northeast areas are predominantly pastures where cattle often use the creek as a water source. The fence in Figure 2.15 was rebuilt along the edge of the pasture to prevent cattle from moving down stream but allow access to the water. The USGS gage located on Farm Road 148 Bridge was removed in September, 2005 and the bridge was rebuilt. The construction process introduced more sediment to the stream at this location and Figure 2.15 shows the newly seeded stream bank which continues along the water's edge. Several sinkholes within the city of Springfield to the west have been dye traced and shown to drain into the Pearson Creek basin (Aley and Thompson 2002).

Figure 2.15: Pearson Creek (11). Stream bank at edge of new Farm Road 148 Bridge (February 5, 2006)

Bull Shoals Basin Watershed (HUC 11010003). Bull Shoals Basin is the area that encompasses the UWRB tributaries east of the James River Basin, generally flowing parallel to the James River and watersheds that flow north out of Arkansas into Bull Shoals and Taneycomo Lakes (Figures 2.1 and 2.2). This study sampled 4 sites in the Bull Shoals Basin. Bull Creek (8) and Beaver Creek (9) were in streams that flowed south, located east of the James River Basin in Missouri. Bear Creek (19) flows north from Arkansas into Bull Shoals Lake while White River-below Table Rock Dam (7) is a lake sampling site.

Bull Creek (8) at USGS gage 07053810 is one of the least developed stream reaches in this study. A beaver dam shown in Figures 2.16 and 2.17 is one of the non-human developments found in this watershed. Many bass, perch and other fish species are visible in the pools along this stream. The drainage area is approximately 500 km^2 in size and is dominated by forest with only a small area of urban. This watershed is threatened by rapid expansion due to its proximity to Highway 65, connecting the area to Springfield and Branson, MO. Beaver Creek (9) basin contains more pasture than Bull Creek watershed and supports a large number of beef cattle operations. The basin is 770 km^2 in size and receives effluent from Ava, MO WTP. The water sampling location at Beaver Creek (9) is at USGS gage 07054080 (Figure 2.18). Also visible in Figure 2.18 is the large gravel bar filling up a portion of the streambed. Gravel mining has been taking place in this area as evident by the tire marks from hauling trucks. Geology types in the Bull Creek and Beaver Creek basins are similar to those found in the James River watershed, mainly carbonate limestone and dolomite, with Beaver Creek watershed containing some sandstone formations.

Figure 2.16: Bull Creek (8). USGS gage site with beaver dam (November 12, 2005)

Figure 2.17: Beaver dam. Bull Creek (8) (November 12, 2005)

Figure 2.18: Beaver Creek (9). Site at Bradleyville, Missouri (February 5, 2006)

The Bear Creek sample site at USGS gage 07054410 is off the Highway 14 bridge near Omaha, AR (Figure 2.19). This location has also been used as a dump for old furniture, appliances and animal carcasses during the hunting season. The highest nutrient readings for this stream were from samples collected during the fall, 2005 hunting season when the creek was used as a dump for deer carcasses (Figure 2.20). The Bear Creek watershed reaches into the dolomite formations (33% of the drainage area) characteristic of the northern and eastern portions of the UWRB. Geology in this watershed is also composed of 49% limestone and 18% sandstone. Land use is primarily forested (65%) and pasture/grasslands (31%) with just over 1% urban area.

Figure 2.19: Bear Creek (19). Site at Highway 14 Omaha, AR (November 13, 2005)

Figure 2.20: Deer carcass. Bear Creek during the fall hunting season which coincided with higher nutrient readings in the water samples (November 13, 2005)

White River-below TR Dam (7) (USGS gage 07053400) is distinct from other sampled sites in this study due to its being taken from a reservoir rather than a stream (Figure 2.21). Nutrients, the main focus of this study, behave differently in these lentic systems than in flowing or lotic systems. Phosphorus is often associated with turbidity and sediment particles which will settle out in a reservoir while in a stream they are moved with the current. Nitrates are also less variable in reservoirs and may also be converted through respiration of aquatic organisms or through chemical denitrification in the oxygen-poor sediment zone or deeper regions of the reservoir. The UWRB watershed above Table Rock Dam is over 10,390 km^2 and encompasses the Beaver Lake watershed and the James River watershed.

Table Rock Lake watershed contains more than half forest area with intensive agricultural operations and grazing in the open grasslands and in the poultry producing regions of northwestern Arkansas. Often the flood plains are used as pasture in the James River Basin region as shown in Figure 2.22 where cattle graze near Wilson Creek. The Cities of Springfield and Fayetteville are the major urban centers, but there are also numerous towns and communities that add to the overall percentage of urban land use in the watershed. Beaver and Table Rock Lakes have a large amount of development around their shores from construction of vacation homes, condos and resorts near the water. This corridor of development around the lakes is increasing the overall urban land use area in this watershed. Figure 2.23 shows the numbers of municipal wastewater plants in the UWRB and also shows many communities around the lakes that do not have municipal plants. These communities rely on septic systems or neighborhood wastewater plants to treat their sewage.

Figure 2.21: White River-below Table Rock Dam (7) (November 12, 2005)

Figure 2.22: Cattle in the flood plain. Near Wilson Creek in the UWRB watershed

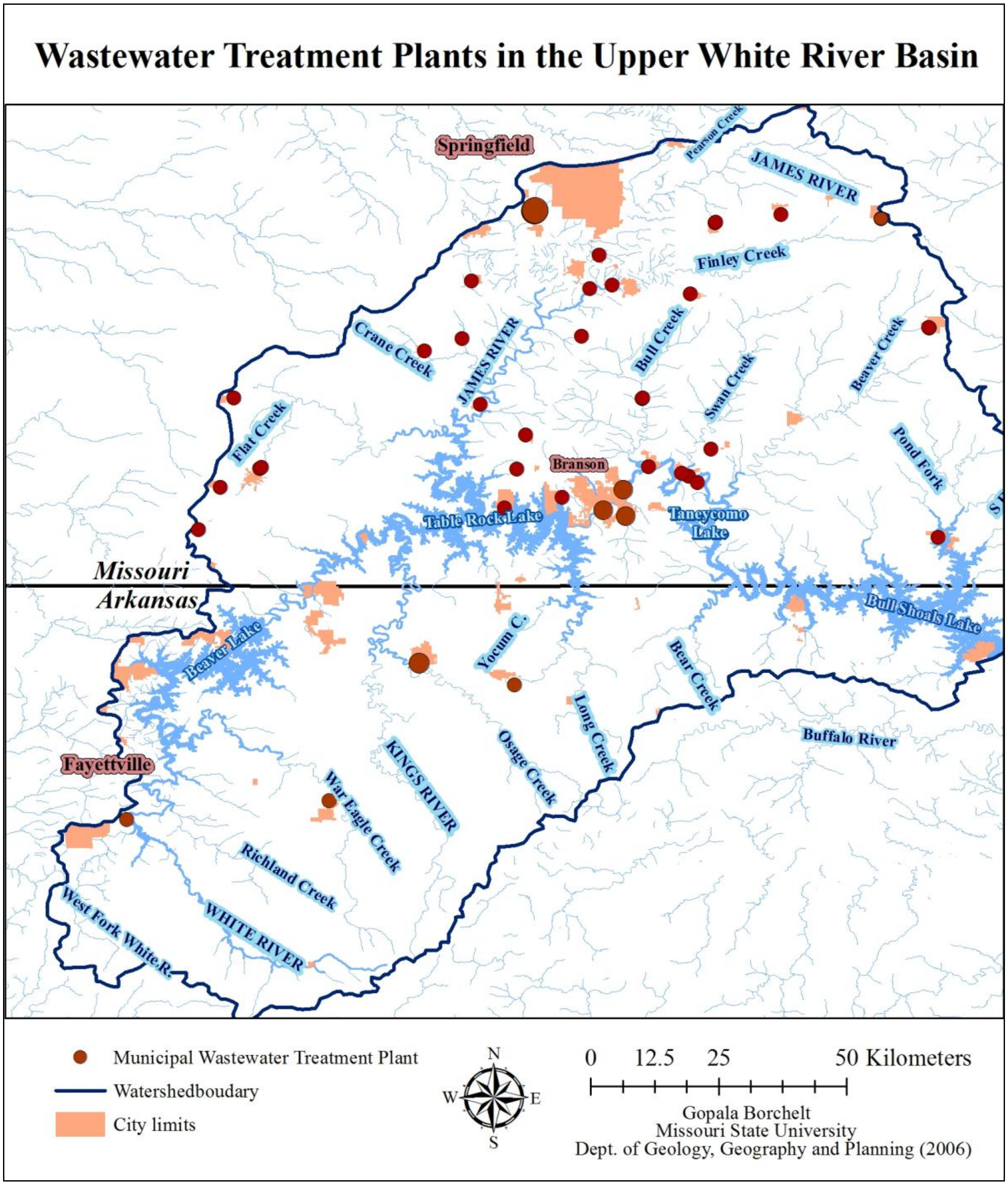


Figure 2.23: Municipal WTP map. Wastewater treatment plants in the Upper White River Basin (data from the Missouri Department of Natural Resources and the Arkansas Department of Environmental Quality). Circles indicate relative volume of discharge.

Beaver Lake Basin Watershed (HUC 11010001). Beaver Lake Basin watershed consists of the headwaters of the White River, Beaver reservoir and all of the tributaries to the White River and Table Rock above Table Rock Dam excluding the James River Basin. Arkansas tributaries flow from the Boston uplands northward into the White River. The headwaters of the White River originate from the shale bedrock in the Boston uplands and flow north into Beaver reservoir, Table Rock reservoir and eventually southward again into Bull Shoals. The Yocum Creek tributary does not contain a significant amount of shale bedrock since this stream originates outside of the Boston shale uplift. Kings River, War Eagle Creek, Richland Creek and the two forks of the Upper White River contain shale bedrock in their headwaters reaches and limestone bedrock in lower reaches. Kings River watershed also contains sandstone formations in the mid reaches of its drainage area.

Long Creek (12) at USGS gage 07053207 is slow-moving and relatively deep (Figure 2.24). The banks are lined with river cane, a prolific bottomland species, which helps hold erodeable, sandy soils. Long Creek basin drains karst limestone and some shale bedrock. The shale formations extend throughout much of the headwaters. Urban areas make up a small portion of this 265 km^2 watershed, while limestone quarries and road construction sites cover a significant area, 2%. Poultry is a major farm product in this region and pastures are often fertilized with litter, to boost forage production and provide for poultry litter disposal (Figure 2.25). This practice, with its associated strong odor, was observed on several occasions while sampling in the Long Creek watershed.

Figure 2.24: Long Creek (12). Site near Denver, Arkansas (November 13, 2005)

Figure 2.25: Poultry houses near Long Creek. (February 6, 2006)

Yocum Creek (13) is located off of the gravel County Road 614 at USGS gage 07053250 (Figure 2.26). This reach is relatively fast moving at baseflow and is composed mainly of deep gravel sediments with the deepest pools reaching bedrock. The drainage basin for this site is 117 km^2 and contains mostly pasture land with scattered forest mainly on the steep slopes. Urban areas are small and include the towns of Oak Grove and Green Forest. Yocum Creek watershed also contains a relatively large amount of barren area from the many quarries mining the limestone bedrock for construction and development throughout the UWRB watershed. As in the Long Creek watershed, poultry and cattle operations are a major industry in the Yocum Creek watershed.

Figure 2.26: Yocum Creek (13). Near Oak Grove, Arkansas at County Rd. 614, (February 6, 2006)

The Kings River watershed is more than 1,370 km^2 in size and the second largest watershed in this study, after the James River Basin. Kings River (14) is located on State Highway 143 at the USGS gage station 07050500 (Figure 2.27). The majority of this watershed is forested with the Ozark National forest covering some of the headwaters region of the river. Remaining land use is pasture and some urban. Berryville WTP is a point source discharging 2.4 million gallons per day into Kings River. As with the other watersheds in this region of the UWRB, northwestern Arkansas, Kings River watershed sustains a large poultry industry which produces tons of litter often used as fertilizer on cattle pastures.

Figure 2.27: Kings River (14). Site at Highway 143 near Berryville, Arkansas (November 13, 2005)

War Eagle Ck (15) sample site is downstream of USGS gage station 07049000 and has a watershed of 685 km². This sample site was accessible from State Highway 45 (Figure 2.28). The drainage area contains mostly forest in the headwaters and cattle pastures in the flat bottom lands. Poultry production and cattle farming are also major industries in the War Eagle Creek watershed which is located west of Kings River watershed. A typical poultry operation in the War Eagle Creek area is seen in Figure 2.29. War Eagle Creek watershed also receives WTP effluent from Huntsville municipality which discharges approximately 2 million gallons per day. War Eagle Creek (15) has a forked streambed around the Hwy 45 bridge supports with large tree trunks and woody debris caught against the supports indicating very powerful storm water flows (Figure 2.28). The left bank at this reach was steeply incised from erosion and mass wasting. The right bank had depositions of fine and coarse gravels.

Figure 2.28: War Eagle Creek (15). Site at Hwy 45, Arkansas (November 13, 2005)

Figure 2.29: Poultry houses near War Eagle Creek. (February 6, 2006)

The Richland Ck (16) sampling site had a similar appearance to the Long Creek sampling location with thick stands of river cane on both sides of the stream and nearly stagnant water during base-flow conditions (Figure 2.30). This sampling location is on Highway 45 near Goshen, AR at the USGS gage 07058800. The streambed is composed of smoothed limestone bedrock with thick colonies of slippery, attached alga and biofilms completely covering the surface. Land use in the Richland Creek watershed is mainly forest with areas of grassland/pasture and some urban areas closer to Fayetteville, AR. The geology type changes throughout the watershed similar to War Eagle Creek where shale bedrock makes up the headwaters and limestone is predominant in the downstream reaches. This watershed is threatened by increasing confined animal, agricultural operations and urban growth from the nearby city of Fayetteville, AR.

Figure 2.30: Richland Ck (16). Site near Goshen, Arkansas (February 6, 2005)

The headwaters of the White River originate in the Ozark National Forest and flow past the Cities of Fayetteville and Springdale which are located on the southwestern edge of the UWRB watershed. The White River-Fayetteville (17) sampling site is at the East Wyman Road Bridge at USGS gage 07048600 (Figure 2.31). The watershed area is approximately 1,038 km^2 in size. In the lower reaches where the landscape flattens into wide valleys and broad ridges, intensive agricultural operations dominated by cattle grazing, poultry farms and confined hog operations occupy much of the bottomland areas. Land use is primarily forested and agriculture but contains an increasing amount of urban residential area from the spreading suburbs of Fayetteville, AR. The water in this reach is slow-moving and very turbid. Similar to the James River near Springfield, the White River is used as trash dump by the local population for old appliances, tires and

batteries (Figure 2.32). The West Fork of the White River passes closer to the town of Fayetteville and drains an area over 325 km². This watershed is encompassed by the White River-Fayetteville (17) watershed. West Fork White River (18) is located off of the gravel Harvey Dowell Road at the USGS stations 07048550 (Figure 2.33). Urban land use increases in this watershed to approximately 11% due to its vicinity to Fayetteville, Arkansas. Forest areas still cover 70% of this watershed and the remainder is grassland/pasture (18%) and barren/transitional areas (1.4%). This stream is also littered with trash from local dumping.

Figure 2.31: White River-Fayetteville (17). Site near Fayetteville, Arkansas off of Wyman Road (February 6, 2006)

Figure 2.32: Trash thrown in White River. White River-Fayetteville (17) (February 6, 2006)

Figure 2.33: West Fork White River (18). Site near Fayetteville showing the USGS gage sensors extending into the water on the right (November 13, 2005)

CHAPTER 3: METHODOLOGY

This section describes the research design and methods used to collect and analyze data for this study. Studying the relationships between watershed characteristics and nutrient concentrations from the 19 selected sites required extensive field sampling, laboratory analysis, geographic information systems (GIS) development and statistical analysis. The field sampling methods and laboratory procedures used in this study followed Standard Operating Procedures (SOPs) approved by the United States Environmental Protection Agency. Field collection was done using a multi-probe water quality meter, by collecting grab samples, collecting duplicate and blank samples, measuring stage, and by taking field notes at each sampling site.

Laboratory methods included preparation of standards for quality control and sample analysis to estimate Total Nitrogen (TN) and Total Phosphorus (TP) concentrations. Geographic information processing was very intensive for this project and involved gathering spatial data layers from various sources, integrating these layers across states and county boundaries to cover the study area, and extracting quantitative information from these spatial layers. Microsoft Excel software was used to tabulate data and study relationships between watershed characteristics, water chemistry and nutrient concentrations. The Standard Operating Procedures (SOPs) used in this study are available online at www.oewri.missouristate.edu.

Field Methods

Nineteen sampling sites were established across the Upper White River Basin at existing USGS gages along the main stem and 9 major tributaries of the White River (Figure 2.3). The GPS location coordinates for these sites are available at the USGS water quality website (http://mo.water.usgs.gov/). Eight sample sites were located in the James River arm of the UWRB including: (1) three sites on Wilson Creek, a tributary of the James River draining Springfield: (2) one site on Pearson Creek: (3) one on Finley Creek: and (4) three sites in the main channel of the James River. One sample site each was located on Beaver and Bull Creeks, major tributaries that flow south into the White River from Missouri. Tributaries that flowed northward from Arkansas included Bear Creek, Long Creek, Yocum Creek, Kings River, War Eagle Creek, Richland Creek, West Fork of the White River and the White River near Fayetteville, Arkansas. In total, 11 sites were sampled in Missouri and 8 sites were sampled in the Arkansas portion of the watershed (Figure 2.3).

Sample sites were numbered by chronology of sample collection. Water samples were collected from sites 1 through 11 creating a travel loop from Missouri State University through the Missouri sites and back to Springfield on one day of sample collection. Sites 12 through 19 were collected on the second day of sampling after taking highway 65 south from Springfield into Arkansas. Weekends were chosen for sampling in order to keep sampling times for all sites as close together as possible since this presented more free time from work and class schedules. Water sampling was conducted within the first half of each month for one year form March, 2005 to February, 2006. This

yielded 12 monthly datasets of water chemistry and nutrients for each site. Laboratory analysis was performed within 28 days of sampling as required by quality control.

Sample Collection. Five hundred milliliter (mL) sample bottles were cleaned before each sampling run with an acid wash of 2% diluted hydrochloric acid and properly labeled with the site name, date and sample type (Figure 3.1). Water samples were collected as grab samples at a wadeable depth at each stream site. Using this method, the sample bottle was rinsed three times in the stream to remove any cleaner or acid wash solution. The bottle was then inserted into the water at approximately 1/3 of the stream depth below the surface and orientated into the stream flow. Care was taken not to collect sediments that had been disturbed while wading into the stream. The sample bottle was held in the water until approximately 80% of the bottle was full and then quickly removed and capped. This prevented sediment and dissolved solids carried in the flow from accumulating in the bottle beyond what was present in the average unit of water.

Figure 3.1: Labeled sample bottles. Containers used for water quality grab sampling

Quality Control. Duplicate samples were taken for two different sites on each sampling date. These sites were split between Missouri and Arkansas sites. Collection of duplicate samples is used to compare and confirm nutrient readings taken during analysis. Field blank samples were prepared at the same place and time as duplicate samples. This was done by using a container of deionized water brought from MSU Geomorphology Laboratory, which was poured into appropriately labeled bottles while at the field site. Field blank samples were used to check for contamination introduced into the water samples through collection error. All samples, duplicates and blanks were preserved from further biological and chemical activity by lowering the pH to approximately 2 using drops of sulfuric acid and pH paper. Samples were transferred to an ice cooler while in the field and stored in a refrigerator at the Geomorphology Laboratory prior to analysis.

Water chemistry measurements including pH, water temperature, turbidity, dissolved oxygen (mg/L), total dissolved solids (g/L) and conductivity (µS/cm) were collected using a Horiba U-22 Multi-Parameter probe (Figure 3.2). The U-22 is a handheld instrument with a digital readout screen that shows the values of simultaneously collected water chemistry variables by the submersible probe. The U-22 probe was orientated into the water flow, submerged, and all parameters were recorded in a field book and saved in the memory of the unit. Data from the U-22 was downloaded to a computer upon returning to the laboratory. The Horiba U-22 system is accurate to within ± 0.3º C for water Temperature, ± 1 percent for conductivity, ± 0.1 mg/L for dissolved oxygen, ± 0.05 for pH and ± 5 percent for turbidity. The Horiba U-22 was calibrated before field sampling using standard solutions provided by the manufacturer.

Figure 3.2: Horiba U-22. Unit displays digital readout screen (left) and probe (right)

Stream Stage Measurements. Metered stadia rods were used to measure water depth at each sampling site. On the first sampling run in March, 2005 an in-stream location with a stationary bottom was established from which to measure water depth. At many sites, the footers of bridges presented a stationary location from which stage was measured. Chosen stage recording locations were noted and stream depth was taken from the same location for each sampling run. Using USGS real-time data (website at www.usgs.org) the antecedent major stream flow events before each sampling date were examined for each site in order to examine the possible lingering effects of recent high flow events.

Laboratory Methods

Water samples were tested for TN and TP concentrations using a persulfate digestion and spectrophotometer procedure. All laboratory methods used in this study followed procedures accepted by the EPA for the Total Maximum Daily Load (TMDL) study on the James River watershed. These methods area described in the Standard Operating Procedure (SOP) for Total Nitrogen Version 1 and the SOP for Total Phosphorus Version 1 prepared by Dr. Biagioni of the MSU Chemistry Department (Appendix C).

Total Nitrogen (TN). The analysis method for Total Nitrogen (TN) was based on the persulfate oxidizing and digestion procedure described by Crumpton et. al. (1991). This method measures all forms of nitrogen (TN) present in a sample by converting all forms to inorganic nitrate and then deriving the concentrations of this compound. This method is becoming more readily accepted than the older, TKN or Kjeldal nitrogen digestion process which not only uses more toxic acids and chemicals but has a tendency to be less accurate. This inaccuracy is due to the Kjeldal digestion method measuring TN by addition of measurements of both the TKN nitrogen and NO3/NO2 (nitrate/nitrite) nitrogen present in a sample. However, during the Kjeldal digestion some of the nitrogen is converted to NO3 so that nitrogen is double counted causing an overestimation of the amount of TN (Patton and Kryskalla 2003). Total Nitrogen concentrations for this water quality study were measured using an alkaline persulfate digestion and second-derivative spectroscopy (Patton and Kryskalla, 2003)**.** It is a measure of all forms of nitrogen present in a sample. Water samples were first neutralized having been previously preserved with sulfuric acid upon collection. Samples were neutralized using NaOH

(sodium hydroxide) up to between pH 6 and 8. Ten milliliters of each sample was then combined with an alkaline persulfate oxidizing solution (digestion reagent) and heated to 120º C in an autoclave. This process quantitatively converted most of the organic nitrogen compounds into nitrate, an inorganic nitrogen form. The digested samples were then acidified again using hydrochloric acid to break down any remaining solids from the digestion process into solution. A spectrophotometer which had first been calibrated with known concentrations of standard reagents through digestion procedure was used to detect the absorbance of nitrate molecules in the water samples measured at three wavelengths; 230, 225 and 220 nm. The second derivative was then calculated to obtain concentrations of TN in water samples based on the absorbance. The established detection limit for this method is a minimum of 0.1 mg TN/L with the upper range of 5 mg TN/L which can be extended for some samples that have higher TN concentrations by dilution with deionized water.

Total Phosphorus (TP). Analysis for concentration of total phosphorus was performed by acid persulfate digestion. This method measured the amount of orthophosphate in a water sample after all forms of phosphorus had been quantitatively converted to this form (Patton and Kryskalla 2003). Neutralized samples were combined with 0.2 mL sulfuric acid and 0.08g ammonium persulfate and heated to 120 C° for digestion to convert phosphorus to orthophosphate. The samples were then returned to neutral using NaOH and phenolthaline as an indicator of acidity. A combined molybdate solution (sulfuric acid, ascorbic acid, antimony potassium and ammonium molybdate) was added to the water samples, six standard solutions and three blanks which were used to calibrate the spectrophotometer. The molybdate solution caused samples to show a

blue color proportionate to the phosphorus concentration in the sample when analyzed at 880 nanometer wavelengths. Absorbance readings from the spectrophotometer at the 880 nanometer wavelength were entered into an Excel spreadsheet and concentrations of TP were calculated using the standard calibration. Quality control procedures used in this study are outlined in the Quality Assurance Project Plan for this work and approved by the EPA (Appendix C). This includes preparation of laboratory standard solutions of known concentrations for instrument accuracy assessment. Laboratory blank samples were prepared for both the TN and TP methods to ensure that contamination was not being introduced through human error during laboratory procedures. At least one quality control check, one laboratory blank, one matrix spike, one laboratory duplicate, one field duplicate and one field blank were analyzed for every ten samples.

Upon completion of laboratory analysis, the method detection limits for this study were calculated using the standard deviation of the laboratory blank standards multiplied by 3. Table 3.1 shows the method detection limits for TN and TP analysis on each set of monthly samples. The overall detection limits for TN and TP in this study was also calculated from the standard deviation of all of the blank standard samples. This detection limit was used as the standard from which to compare all other nutrient concentration values. According to the SOPs for TN and TP analysis (Appendix C) the Method Detection Limit (MDL) is calculated to establish the method's ability to detect the analyte. This is performed by carrying through 7 or more separately prepared reagent blank solutions through all of the analysis preparation, digestion and spectrophotometer procedures.

Table 3.1 Method detection limits (MDL). Detection limits for the laboratory procedures are shown for each sample analysis date. Method detection limits were calculated as 3x the standard deviation of the blank laboratory standards.

Sampling Date	**TN mg/L**	**TP μ/L**
March-2005	0.06	2
April-2005	0.00	0
May-2005	0.05	6
June-2005	0.04	3
July-2005	0.00	1
August-2005	0.05	7
September-2005	0.00	1
October-2005	0.16	1
November-2005	0.03	2
December-2005	0.17	1
January-2006	0.00	0
February-2006	0.01	1
Method Detection Limit	**0.1**	**4**

This study used 12 separately prepared sets of reagent blanks for both the TN and TP detection limits. The MDL was then calculated as 3 × standard deviation of all of the blanks. MDL values for this study are 0.1 mg/L TN and 4 μg/L TP. Detection limit for field sampling was also calculated as 3x the standard deviation of the blank field samples (0.3 mg/L for TN and 7 μg/L for TP). Field sample detection limits indicate that some of the field sampling may have additional nutrients from sampling error or the deionized water used for blank field samples. The general rule while examining the data from this study has therefore been to look at trends in data rather than pinpoint particular data values especially when these are extremely low.

GIS Data Compilation

A Geographic Information System (GIS) was produced and used in this study to display and quantify spatial data including watershed characteristics. All GIS data compilation was performed using the ArcGIS suite of mapping software and ArcInfo licensed to the MSU Spatial Analysis Laboratory. Most of the spatial data layers were downloaded from the Missouri Spatial Data Information Service (MSDIS at http://msdis.missouri.edu) which is a web-based distribution center for spatial data created by Missouri Resources Assessment Partnership, the USGS, MODNR and others. University of Arkansas Center for Advanced Spatial Technologies (CAST) was another source of spatial data that was downloaded through Geostor clearinghouse website at http://www.geostor.arkansas.gov. Other datasets were extracted from original GIS layers or produced by manually digitizing or plotting GPS coordinates. Datasets were collected on both the Missouri and Arkansas portions of the UWRB and often did not match well across state boundaries. Data used in this project included land use, geology, elevation, National Pollution Discharge Elimination Systems (NPDES) point sources, river and stream networks, sub-watershed boundaries, political boundaries and sampling locations.

Sampling locations were plotted using a table of the GPS coordinates which were obtained directly from the USGS real-time stations and water quality website (http://waterdata.usgs.gov/mo/nwis/rt). Land use data from 2004 for Missouri and Arkansas was downloaded from the MSDIS and CAST web servers, respectively. These data were produced using high-resolution satellite imagery of the states and extensive field verification of land use classification (Blodgett 2005; Gorham 2005). However, the original land use datasets did not match across state boundaries due to different

classification systems and a different number of classes between the two states. Arkansas data had 15 classes with more agricultural distinctions while Missouri land use data contained 13 classes with more distinction between different levels of urban land use. In order to match the project study area across state boundaries, the land use classifications for both states were simplified to produce eight basic classes that were consistent across both states. The accuracy of this reclassification was tested by how well the two state land use datasets matched across the state boundary lines when combined. The eight classes, urban impervious, urban residential, barren, cropland, grasslands, forest, scrublands/young forest and open water were quantified by each sub-watershed in this study as percentage of total land use.

Through examination of land use data and preliminary data exploration even the eight simplified classes of land use presented redundant relationships. A study by Baginska et. al. (2003) about the role of land use resolution on nutrient concentrations found that only four or five major land use categories were required to estimate potential nutrient inputs from land use within a watershed basin. In order to cut down on the excessive amount of land use data processing, as well as reduce redundancy, the eight classes were further summarized into 1) “urban” (including both urban categories), 2) “barren/transitional”, 3) “agricultural” (including both grasslands and croplands) and 4) “forested” (forest and scrubland/young forest). Since the Land use data was based upon 2003-2004 aerial imagery, the assumption in using this data set was that the amount of change in land use was not significant enough to measurably alter the conclusions obtained when used at the large scale of this study.

Geology data used for this project was also obtained from MSDIS and Geostor. This information consisted of bedrock types, their attributed classification and extent. As with the land use data, state geology classifications for Arkansas did not match the geology classifications for Missouri. While this data matched visually in the ArcGIS mapping software, the attribute information associated with the geology layers was inconsistent from one state to the other. Again, the classification scheme was simplified and the data attributes were interpreted as belonging to one of several predominant bedrock types including limestone, dolomite, shale and sandstone. Elevation data from MSDIS and CAST which were used as digital elevation models (DEM) were created by the USGS Eros Data Center’s National Elevation Dataset (NED, 1999). This information was available by county and was created using stereo pairs of aerial photographs. All of the counties of the UWRB in Missouri were combined with the Arkansas counties to form a continuous surface. This digital elevation model had a resolution of 30 meters to each pixel. Based on sampling point locations and elevation data, ArcHydro analysis software was used to delineate the 19 watersheds within the UWRB study area.

Using watershed boundaries, land area in square kilometers, percentage of land use class and percentage of geology type were calculated for each watershed. Arkansas Department of Environmental Quality (ADEQ) and the Missouri Department of Natural Resources (MODNR) provided the National Pollution Discharge Elimination Systems (NPDES) data on wastewater treatment plants and discharge volumes. Additional spatial data including river and stream networks, roads and political boundaries were obtained from the USDA Spatial Data Gateway, the USGS National Hydrology Dataset, MSDIS, and the University of Arkansas CAST (USGS 1993; Blodgett 2005; USDA/NRCS 2005).

Least Squares Linear Regression Analysis

A commonly used correlation equation is Least Squares Linear Regression. It is designated by the letter "R^2" which represents the degree of correlation between variables. It ranges from 0 to 1with a higher R^2 value indicating a stronger correlation between the variables, one or more being the predictor variables and the other predicted. This value is interpreted in the following manner: an R^2 value of 0.4 indicates that the predictor variable (y) account for 40% of the variability in the predicted value (x). This leaves 60% of the residual variability not accounted for by the equation or not explained. Ideally, the equation should explain most if not all of the variability in the x variables which in this study are the nutrients concentrations. The R^2 value is therefore an indicator of how well the model fits the data (e.g., R^2 close to 1.0 indicates that the model has accounted for all of the variation between the specified variables) (Fox 1997).

The performance or significance of the regression is indicated by the p-value, a measure of the probability of non-correlation or no relationship between the variables in the regression equation. A low p-value (< 0.05) therefore indicates that the correlation is significant. However, a strong significant correlation does not necessarily indicate a cause and effect relationship. The relationship between variables can also be due to a common causative factor or a coincidental common trend. Least Squares Linear Regression analysis was performed to examine relationships between water quality and watershed variables in this study.

Data Management

All data collected from field sampling, Horiba U-22 unit, GIS spatial analysis and laboratory analysis was entered into Microsoft Excel spreadsheets. Water quality data was entered into the spreadsheet and stored by site. Spatial data for each watershed obtained from GIS was also compiled in a spreadsheet by site for comparison to water quality data. Data exploration and verification was performed to ensure that all data entered into the excel spreadsheets and all calculations, dates and parameters were compiled correctly. This required comparison of field notes to digital data, formula verification etc. Water quality and geospatial data for this study are available on the Ozarks Environmental and Water Resources Institute (OEWRI) website at www.oewri.missouristate.edu.

CHAPTER 4: RESULTS & DISCUSSION

This chapter presents the results of a one-year water quality study to evaluate relationships between nutrient (TN and TP) concentrations and watershed characteristics in 19 watersheds of the Upper White River Basin. Watershed characteristics include land use, bedrock, wastewater treatment plant discharge, and stream discharge (Q). Water quality parameters evaluated in this study are conductivity, turbidity, dissolved oxygen (DO) and water temperature. Results are divided into 11 sections: 1) GIS data analysis results 2) water quality at each site, 3) watershed classification by pollution source, 4) spatial trends in water quality, 5) seasonal trends in water quality, 6) hydrologic influence, 7) correlation among water quality indicators 8) bedrock influence, 9) wastewater treatment plant influence, 10) land use influence and 11) water chemistry and nutrients in the UWRB watershed. A description of future work that will further improve our understanding of water quality in the UWRB is also presented in this chapter. All data gathered in this study are contained in Appendix-A, water chemistry data and Appendix-B, GIS maps.

GIS Data Analysis Results

The general distribution of geology types was based on shape files obtained from Missouri Spatial Data Information Service (MSDIS) and Geostor spatial data clearinghouses at (http://msdisweb.missouri.edu & http://www.cast.uark.edu/). Data was produced from geological maps of Missouri and Arkansas. Table 4.1 shows percentage of bedrock types that make up the drainage area geology for each sampling site. Thirteen sites have primarily limestone and dolomite bedrock, located in the middle and northern portions of the UWRB. Three watersheds have mixed

carbonate and shale bedrock types, Kings River, Long Creek and War Eagle Creek watersheds. Headwaters of these streams emanate from the Boston Mountain shale. The headwaters of the White River and Richland Creek watershed have predominantly shale bedrock. Land use data obtained from the Missouri Resources Assessment Partnership (MORAP) and Center for Advanced Spatial Technologies (CAST) for 2004 was simplified and quantified for each of the 19 sample watersheds (Table 4.2). Urban land use is approximately 4% of the UWRB watershed. With rapidly growing urban areas, this percentage is expected to increase while agricultural areas around towns are being reduced. Watersheds draining Springfield, Ozark, Branson and Fayetteville have a greater percentage of urban land use while sub-watersheds around these areas contain higher percentages of grassland/pasture land use. The predominant agriculture involves cattle operations in the Missouri portion of the watershed and poultry production in the Arkansas portion of the watershed. There is also a large amount of urban area developing around the lakes which is made up of resorts, retirement communities and condominiums, a reaction to the booming tourist industry. As expected, forested watersheds are predominant in the rural areas farther from major population centers and in areas near national forests.

Water Quality at Each Sample Site

Nutrients and water chemistry from each of the 19 sample sites throughout the UWRB are presented in this section. Data is divided into the three major Hydrologic Unit Codes (HUC) that make up the UWRB, the James River Basin, Bull Shoals Basin and Beaver Lake Basin (see Figure 2.1 in chapter 2).

Table 4.1: Geology by site. Percentage of general geology type by sample drainage area.

Site	Dolomite	Limestone	Sandstone	Shale
WC-Springfield (1)	0	100	0	0

WC-above SWTP (2)	0	100	0	0
WC-at SWTP (3)	0	100	0	0
JR-Boaz (4)	31	64	5	0
Finley R (5)	34	66	0	0
JR-Galena (6)	34	60	6	0
WR-below TR Dam (7)	28	51	5	16
Bull Ck (8)	44	56	0	0
Beaver Ck (9)	52	44	5	0
JR-above Springfield (10)	38	62	0	0
Pearson Ck (11)	0	100	0	0
Long Ck (12)	0	53	0	47
Yocum Ck (13)	23	76	0	1
Kings R (14)	17	42	14	26
War Eagle Ck (15)	0	44	0	56
Richland Ck (16)	0	35	0	65
White R-Fayetteville (17)	0	36	0	64
West Fork White (18)	0	38	0	62
Bear Ck (19)	33	49	18	0

Table 4.2: Land use by site. Percent of land use in drainage basin area of each water sampling site.

Site ID	Urban	Barren	Agriculture	Forest
WC-Springfield (1)	87	0	8	4
WC-above SWTP (2)	71	0	20	9
WC-at SWTP (3)	67	1	24	9
JR-Boaz (4)	17	1	56	25
Finley R (5)	5	1	63	31
JR-Galena (6)	10	1	60	29
WR-below TR Dam (7)	4	1	36	56
Bull Ck (8)	2	1	24	73
Beaver Ck (9)	1	1	47	50
JR-above Springfield (10)	5	1	59	35
Pearson Ck (11)	18	1	66	15
Long Ck (12)	1	1	31	66
Yocum Ck (13)	3	2	65	29
Kings R (14)	1	2	22	75
War Eagle Ck (15)	1	2	27	70
Richland Ck (16)	1	1	26	72
White R-Fayetteville (17)	4	1	15	79
West Fork White (18)	11	1	18	70
Bear Ck (19)	1	2	31	65

James River Basin (HUC 11010002). The James River Basin is a major tributary of the UWRB which flows south into Table Rock Lake. This watershed is approximately 3768 km² in size. Portions of seven counties (Stone, Christian, Barry, Lawrence, Greene,

Webster, and Douglas) drain into the James River. There are approximately 465 kilometers of streams with permanent flow, 119 kilometers of intermittent streams, and numerous losing streams within the James River Basin (MODOC 2001; MODNR 2001). This watershed encompasses most of the metropolitan area of Springfield and many rapidly growing communities such as Ozark and Nixa. Tourism also has a major impact on local economy of the James River Basin where tributaries are used for floating, swimming, and fishing and camping. Many streams in the James River Basin including Wilson Creek are loosing streams where all of the surface flow of the stream enters subsurface channels and cracks in the limestone bedrock. During baseflow conditions, streams are fed by springs and ground water flow as it emerges from the karst aquifer. James River sites are influenced by many point and non-point sources of water pollution and also by stormwater run-off from impervious area. Streams show the affects of flashy high water from storm events where precipitation rapidly flows into streams draining extensive impervious areas causing massive bank erosion.

Water quality is also affected by developed areas where nutrient loading is generally higher than that of non-developed areas. Data from the Lakes of Missouri Volunteers Program (LMVP) shows that nutrient pollution from populated areas near the headwaters around Springfield is flushed downstream feeding excessive algal growth and eutrophication. James River has therefore been listed according to the Clean Water Act, section 303(d) as impaired due to nutrients. A Total Maximum Daily Load (TMDL) for nutrient concentrations in the James River was developed through examination of the relationships between excessive algal growth and nutrient concentrations in the river (MODNR 2001). The James River TMDL states that TP concentrations should not

exceed 75 µg/L and the TN concentrations should stay below 1.5 mg/L in order to keep algal growth at acceptable levels, between 100-200 mg/m² (MODNR 2001).

Wilson Creek drains a major portion of Springfield, MO and is 50% urban and less than 20% forest. Springfield's Southwest Wastewater Treatment plant (SWTP) discharges more than 30 million gallons of effluent per day into Wilson Creek greatly affecting water quality below the plant. The first two sample sites, WC-Springfield (1) and WC-above SWTP (2) are located 6 km apart and are upstream of the SWTP. Water quality is similar at these sites with TN concentrations at 1.4 mg/L and 1.2 mg/L and average TP at 56 µg/L and 59 µg/L respectively (Table 4.3). Downstream of the plant, WC-at SWTP (3) yielded the highest average TN concentrations (11.7 mg/L) and second highest average TP of all sample sites in this study (175 µg/L). These nutrient levels exceed James River TMDL limits. In addition to increased nutrient concentrations, WC-at SWTP (3) also has water chemistry typical of wastewater treatment plant (WTP) discharge. Average water temperature at WC-at SWTP (3) is 19° C while the average water temperature at WC-above SWTP (2) is 14° C. The higher water temperature below the WTP outflow is caused by controls at the plant during the bio-treatment process. WC-at SWTP (3) has average DO concentrations of 16 mg/L, a result of effluent being oxygenated at the plant before release, while WC-above SWTP (2) has 10 mg/L DO. Residual salts from household and industrial wastes remaining in wastewater effluent also cause higher conductivity below the SWTP than at other sites (Table 4.3).

Table 4.3: Water quality indicators for the James River Basin. Summary of sample data by site (complete data tables in Appendix A). *Underlined nutrient values exceed James River TMDL limits of 75 µg/L TP and 1.5 mg/L TN. ^dl = below method detection limits (0.1 mg/L TN and 4 µg/L TP).

Site	Value	TN	TP	pH	Conductivity	Turbidity	DO	Temp	Depth	Q

		mg/L	µg/L		mS/sec	NTU	Mg/L	C°	m	m^3/sec
WC	Mean	1.4	56	7	729	17	9	14	0.43	0.4
Springfield (1)	Min	0.8	^dl	7	314	6	5	3	0.07	0.04
	Max	2.5	194	8	999	61	14	23	1.14	2.92
	Median	1.2	37	7	743	8	8	16	0.4	0.08
WC-above	Mean	1.2	59	8	607	24	10	14	0.23	0.55
SWTP (2)	Min	0.6	2	7	266	6	0	4	0.01	0
	Max	2.3	186	9	900	78	18	24	0.85	1.61
	Median	0.9	38	8	666	10	9	12	0.15	0
WC-at	Mean	11.7	175	8	1045	14	16	19	0.52	1.28
SWTP (3)	Min	2.5	35	7	562	0	10	13	0.42	0.71
	Max	17.7	325	8	1520	32	22	23	0.95	3.54
	Median	12	175	8	975	17	16	20	0.48	1.03
JR-Boaz (4)	Mean	6.3	125	8	778	18	11	17	0.47	4.94
	Min	1.6	12	7	497	3	8	3	0.34	1.44
	Max	14.6	327	8	1110	55	17	28	0.95	19.74
	Median	5.2	103	8	840	12	10	17	0.41	2.51
JR-above	Mean	0.9	18	8	518	15	11	15	0.73	1.32
Springfield (10)	Min	0.5	2	8	323	1	7	4	0.36	0.16
	Max	1.1	36	9	666	68	16	25	1.51	7.08
	Median	1	18	8	549	9	10	16	0.53	0.44
JR-Galena (6)	Mean	2.8	56	8	617	14	11	17	0.48	11.87
	Min	1.1	4	8	331	2	7	2	0.1	3.31
	Max	6.6	125	9	969	63	17	29	1.68	59.18
	Median	2.2	56	8	594	5	10	17	0.15	4.66
Pearson C (11)	Mean	2.2	45	8	589	31	11	15	0.56	0.21
	Min	1.7	1	7	415	0	7	7	0.24	0.03
	Max	2.8	310	9	771	155	17	24	0.93	0.82
	Median	2.1	24	8	581	14	10	16	0.56	0.11
Finley R (5)	Mean	1.1	28	8	502	19	11	15	0.4	2.53
	Min	0.6	dl	8	317	0	9	3	0.23	0.47
	Max	1.5	51	9	687	93	16	27	0.87	11.67
	Median	1.1	28	8	490	11	10	13	0.28	0.68

Two sample sites located along the James River further show the strong influence of wastewater effluent from the Springfield WTP. JR-above Springfield (10) is upstream of the Wilson Creek confluence and has average TN of 0.9 mg/L and TP of 18 µg/L.

James River-Boaz (4), below the confluence with Wilson Creek at has much higher average nutrient concentrations at 6.2 mg/L TN and 125 µg/L TP. Further downstream in the James River, JR-Galena (6) also had elevated levels of nutrients compared to JR-above Springfield (10) with mean of 2.8 mg/L TN and 56 µg/L TP (Table 4.3). The Galena WTP discharges approximately 35,000 gallons per day just upstream of this location, a much smaller plant than SWTP (MODNR 2004; SWTP 2006). The influence of the SWTP on Wilson Creek extends to Galena but is diluted by 4 to 5 times when it reaches JR-Galena (6). Dilution causes nutrient levels at JR-Galena (6) to be significantly lower than those found 47 kilometers upstream at JR-Boaz (4). Deposition of phosphorus as it sorbs with sediments and is taken up by aquatic plants decreases TP loading in downstream reaches. Total N is diluted with increased discharge and also removed from the water by aquatic organisms and plants as the river flows downstream, but this nutrient is not as dramatically reduced in the JR-Galena (6) samples as TP since it is more mobile (Benfield 1996; USEPA 1999).

Total P and TN levels at JR-Galena (6) can be compared to nutrient concentrations sampled by the Lakes of Missouri Volunteers Program (LMVP) in 2005 at a site approximately 18 kilometers downstream of JR-Galena (6). LMVP data shows average TP at 76 µg/L, slightly higher than baseflow average found in this study (Thorpe et. al 2006). LMVP values represent all water levels sampled during the warm season, from spring to fall including low and high flows. High stream discharge may contain higher nutrient concentrations than baseflow, especially during the first flush of run-off from land use sources. Nutrients may also become diluted with further run-off in the latter part of storm events as streams levels have raised, but contamination from the land

use is dissipated down stream (Petersen et. al. 1998). Baseflow influenced by point sources such as WTP may also have high nutrient loading due to more concentrated point-source effluent. The LMVP TP data was from the 2005 warm season which did not have many run-off events due to this year being very dry. The few high-flow samples captured by the LMVP volunteers may have been very high in nutrient loading from a build-up of land use sources causing this data to have a higher average.

Data from LMVP for the James River downstream of Galena showed average TN values around 1.3 mg/L in 2005, lower than JR-Galena (6) values (2.8 mg/L). The LMVP site in the James River is in the transition zone from James River to Table Rock Lake reservoir. Slower current at the LMVP site allows nitrogen in the water to be quickly assimilated by algae and other organisms, lowering TN in this part of the river. In addition, LMVP data collectors often work more during the summer months when the assimilation of TN by aquatic organisms is high. Total N levels tend to be higher at baseflow and then decrease with dilution during higher Q, the opposite of TP.

Finley Creek and Pearson Creek are tributaries of the James River that contain major construction and development south and east of Springfield, MO. Pearson Ck (11) is 56 km^2 in size and contains 18% urban area and 15% forest. Finley Ck (5) watershed is larger, with an area of 665 km^2 that is 5% urban and 31% forest (Table 4.2). Pearson Ck (11) samples average 2.2 mg/L TN and 45 µg/L TP while Finley Ck (5) samples contained approximately half of these levels (1 mg/L TN and 28 µg/L TP). Pearson Creek as no WTP while there are 5 WTP in the Finley Creek watershed which discharge a combined 1.5 million gallons of effluent daily. The closest of these is 7 miles upstream of the sample site at Nixa. However, Finley Creek basin with its 5 WTP is not affected as

severely as the smaller Pearson Creek basin with its larger percentage of urban area or Wilson Creek with the much larger SWTP. Besides drainage basin sources of nutrient loading, Pearson Creek also receives drainage from distant sink holes within the city of Springfield, outside of its surface drainage (Aley and Thompson 2002). This adds nutrients from parts of Springfield to the Pearson Creek watershed that is not reflected in the topographic drainage basin. Independence of the subterranean drainage system from surface drainage is a common characteristic of karst landscapes in the Ozarks further complicating relationships between water quality and drainage basin factors.

Comparison of nutrient concentrations showed that there were several sites which had samples below method detection limits. Method detection limits were calculated to show the lower limit beyond which the laboratory analysis was unreliable due to limitations of the analysis process. This limit was 0.1 mg/L TN and 4 µg/L TP. Samples that read below method detection limits were few and were simply included in the equations, graphs and tables as the original analysis values.

Bull Shoals Basin, Missouri and Arkansas (HUC 11010003). Bull Shoals Basin encompasses the UWRB tributaries east of the James River Basin that flow south into Taneycomo and Bull Shoals Lakes. The watersheds that flow north out of Arkansas into Bull Shoals Lake and Taneycomo Lake are also part of this basin. Bull Shoals Basin is downstream of the James River Basin (HUC 11010002) and the Beaver Lake Basin (HUC 11010001). This study sampled 4 sites in the Bull Shoals Basin; Bull Ck (8), Beaver Ck (9), Bear Ck (19) and White River-below Table Rock Dam (7), a lake site. Watershed characteristics in the Bull Shoals Basin are similar to that of the James River Basin with karst carbonate bedrock, primarily forest land use and generally less urban area than James River Basin watersheds.

Bull Ck (8), with a drainage basin of 503 km², has 2% urban area and 72% forest (Table 4.2). This site produced low nutrient concentrations with average TN at 0.4 mg/L. Similarly, five samples out of the twelve taken at Bull Ck (8) had TP concentrations that dipped below sample and method detection limits (4 µg/L) with average TP concentrations only 6 µg/L (Table 4.4). East of Bull Creek watershed is the Beaver Creek basin where TN concentrations were found to be similar. This watershed is larger than Bull Ck (8), 771 km², with 2% urban area but only 50% forest. Open grassland and pasture areas make up the remaining watershed area (Table 4.2). The Beaver Ck (9) samples also had slightly higher average TP (10 µg/L) than those at Bull Ck (8). Bear Ck (19) watershed is 344 km² with less than 2% urban and 65% forest. Many poultry farms dot the landscape in this basin as this is a major agricultural industry in the Arkansas portion of the UWRB (Figure 4.2). Bear Ck (19) samples generally had low TN with values below 1 mg/L except for the June sample which was 2.8 mg/L and a high spike in

the November sample, over 13 mg/L. The high TN spike in November may have been from the deer hunting season when butchered deer carcasses had been thrown into the water near this site. Total P concentrations were 10 µg/L, equal to those at Beaver Ck (9) (Table 4.4). White River-below Table Rock Dam (7) sample site is unique since it is the only lake site in this study. These samples are colder water drained through the power plant from the lower depths of Table Rock Lake. Water temperatures average 7° C below those at the other sites. Average nutrient levels were 0.9 mg/L TN and 11 µg/L TP.

Table 4.4: Water quality indicators for Bull Shoals Basin. Summary of sample data by site (complete data tables in Appendix A) ^dl = below method detection limits (0.1 mg/L TN and 4 µg/L TP) *Underlined nutrient values exceed James River TMDL limits of 75 µg/L TP and 1.5 mg/L TN.

Site	Value	TN mg/L	TP µg/L	pH	Conduc-tivity mS/sec	Turbidity NTU	DO Mg/L	Temp C°	Depth m	Q m^3/sec
Bull Ck (8)	Mean	0.4	6	8	494	8	10	17	0.83	1.41
	Min	0.1	^dl	8	415	0	6	3	0.64	0.04
	Max	1.1	11	9	685	34	15	28	1.22	6.51
	Median	0.2	7	8	486	5	9	19	0.73	0.28
Beaver Ck (9)	Mean	0.4	10	8	531	10	11	17	0.5	3.38
	Min	0.1	dl	8	468	1	9	4	0.24	0.71
	Max	0.9	25	9	656	25	16	29	1.22	17.61
	Median	0.4	9	8	528	7	10	17	0.42	1.33
White River below TR Dam (7)	Mean	0.9	11	8	352	23	10	9	0.71	67.08
	Min	0.5	4	7	287	3	5	7	0.36	25.57
	Max	1.1	25	9	444	72	15	11	1.67	121.14
	Median	0.9	10	8	330	13	9	9	0.49	61.76
Bear Ck (19)	Mean	1.8	10	8.0	486	11	10	18	0.33	1.11
	Min	0.08	dl	6.8	420	0	7	7	0.20	0.11
	Max	13.84	36	8.5	607	52	13	30	0.54	6.12
	Median	0.54	6	8.1	488	5	10	19	0.32	0.28

Beaver Reservoir Basin, Arkansas (HUC 11010001). Beaver Reservoir watersheds consists of the headwaters of the White River, Beaver Lake, Table Rock Lake and all of the tributaries of the White River above Table Rock Dam excluding the James River Basin. Geology in these watersheds are similar with bedrock in headwater reaches consisting primarily of shale, transitioning to karst limestone/dolomite in the middle and lower reaches as streams flow toward the main stem of the White River (Table 4.1). Predominant land covers are forest and agricultural pastures with the headwaters and elevated topography mainly forested and wide river valleys or bottom lands often used as pasture for livestock. Long Creek (12) watershed, west of Bear Creek basin, also contains a large poultry farming industry. The numbers of these farms are indicated on the map in Figure 4.2. On average, each poultry house produces over 100 tons of litter (poultry fecal matter mixed with straw or other organic material) annually (Chaubey et. al. 2000). Nutrient-rich poultry litter is applied to many of the agricultural pastures and fields in this region. Excessive land application of litter may occur due to the need for disposal of the excessive amount of litter generated (Edwards et. al. 1996; Mallarino et. al. 2004).

Although land application is seen as a solution to litter disposal, over-application or application before a rainfall event can increase nutrient loading into streams through storm water run-off, leaching and erosion. The high nutrient values found at Long Ck (12) and Yocum Ck (13) may be indicators of the impact that this practice can have on nutrient loading in the watershed. Samples from Long Ck (12) had average TP of 178 µg/L, the highest average TP out of all 19 sample sites. This site also had elevated TN concentrations with an average of 1.7 mg/L. TP concentrations greatly increased at the Long Ck (12) site during the latter part of the sampling year from November 2005 to

February 2006 (Appendix A). This may have been due to fall litter applications on pastures or the end of the growing season when vegetation is least available to assimilate TP (Edwards et. al. 1996). Agricultural land use is approximately 31% of this watershed (Table 4.2). Due to the significant increase in TP concentrations at this site and not at other sites with similar land use, another source of nutrients in addition to agricultural litter applications is suspected. Some local inhabitants near Long Creek have alluded to the recent construction of a poultry processing plant in the Long Ck watershed as a source of nutrient loading, but this has not been confirmed. Another possible nutrient source is extensive highway construction on U.S. Highway 65 where this road is being changed from two lanes to a four lane highway. This section is on the eastern edge of the Long Ck basin and runs 7 miles south from the Arkansas-Missouri border. Much of the road clearing for this construction is upstream of the sample site and was ongoing throughout the latter part of the sample period. Figure 4.1 shows extensive road construction and clearing on the right side of the image near U. S. Highway 65.

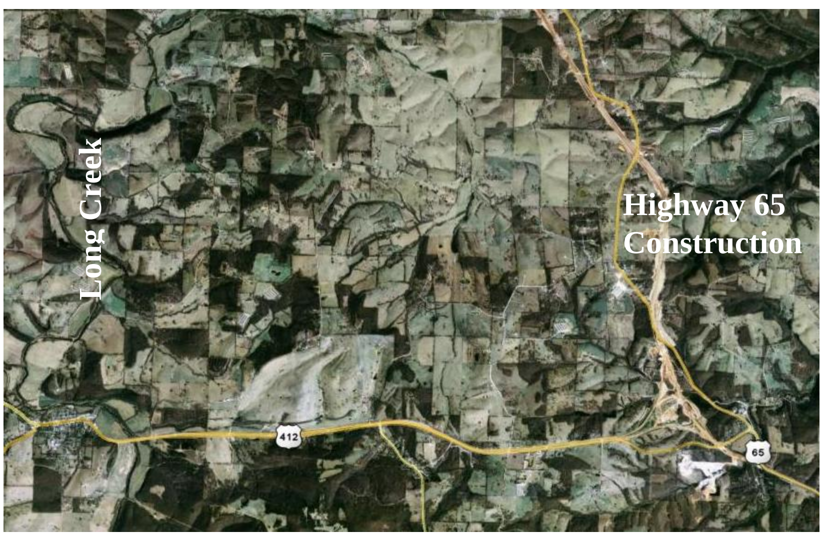


Figure 4.1: Highway construction in Long Creek (12) watershed. Imagery by Google Earth shows U.S Highway 65 construction zone on edge of Long Creek drainage basin

West of Long Ck is the Yocum Ck watershed which has similar land and agriculture to Long Creek. Average TN at Yocum Ck (13) was much higher than at Long Ck (12) at 4 mg/L. Total P was significantly lower at only 35 µg/L (Table 4.5). One apparent difference between the Long Ck (12) and Yocum Ck (13) is stream bed material and water clarty. Long Ck was turbid with sandy banks, dark soils and silty sediment deposit on the streambed. Yocum Ck, however, contained massive gravel bars, clear water and banks of reddish clay and silt overlying embedded chert gravel deposits more typical of Ozarks streams. Another factor determining differences in nutrient concentrations may be drainage basin size. Long Ck drainage basin is 265 km^2 while the Yocum Ck (13) basin is 117 km^2. The larger area of the Long Ck (12) watershed creates a larger stream making it more likely to contain higher amounts of dissolved and suspended solids compared to Yocum Ck with its lower discharge (Vannote et. al. 1980).

Yocum Ck (13) watershed also contains 65% pasture land use compared to the 31% pasture area in Long Ck (12). This makes Yocum Ck (13) the highest in percentage of agricultural land use which may also increase the risk of N leaching from litter applied to pastures (Table 4.3). The Yocum Ck (13) drainage area is less than 30% forest while Long Ck (12) is 66% forested (Table 4.2). Increased forest area is associated with lower TN concentrations (Boyd 1996; Binkley et. al. 2004). Nitrogen is more readily dissolved in water and can move downstream quickly with the flow of Yocum Ck (13) while in the slow-moving water at Long Ck (12) nitrogen has more opportunity to be taken up by aquatic plants and organisms. Differences in stream channel composition, land use, drainage basin size and discharge may therefore explain differences in nutrient concentrations between the sample sites at Long and Yocum Creeks.

Table 4.5: Water quality indicators for Beaver Reservoir Basin. Summary of sample data by site (complete data tables in Appendix A). ^dl = below method detection limits (0.1 mg/L TN and 4 µg/L TP) *Underlined nutrient values exceed James River TMDL limits of 75 µg/L TP and 1.5 mg/L TN.

Site	Value	TN mg/L	TP µg/L	pH	Conduc-tivity mS/sec	Turbidity NTU	DO Mg/L	Temp C°	Depth m	Q m^3/sec
Long Ck (12)	Mean	1.66	178	7.8	475	21	10	16	0.68	0.92
	Min	1.18	14	7.3	404	5	6	6	0.61	0.31
	Max	2.45	592	8.2	593	96	15	23	0.79	3.79
	Median	1.45	88	7.7	425	9	10	16	0.69	0.47
Yocum Ck (13)	Mean	4.3	35	8.1	451	18	11	16	1.07	0.42
	Min	1.28	^dl	7.8	326	3	8	4	1.00	0.1
	Max	17.43	65	8.6	519	82	15	28	1.15	2.27
	Median	2.9	36	8.0	457	7	10	16	1.07	0.11
Kings R (14)	Mean	0.38	77	8.4	402	20	11	18	0.55	4.82
	Min	0.3	dl	8.0	276	3	8	4	0.24	0.51
	Max	0.76	161	8.8	533	83	17	31	1.32	19.85
	Median	0.3	87	8.4	405	12	10	18	0.34	1.23
War Eagle Ck (15)	Mean	0.98	40	8.1	351	23	10	17	0.28	2.29
	Min	0.38	dl	7.7	181	6	7	5	0.10	0.31
	Max	1.4	99	8.6	563	88	16	28	0.82	11.52
	Median	1.02	36	8.0	332	14	10	18	0.15	0.54
Richland Ck (16)	Mean	0.41	12	8.4	288	20	11	19	0.27	3.39
	Min	dl	dl	7.9	148	3	9	5	0.05	0.03
	Max	0.96	24	9.1	445	78	18	32	0.76	16.32
	Median	0.3	13	8.5	272	12	11	18	0.14	0.72
White R-Fayetteville (17)	Mean	0.42	18	8.0	264	26	10	18	0.66	1.11
	Min	0.12	dl	7.4	123	11	5	4	0.14	0.04
	Max	0.87	39	8.3	486	101	15	30	1.15	5.18
	Median	0.41	17	8.0	281	20	10	20	0.61	0.16
West Fork-White R (18)	Mean	0.47	20	7.6	355	31	9	18	0.44	3.74
	Min	0.19	dl	6.6	207	9	5	5	0.08	0.03
	Max	0.92	48	8.3	646	96	15	32	1.26	19.14
	Median	0.4	19	7.7	362	18	9	19	0.25	0.23

Kings R (14) drainage basin is the largest White River tributary in Arkansas with over 1,370 km². This watershed is 75% forest with headwaters located in the Ozarks National Forest. Average TN at Kings R (14) was 0.4 mg/L and average TP was slightly higher than Yocum Ck (13) at 75 µg/L (Table 4.5). Berryville WTP is located nearly 23 kilometers upstream of the sample site. Phosphorus levels may be affected at baseflow from the WTP discharge and sediment carried in this large stream. Non-point source nutrients may also affect this watershed from poultry litter applications (Figure 4.2).

War Eagle Ck (15) drainage basin ranks third in size for the Arkansas sites. This watershed receives the Huntsville WTP effluent located 26 kilometers upstream of the sample site. Average TN was 1 mg/L and TP was around 40 µg/L at this site. As seen in Figure 4.2, both War Eagle Creek and neighboring Richland Creek basin contain large numbers of poultry barns, as do the watershed farther west near Fayetteville, AR. Both of these streams had very low flow throughout the sampling period. The extremely shallow and low discharge at Richland Ck (16) allowed for very little transport of nutrients. Average TN concentrations were 0.4 mg/L and average TP was 12 µg/L, much lower than most other Arkansas sample sites. Most of the TP may bind to sediments and settle out of the almost stagnant water.

White R-Fayetteville (17) is located on the main channel of the White River, approximately 1 mile downstream of Lake Sequoya reservoir and the confluence of the eastern and western branches of the White River. Lakes often act as detention basins for nutrients and sediment (Segarra-Garcia and Loganathan 1992; Meals and Budd 1998). Lake Sequoya may act as a detention basin for nutrients flowing into this watershed from

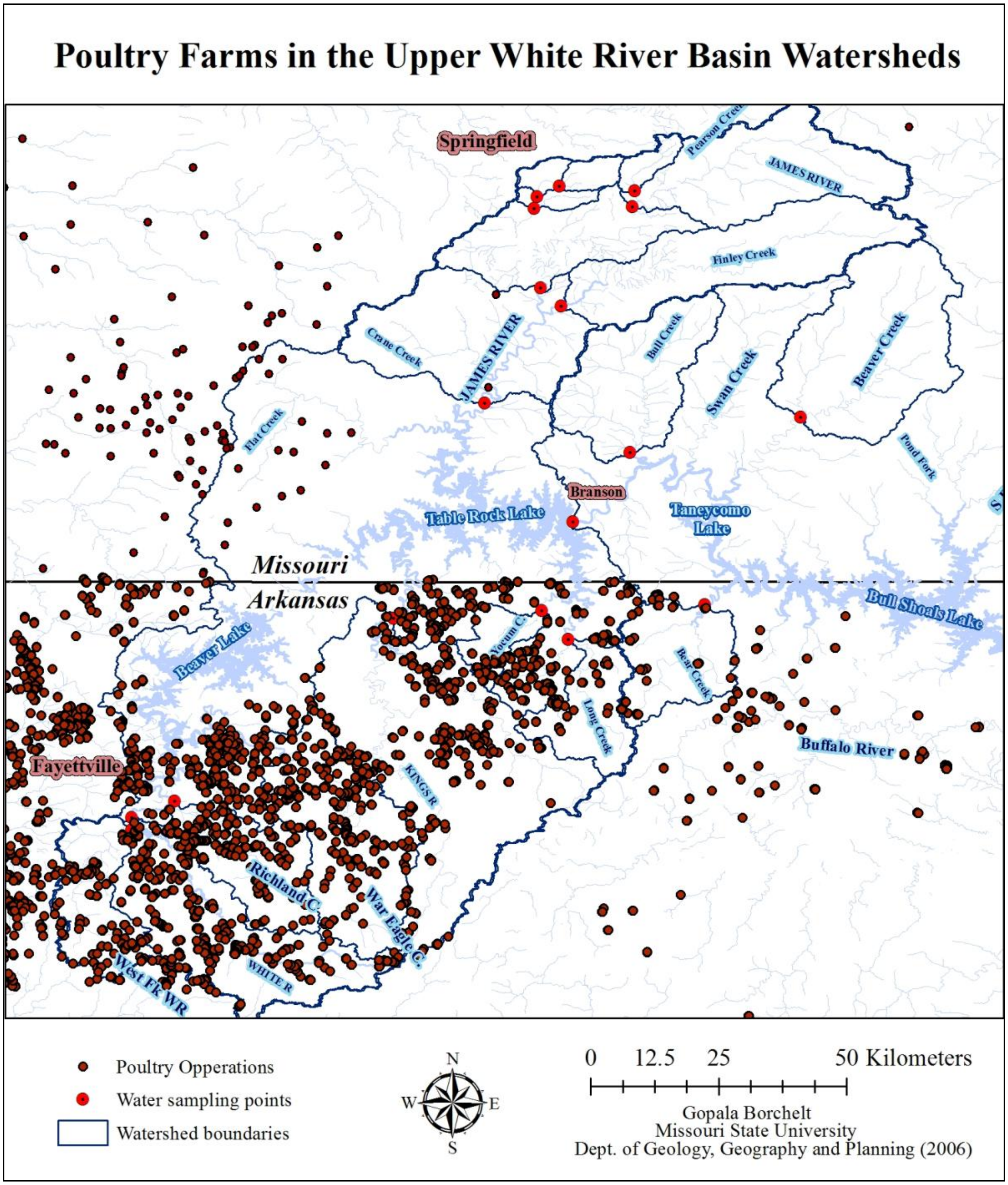


Figure 4.2: Poultry farms in the UWRB. Individual poultry houses in northwest Arkansas and poultry farms in southwest Missouri (data provided by the University of Arkansas CAST 2005 and Missouri Department of Natural Resources NPDES Permits)

the cattle and poultry producing areas and the urban growth in the basin, lessening nutrient impacts during baseflow conditions at this site. White River-Fayetteville (17) samples had TN concentrations below 1 mg/L for all sampling dates and TP did not exceed 39 µg/L with an average of 18 µg/L. West Fork-WR (18) is approximately 1.5 miles upstream of the confluence of the West Fork of the White River with the main stem of the White River. Due to its proximity to the City of Fayetteville, AR West Fork of the White River watershed contains more urban land use (11%) but also has more forest than most other Arkansas watersheds. The small WTP for the town of West Fork, Arkansas discharges 100,000 gallons per day into the watershed. However, the Fayetteville WTP, which discharges 12 million gallons per day, is located downstream of the White River-Fayetteville (17) and West Fork-WR (18) thus adding no point source nutrient inputs to the samples from this plant. West Fork-WR (18) also has a large pool just upstream containing masses of aquatic and semi-aquatic plants. Nutrient values sampled at the West Fork-WR (18) were below 1 mg/L TN for all dates and TP did not exceed 50 µg/L with an average of 20 µg/L (Table 4.5). Low baseflow discharge combined with the detention of nutrient-rich sediments in upstream pools or reservoirs may lessen non-point nutrient loading from urban/agricultural areas in the white River sites near Fayetteville.

Watershed Classification by Pollution Source

In order to examine landscape and watershed factors that may be affecting nutrient loading/water quality in the UWRB, the 19 sample watersheds were ranked into groups of high disturbance, elevated disturbance and low disturbance watersheds. This section describes the ranking procedure and landscape characteristics used to classify the watersheds. Table 4.6 shows the ranking database with parameters including, land use , geology and specific wastewater treatment plant discharge (SWD) which is the WTP effluent discharge per day per km^2 in the drainage basin. Ranking was based primarily on percentage of urban and forest land, but was also influenced by agricultural land use SWD.

Ranking of watersheds based on land use is common in scientific studies on nutrient loading and watershed factors (Jordon et. al. 1997; Miller et. al. 1997; Lent et. al. 1998; Meals and Budd 1998; Ourso and Fernzel 2002; Mytyk and Delfino 2004). Baseflow samples such as those taken in this study are composed of the ground water and delayed surface drainage, not directly linked to precipitation-induced surface run-off (Aley and Thompson 2002). In the karst hydrology of the Ozarks, there is a potential for significant storage of nutrients and contaminants that have been washed with run-off into streams, and sink holes during precipitation. Stored nutrients may be later released as baseflow discharge through springs (Miller et. al. 1997; Petersen et. al 1998; Lunetta et. al. 2005). Baseflow sampling can therefore be highly affected by land use. Confined animal feeding operations (CAFOs), primarily poultry, are shown in the ranking database for comparison. However, numbers of poultry farms may not indicate CAFO disturbance since nutrient sources from these is litter which can be transported to other watersheds.

Table 4.6: Ranking system database. Summary of nutrients, land use, bedrock, SWD, and CAFO by site.

Site ID	A_d km²	TN mg/L	TP ug/L	Urban per/A_d	Ag per/A_d	Forest per/A_d	Carbonate per/A_d	SWD gal/day/km²	CAFOs per/A_d
WC-Springfield (1)	51	1.2	37	87%	8%	4%	100%	0	0
WC-above SWTP (2)	92	0.9	38	71%	20%	9%	100%	0	0
WC-at SWTP (3)	132	12.0	175	67%	24%	9%	100%	228,383	0
JR-Boaz (4)	1,199	5.2	103	17%	56%	25%	95%	25,292	0
Finley R (5)	665	1.1	28	5%	63%	31%	100%	1,243	0
JR-Galena (6)	2,567	2.2	56	10%	60%	29%	94%	12,505	3
WR-below TR Dam (7)	10,394	0.2	7	4%	36%	56%	79%	0	24
Bull Ck (8)	503	0.2	7	2%	24%	73%	100%	0	0
Beaver Ck (9)	771	0.4	9	1%	47%	50%	95%	583	0
JR-above Springfield (10)	633	1.0	18	5%	59%	35%	100%	131	0
Pearson Ck (11)	56	2.1	24	18%	66%	15%	100%	0	0
Long Ck (12)	265	1.5	88	1%	31%	66%	53%	0	54
Yocum Ck (13)	117	2.9	36	3%	65%	29%	99%	0	90
Kings R (14)	1,374	0.3	87	1%	22%	75%	59%	1,782	424
War Eagle Ck (15)	685	1.0	36	1%	27%	70%	44%	2,920	383
Richland Ck (16)	361	0.3	13	1%	26%	72%	35%	0	268
White R-Fayetteville (17)	1,039	0.4	17	4%	15%	79%	36%	96	600
West Fork White (18)	325	0.4	19	11%	18%	70%	38%	308	152
Bear Ck (19)	344	0.5	6	1%	31%	65%	82%	0	60

Table 4.7 shows land use ranking categories used to classify watersheds into three basic categories disturbance. As shown, land use of more than 15% urban area and less than 20% forest gas been categorized as a high disturbance indicator. Similarly, low disturbance indicators are rank less than 5% urban and more than 65% forest area. High disturbance criteria includes >50% agricultural land use while low disturbance ranking is <30% agriculture. The elevated (moderate) disturbance criteria rank primarily between the high disturbance and low disturbance indicators for most land use parameters. Only three land use categories are used for watershed ranking because many watersheds have similar percentages of land use. More than these three categories would unnecessarily complicate the ranking by creating categories containing only one or two watersheds.

Water quality was also compared to land use ranking by creating Table 4.8 which shows low, moderate, high and very high categories for median nutrient concentrations. Table 4.8 also shows the TMDL comparison to each of these categories. Low and moderate TN and TP categories are below TMDL levels while the high and very high nutrient rankings are at or above TMDL levels. These tables (Table 4.7 and 4.8) are followed up by Table 4.9 which shows the ranking for each sample watershed by land use percentages and SWD as well as a comparison to median nutrient rankings. Since land use and water quality are related there is a common relationship or variation between nutrient concentration ranking and watershed ranking.

The drainage basins of all three Wilson Creek sites contain a high amount of urban area and low percentage of forest. These sites therefore were ranked as high disturbance watersheds due to non-point or land use influence. Wilson Ck-at SWTP (3) contains additional high disturbance indicator, high point-source or SWD. Wilson Creek water quality ranking also showed that median nutrient concentrations are moderate to very high, supporting the ranking of these watersheds disturbance areas. The moderate nutrient ranking for both Wilson Creek sites above the SWTP is probably caused by baseflow sampling which did not capture urban run-off, but sampled the low discharge of the stream when many sediments and nutrients had settled out of the almost stagnant water. The influence of the SWTP point-source during baseflow is evident in the very high nutrient ranking of watersheds affected by this point-source. JR-Boaz (4) has moderate forest and urban area in its drainage basin, but also was ranked high disturbance due to point-source influence. This site was also ranked as very high nutrient for concentrations.

Table 4.7: Watershed ranking matrix. Categories used for ranking include land use and SWD in the watershed.

Watershed factor	High disturbance	Elevated disturbance	Low disturbance
Forest Land use	< 20%	20-65%	> 65%
Urban Land use	> 15%	5-15%	<5%
SWD	> 1,500 (gal/ per day/km^2)	600-1,500 (gal/ per day/km^2)	< 600 (gal/per day/km^2)
Agricultural Land use	> 50%	30-50%	<30%
*Urban Land use	> 50%	5-50%	<5%

*urban land use categories for watersheds without WTP discharge

Table 4.8: Water quality ranking matrix. Categories used for ranking sites based on relative nutrient concentrations and TMDL comparison

Comparison to TMDL	Ranking	Water quality limits	
		Median TP µg/L	Median TN mg/L
Below TMDL	Low	≤ 20	≤ 0.5
	Moderate	> 20 - 60	> 0.5 – 1.2
~ At TMDL	High	60 - 100	1.2 - 2
Above TMDL	Very high	> 100	> 2

Table 4.9: Watershed ranking and water quality comparison. High disturbance, elevated disturbance and low disturbance watersheds based on percent land use and also showing SWD ranking and ranking of nutrient concentrations from Table 4.8 for comparison

Land Use Ranking		Nutrient ranking	
High disturbance (High Ag or Urban/Low Forest)		***TP***	***TN***
Land use based			
	WC-Springfield (1)	**Mod**	**Mod**
	WC-above SWTP (2)	**Mod**	**Mod**
	Pearson Creek (11) ^Ag	**Mod**	**V high**
Point source			
	WC-at SWTP (3) *H	**V high**	**V high**
	JR-Boaz (4) H, Ag	**V high**	**V high**
Elevated disturbance (moderate forest)			
Land use based			
	Yocum Creek (13) Ag	**Mod**	**V high**
Point source			
	JR-Galena (6) H, Ag	**Mod (close)**	**V high**
	War Eagle Creek (15) H	**Mod**	**Mod**
	Finley Creek (5) *M (close), Ag	**Mod**	**Mod**
	Kings River (14) H	**High**	**Low**
	JR-above Springfield (10) *L, Ag	**Low**	**Mod**
	Beaver Creek (9) L	**Low**	**Low**
Low disturbance (high forest)			
Land use based (+/-)			
	Long Creek (12)	**High**	**High**
	Bear Creek (19)	**Low**	**Low (close)**
	Bull Creek (8)	**Low**	**Low**
	Richland Creek (16)	**Low**	**Low**
Point source			
	West Fork White River (18) L	**Low (close)**	**Low (close)**
	White River-Fayetteville (17) L	**Low**	**Low**
	White River-below TR Dam (7) M	**Low**	**Low**

*Point Source loading factor, (SWD) shown as high (H) moderate (M) and low (L) symbols) based on the categories in Table 4.7. ^Ag = > 50% agriculture (crop and pasture/grassland). Close = the value used in this ranking is nearly in the next category higher, such as the low (close) = almost moderate.

Pearson Creek (11) has low forest area, moderate urban area, but also has a high percentage of agricultural land. This site was ranked under high disturbance watersheds by non-point source and has a moderate to high nutrient ranking. Pearson Creek (11) may be affected during baseflow by spring discharge and concentration of volatile nitrogen. All 5 of the high disturbance watersheds were within the James River Basin and in smaller tributaries that drain Springfield, MO. The main stem of the James River shows some of the eutrophic effects of development in the basin with the large algal blooms which can be seen in the wide sun-lighted streambed at Galena, Missouri (Figures 4.3 and 4.4). JR-Galena (6) has medium percentage of forest and urban land use as do JR-above Springfield (10) and Finley Ck (5). These watersheds also have high percentages of agricultural land use and moderate to high SWD so these sites were ranked under the elevated disturbance category.

Figure 4.3: Channel covered with algae. James River (Galena, MO February 5, 2006)

The JR-Galena (6) site has very high median TN concentrations, indicating that during baseflow conditions this nutrient is dissolved in the water and carried down stream from sources upstream. However, TP sorbs to sediments which settle out of the stream at baseflow and therefore ranked as moderate at this site. Finley Ck (5) ranked as elevated disturbance watershed from agricultural land use and SWD and had low to moderate nutrient concentrations. Yocum Ck (13) was another elevated disturbance site because this watershed contains one of the highest percentages of agricultural land. It is also ranked near the high end of the elevated disturbance category for forest land use (29%). Again, the Yocum Ck (13) had very high TN levels and moderate TP concentrations. Other watersheds ranked in the elevated disturbance category included Kings R (14) and War Eagle Ck (15) which had high SWD and moderate agricultural land use. Beaver Ck (9) also had elevated disturbance from moderate agricultural forest land use area.

Figure 4.4: Strands of attached algae. James River (Galena, MO February 5, 2006)

Watersheds ranked under the elevated disturbance category generally have moderate to high SWD and agricultural land use. Agricultural land in this study consists mainly of open pastures and a small percentage of crop fields. These areas have are potential nutrient sources of erosion, fertilizer and manure run-off. High agricultural watersheds therefore rank under the elevated disturbance category similar to the urbanized watersheds ranking mainly as high disturbance or the very rural, forested basins ranking as low disturbance. In addition, the water quality ranking for these watersheds showed a trend of high to moderate TN and TP concentrations. The high TP ranking for Kings River (14) may be from the Berryville WTP upstream. Beaver Ck (9) was low in nutrient concentration which may have been a factor of the very dry sampling yesr which especially affected this watershed. This can be seen in Figure 4.23.

Ranking of low disturbance watersheds included Bull Ck (8), Long Ck (12), Bear Ck (19), Richland Ck (16), WR below TRD (7), WR-Fayetteville (17), and West Fork-WR (18). These sites all have a high percentage of forest (65%- 79%) and low percentage of urban area except West Fork-WR (18) which has elevated urban area (18%). These watersheds, with the exception of White River sites near Fayetteville have a moderate percentage of agricultural land use. White R-Fayetteville (17) and West Fork-WR (18) contain little pasture land, but have some SWD effects. All low disturbance sites have low nutrients with the exception Long Ck (12) which ranked as low disturbance site by land use, but has a high ranking for nutrient concentrations. Major land use changes due to road construction were occurring in the eastern part of this watershed during the sampling period and may account for high nutrient concentrations.

Spatial Trends in Water Quality

Figures 4.5 through 4.12 summarize water quality indicator values for UWRB sample sites by location in the three 8-digit HUC boundaries. James River TMDL levels for nutrients are indicated for sites in the James River Basin while the mean nutrient values for low disturbance sites are indicated for Bull Shoals and Beaver Lake Basin sites. Low disturbance sites are those ranked according to Table 4.9 and generally have little or no point-source (SWD). Bear Ck (19) and Long Ck (12) were excluded from the low disturbance reference sites due to the several high spikes in nutrient values found at these sites, evidence of occasional high non-point nutrient loading. The 5 reference sites used to calculate average low nutrient levels are Bull Ck (8), Bear Ck (9), Richland Ck (16), WR-Fayetteville (17) and West Fork-WR (18). Hyphens are used in the graphs (Figures 4.5 though 4.12) to show the level of the 3rd highest sample value at each site. This helps to identify sites where one or two samples had very high values compared to the remainder of the samples, indicating a spike not representative of the usual state of the water quality.

Several sample sites have large variation between the high and low nutrient values. These sites are WC-at SWTP (3), JR-Boaz (4) and JR-Galena (6) and Yocum Creek (13). In addition to these, WC-Springfield (1), WC-above SWTP (2), Pearson Ck (11), Long Ck (12), Kings River (14) and War Eagle Ck (15) have a high variation in TP values. Bear Ck (19) and Yocum Ck (13) have a high variation in TN values. All of these sites exceed James River TMDL nutrient levels either for average concentrations or occasional high values.

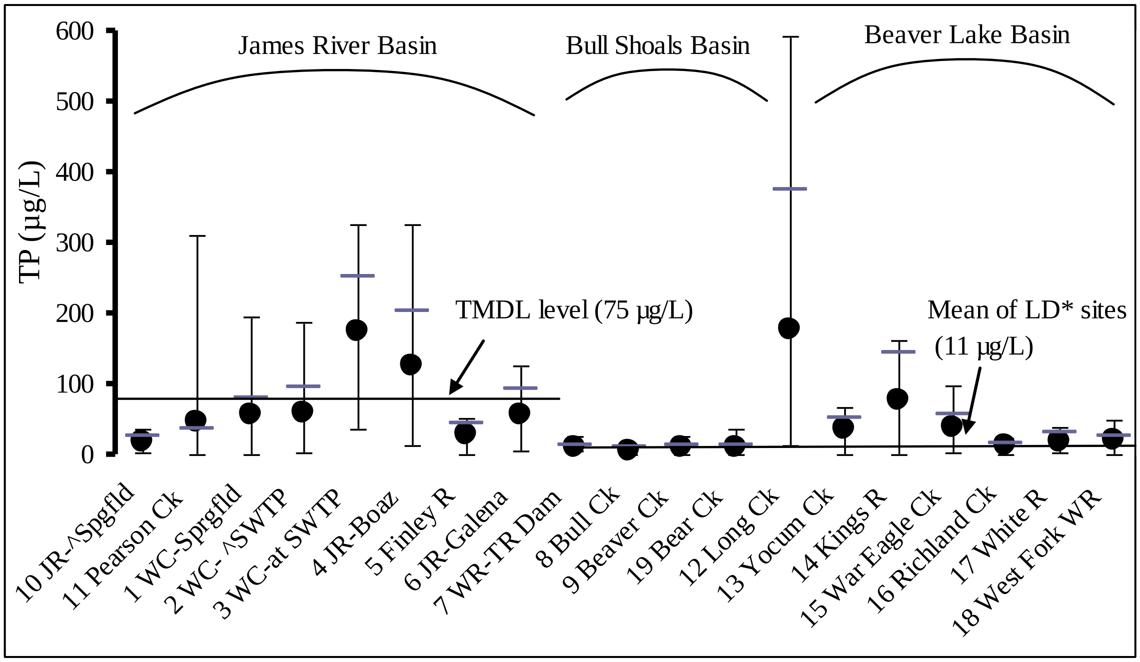


Figure 4.5: Total P values by site and HUC region. A summary of the TP values for each site is shown with maximum and minimum values indicated as vertical bars around the mean (dots). Hyphens mark 3rd highest sampled value. * LD = 5 least disturbed sites

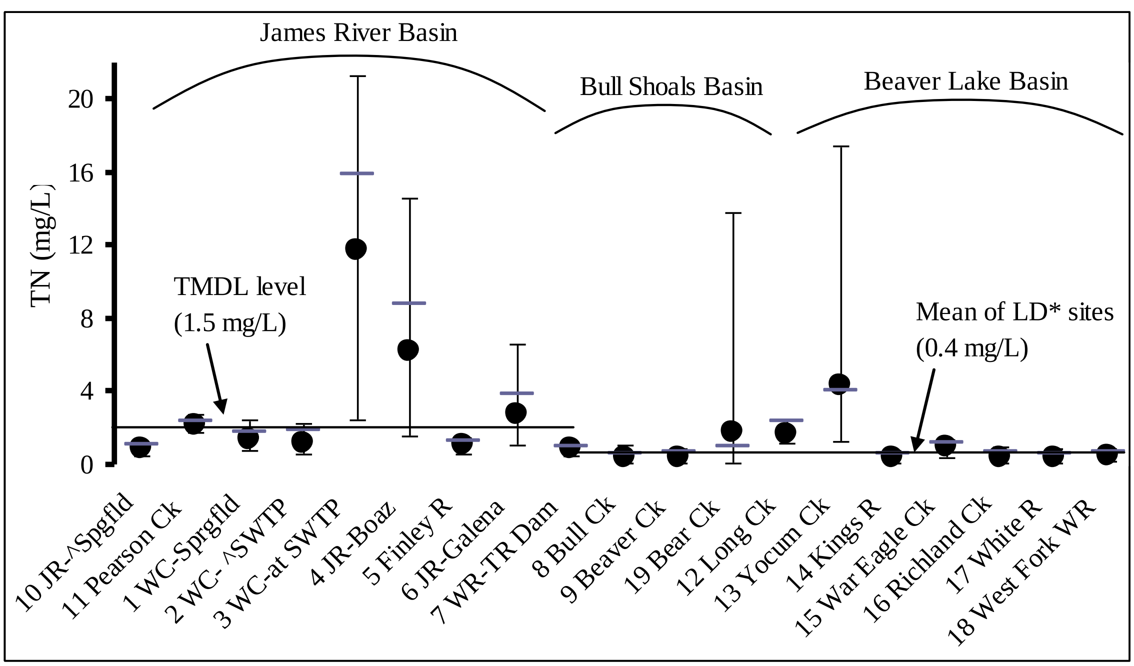


Figure 4.6: Total N values by site and region. Vertical lines represent maximum and minimum values while hyphens mark 3rd highest sampled value. * LD = low disturbance sites

Specific discharge (SQ), calculated as mean sample Q in liters per day/km², varied throughout the 19 watersheds, especially in those with high percentages of urban or agricultural land use (Figure 4.7). High SQ variation is seen in the Wilson Creek sites, Beaver Ck (9), Richland Ck (16) and West Fork-WR (18). The variation was, however, largely caused by one or two sampling dates as evident by the location of the mean values near the low end of the variation indicator lines (Figure 4.7). Smaller drainage basins also have more variability in stream levels than the large watersheds. This is caused by the larger watersheds having more sources, including springs, tributaries and runoff, which add constant flow to the stream. Small creeks in the Ozarks, especially ones that rely on surface drainage of semi-impervious urban and agricultural areas can sometimes dry up on the surface and appear to hold no water at all, a characterization of the WC-above SWTP (2) site. These same streams suddenly flash flood with a local rain storm event.

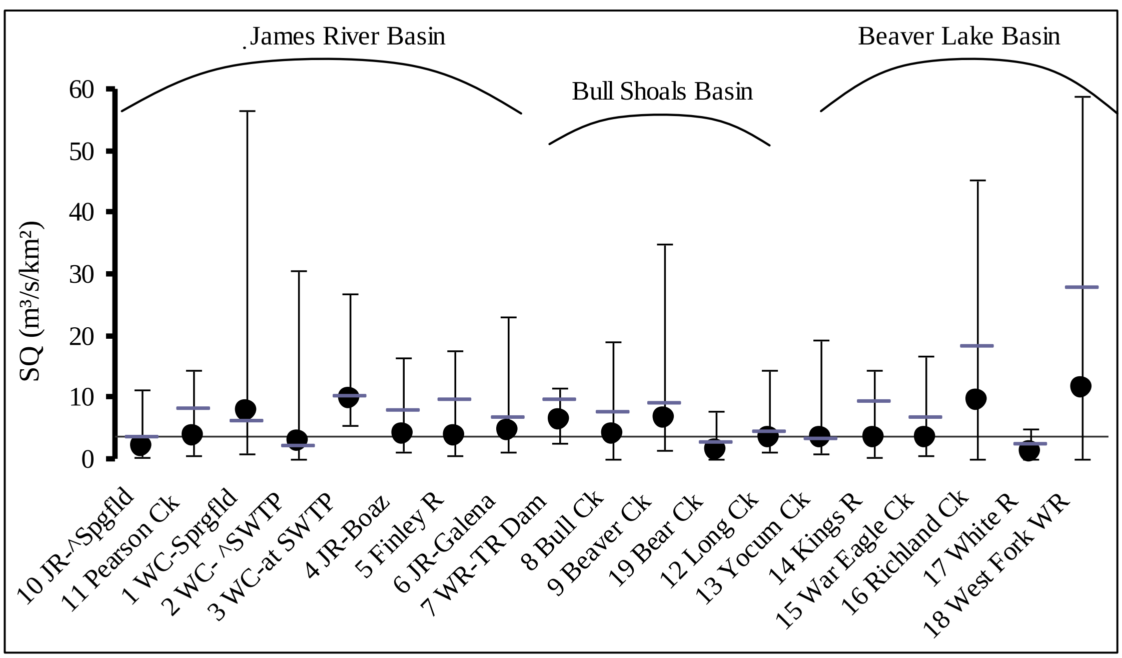


Figure 4.7: Specific discharge by site. Vertical lines show max/min values, hyphens mark 3rd highest value, and horizontal line is overall average SQ (3.8 liters/sec/km²/).

Specific conductivity is more variable in the James River Basin sites, especially in the point-source influenced sites (Figure 4.8). The James River sites have higher overall conductivity while sites near the headwaters of the White River have lower SC. Urban land use may cause the increase in SC at West Fork-WR (18) by loading more salts and sediments from impervious areas. Turbidity was highest in the Pearson Ck (11) samples (Figure 4.9). This was probably caused by construction of a new bridge at this site where soil disturbance stirred up the fine clay which was then suspended in the water. Other than Pearson Creek, there is a slight increase in turbidity at the Beaver Lake Basin sites closer to the headwaters of the White River. There is a decrease in average turbidity at Bull Shoals Basin sites excluding WR-below Table Rock Dam (7).

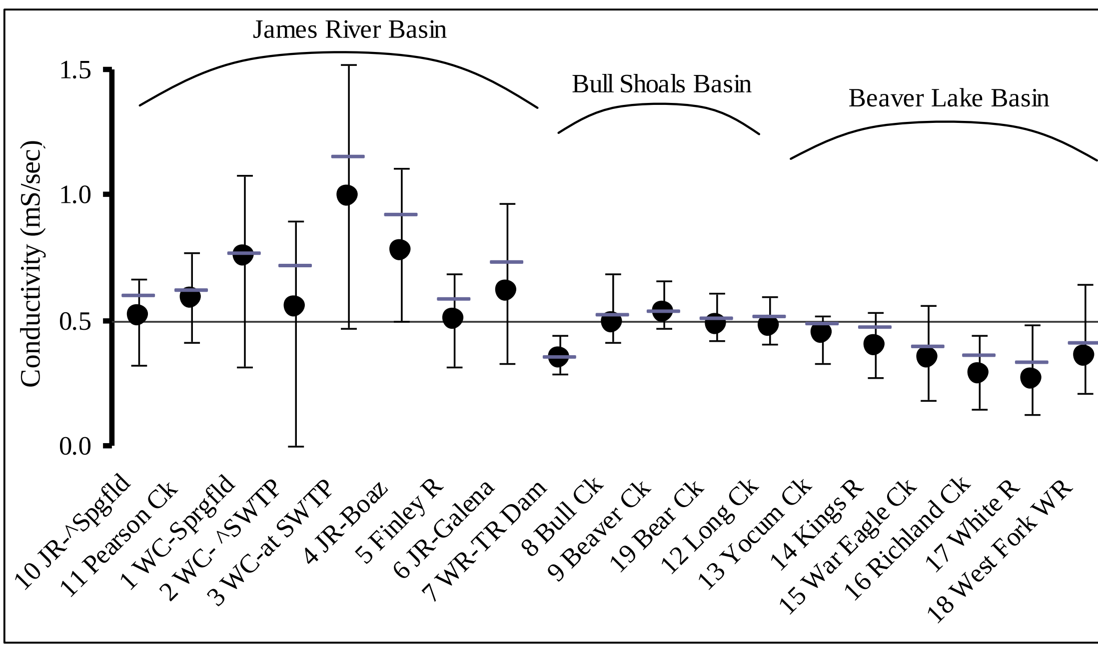


Figure 4.8: Specific conductivity by site. Vertical lines show max/min values while hyphens mark 3rd highest value. Horizontal line is overall average SC (0.49 mS/sec)

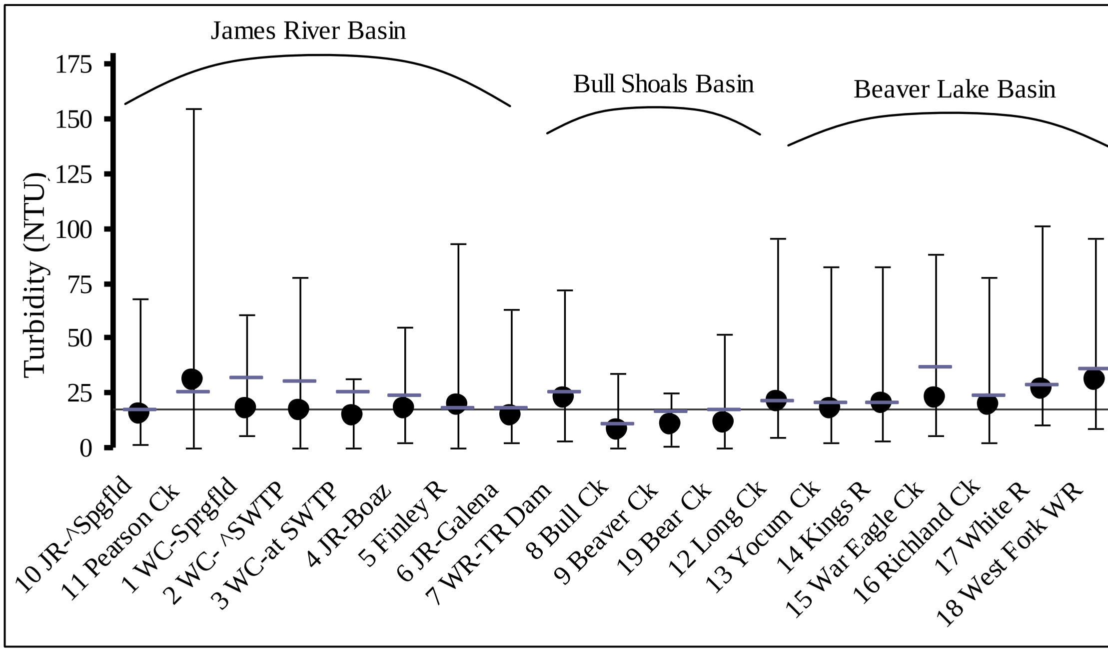


Figure 4.9: Turbidity (NTU) by site. Vertical lines represent max/min values while hyphens mark 3rd highest sampled value. Horizontal line is overall average turbidity.

Temperature variations, shown in Figure 4.10, are similar throughout much of the UWRB. The high temperatures in the summer months drive the maximum values up. As expected, the White R-below Table Rock Dam (7) has the lowest temperatures due to the cool, deep water from Table Rock Lake flowing through the dam. WC-at SWTP (3) has the highest average temperature with the majority of its flow made up of WTP effluent that has been warmed up during the treatment process. There is also a slight trend from cooler water temperatures in the James River Basin to warmer temperatures in the Beaver Lake Basin. This may simply reflect the fact that James River watersheds are farther north than Beaver Lake watersheds and have slightly cooler annual climates. Dissolved oxygen is similar throughout the UWRB watersheds, again with the exception of WC-at SWTP (3) where DO is artificially elevated (Figure 4.11). Abundance of nutrients and bacteria in Wilson Creek quickly use up DO in these urban areas causing levels to drop.

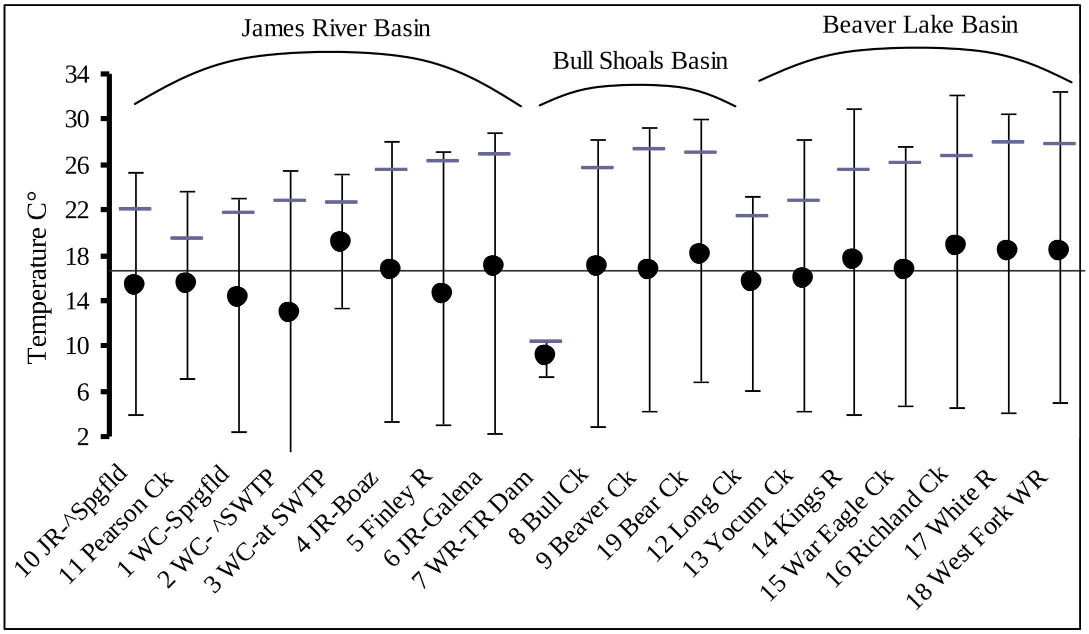


Figure 4.10: Water temperature by site. Vertical lines show max/min values, hyphens mark 3rd highest value, and horizontal line is overall average temp (16.7 C°).

Five out of the 8 sample sites that show mean DO values below the overall average DO level are affected by urban areas. However, the majority of the sample values are well above the DO limits for supporting aquatic life in streams in Missouri, which is 5 mg/L. Only Wilson Ck-above SWTP (2) and Wilson Ck-at SWTP (3) had samples that drop below this limit. Average pH is highly variable among sample sites and also drops where there is a high percentage of urban or agricultural land use. This may be caused by the increase in organic waste material such as animal and human byproducts being added to the water in these areas causing release of acids from the decaying organic material. The buffer created by carbonate bedrock is approximately a pH of 8.2, shown on Figure 4.12. This buffer helps the water in carbonate regions like the Ozarks absorb some of the acidity from organic material. This characteristic causes all of the average sample values to be above the neutral pH (7), which makes them slightly alkaline.

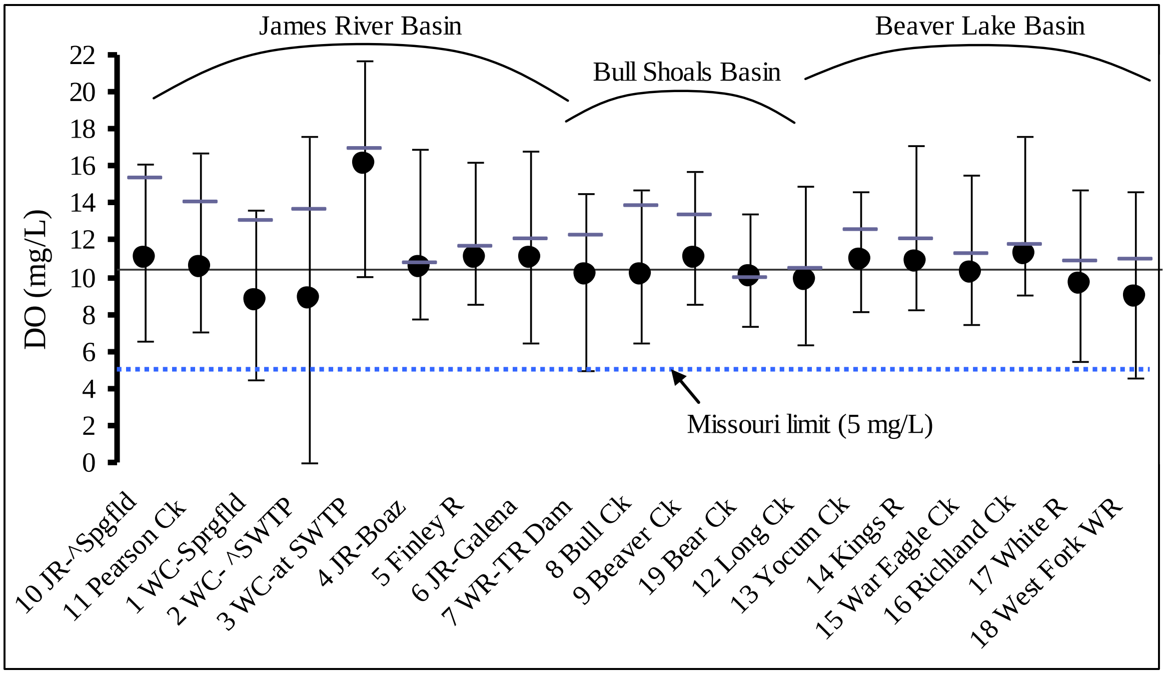


Figure 4.11: DO by site. Vertical lines show max /min values, hyphens mark 3rd highest value and horizontal line is overall average DO (10.5 mg/L).

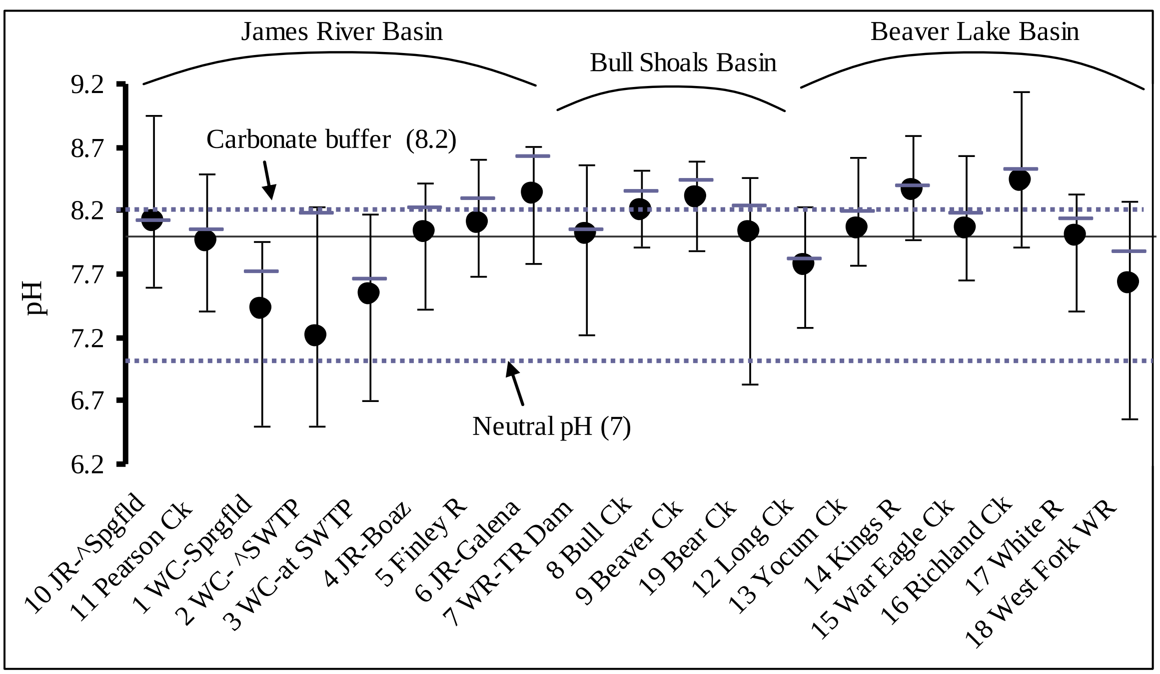


Figure 4.12: pH by site. Vertical lines show max/min values, hyphens mark 3rd highest value and horizontal line is overall median pH (8.0).

Seasonal Trends in Water Quality

Nutrient concentrations have often been found to relate with seasonal patterns (Boyd 1997; Binkley et. al. 2004). Seasonal changes that affect water chemistry include precipitation frequency, temperature and vegetation growth cycles. Drainage basin size may also affect seasonal patterns (Sphar and Wynn 1997; Brezonik and Stadelmann 2002). To show the correlation between water quality indicators and seasons, the three highest values were selected out of all 12 samples for each site. These values were then plotted by month creating a total of 57 high values spread out according to the month in which they occurred (Figures 4.13 through 4.16). The three lowest sample values were also selected and plotted for each water quality parameter.

The highest TP concentrations are often associated with late summer and fall (Figure 4.13). Low stream flow during late summer and fall may increase WTP effluent volume in the stream which is high in phosphorus. Additionally, high temperatures in the late summer and early fall combined with low water levels and less stream flow may induce the release of phosphorus stored in stream sediment (USEPA 1999). Many low TP samples occurred in late winter and early spring, possibly reflecting dilution of nutrient concentrations during the high-precipitation period of the year. High TN concentrations of often occurred during the winter and early spring from January to March with several high samples in July (Figure 4.13). High TN in late winter and early spring may be due to less up-take by plants since most vegetation is dormant during this period. Run-off increases from rainfall during early spring and may also affect TN loading. Low TN values occurred more often in September to December. This may be caused by less consumption of TN by aquatic and terrestrial plants combined with a less run-off inputs.

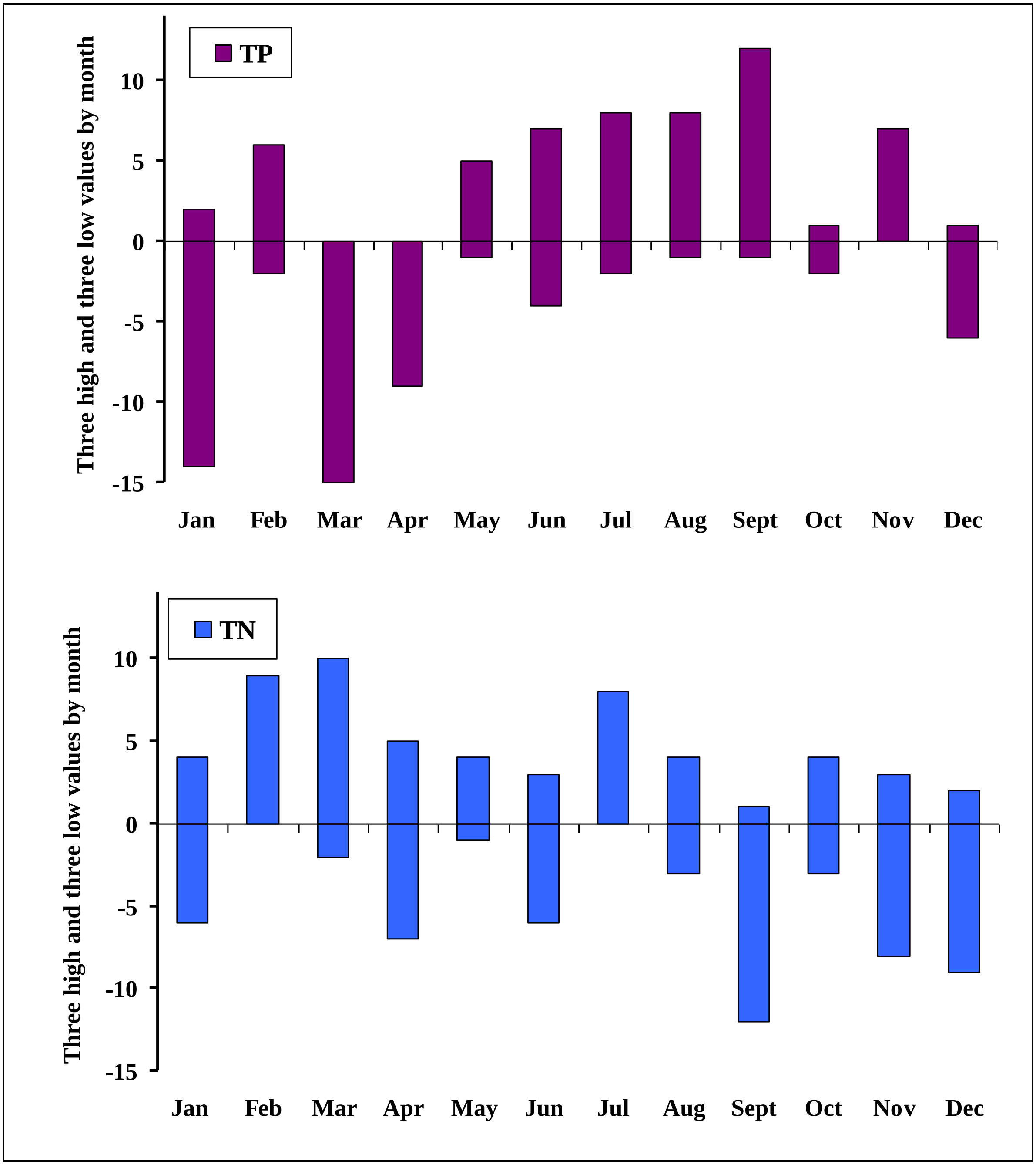


Figure 4.13: Seasonal high and low nutrient concentrations. Addition of the three highest sample concentrations for each site are shown by month above the 0 line. Addition of the three lowest sample concentrations by site are shown by month below the 0 line for comparison.

High sample values for turbidity and SC occurred most frequently in the fall and winter seasons, September through January (Figure 4.14). The February sample was taken on the 5th and 6th and second of this month. The winter and early spring is when leaves dropped from the fall senescence are beginning to break down in the water. The added tannins and decaying leaf matter increases turbidity in the water. During the summer months, pools and runs along rivers and streams may become striated with warmer water near the top and cooler water closer to the bottom of the channel. The change in air temperature from the warm summers to cooler winter also causes the striated water to mix up and reincorporate some of the sediments from the streambed into the water column. Some of the high values in turbidity found in the warm seasons are probably due to excessive algae growth or soil disturbance from construction near the stream. Many low turbidity values occurred in November, possibly also related to the lower stream discharge.

Specific conductivity sample values are often highest during the November through January also possibly related to low stream discharge (Figure 4.16). The lower stream flow during this period may have allowed dissolved minerals, salts and limestone in the water to concentrate and cause increased conductivity. The months with the lowest SC, March- May, were also the months with the highest stream discharge. The dilution of minerals and other conducting dissolved solids by the increased precipitation and run-off also may be the reason for low SC in the early spring.

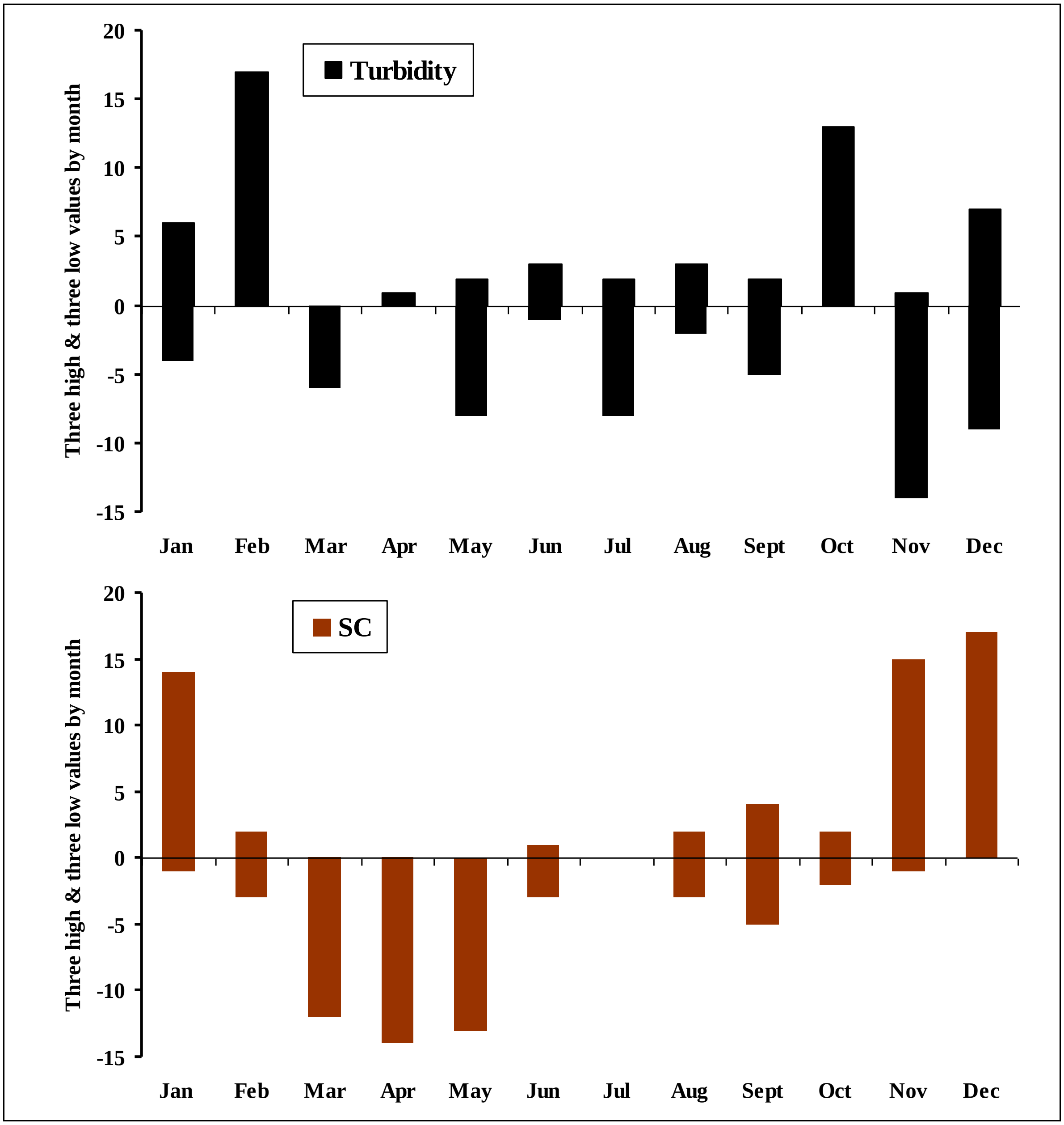


Figure 4.14: Three highest and three lowest turbidity and SC. Addition of the three highest sample concentrations for each site are shown by month above the 0 line. Addition of the three lowest sample concentrations by site are shown by month below the 0 line for comparison.

June through September is the warmest time of the year in the Ozarks as shown by the number of high water temperatures sampled during these months (Figure 4.15). Water temperatures gradually heat up, becoming warmest around August, and then quickly decline as the season progresses. Seasonal high DO reflects the water temperature changes. Since lower water temperatures are able to absorb more dissolved oxygen, the high DO samples tend to be during the cooler moths of March, December and January when colder water temperatures prevail. High DO samples in March are generally found in the southern portions of the UWRB in the Arkansas watersheds that are less affected by urban growth. High DO is also found in Wilson Creek near Springfield where it is added to the SWTP effluent. High DO samples in December and January are generally found in the northern watersheds of the UWRB including the James River and Bull and Beaver Creeks.

Sixteen out of 19 samples had high stream discharge (Q) values in March-May (Figure 4.16). The March-May samples were collected only a week after a rainfall event for most sites, making these samples most likely to contain higher Q. April though June also historically receives the most rainfall out of the year (MODOC 2001). The Low Q samples occurred most frequently in the late summer and during winter months when rainfall was less frequent. High and low pH values showed a pattern of high values in the early part of the year and gradually decreasing pH as the year progressed (Figure 4.16). The stream Q may have had an effect on this water quality parameter since higher Q in the beginning of the year may have increased mineral and salts inputs from run-off and diluted the acidic, organic material.

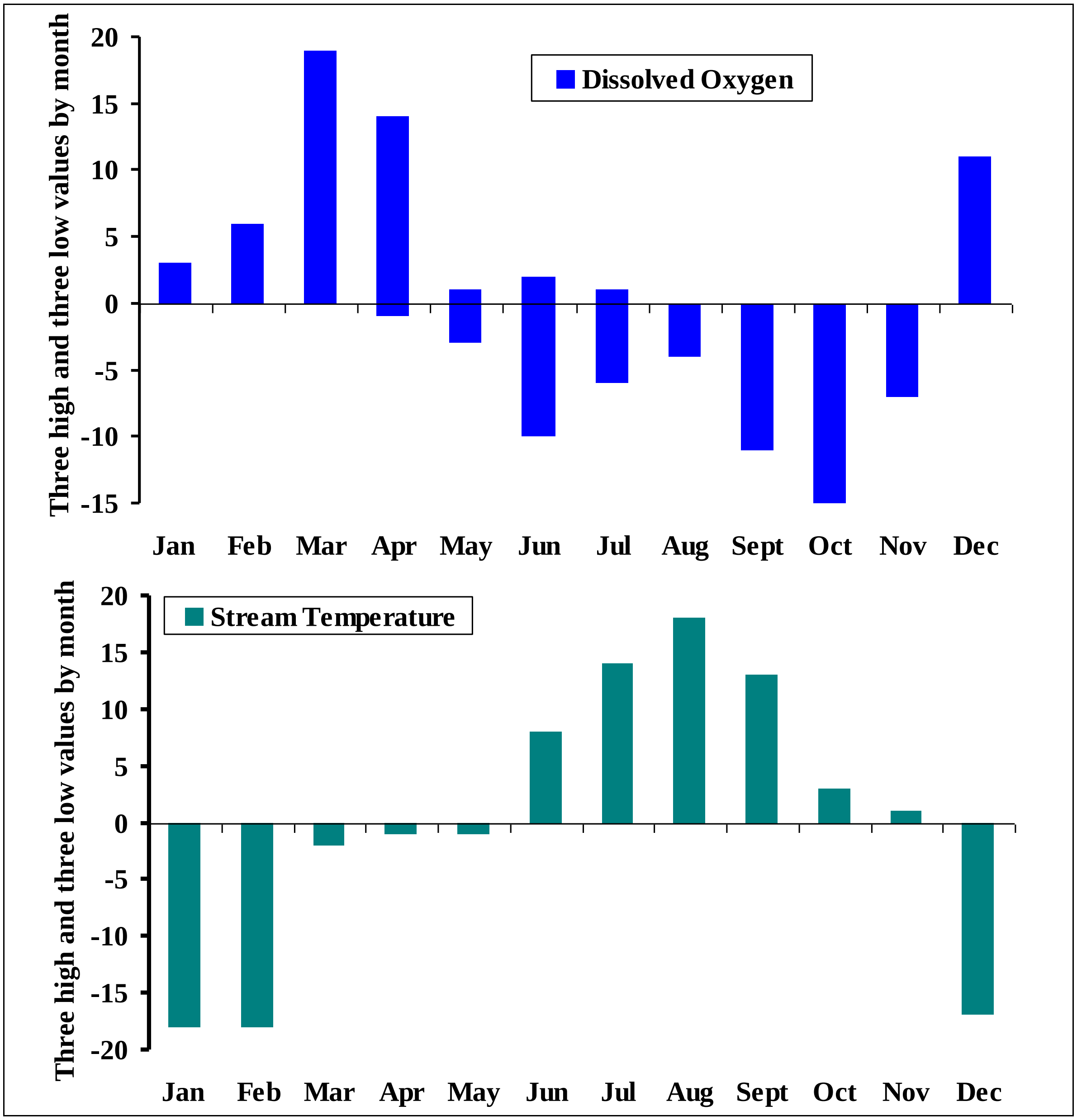


Figure 4.15: Seasonal high and low DO and stream temperature. Addition of the three highest sample concentrations for each site are shown by month above the 0 line. Addition of the three lowest sample concentrations by site are shown by month below the 0 line for comparison.

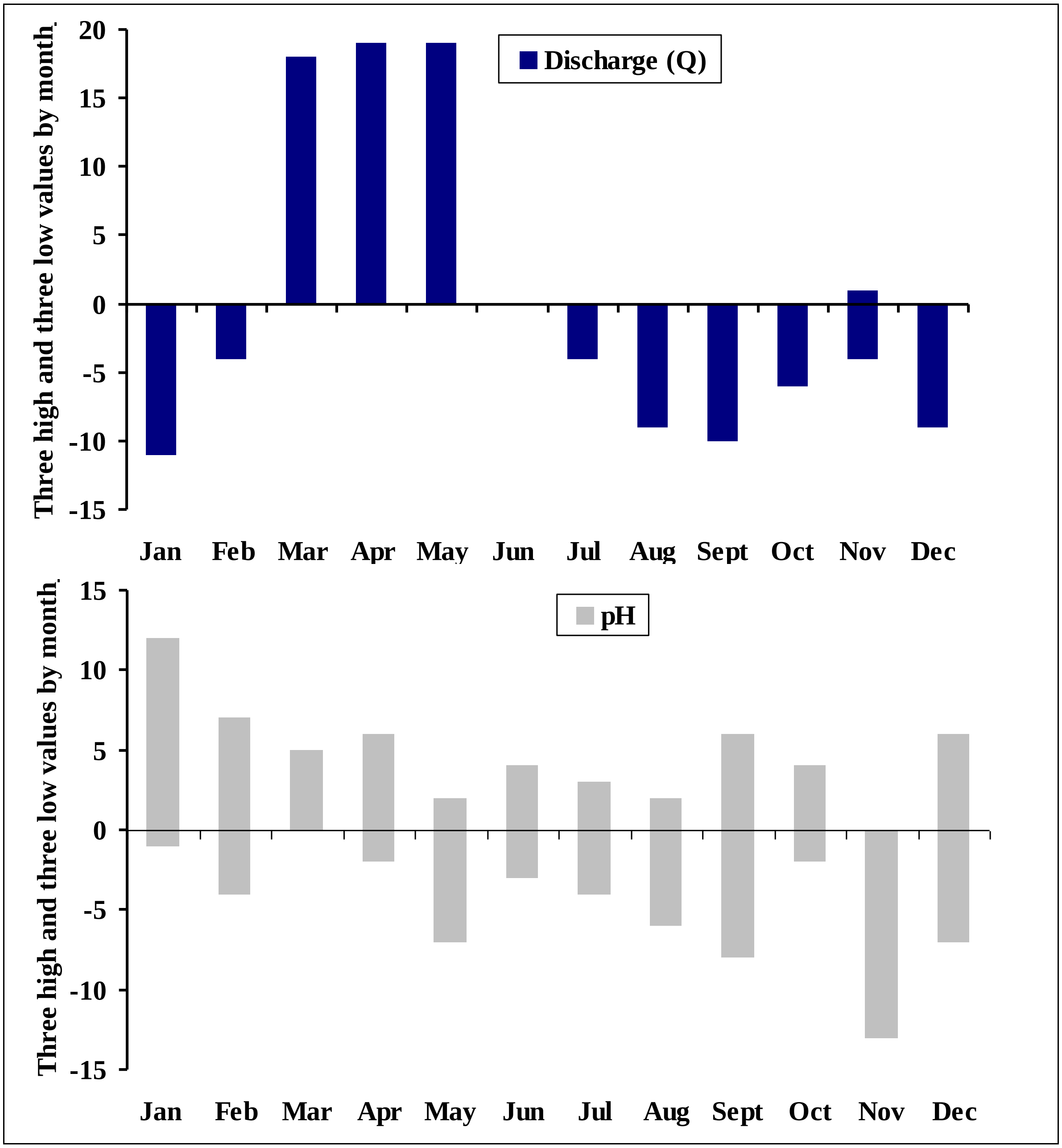


Figure 4.16: Seasonal high and low stream discharge and pH. Addition of the three highest sample concentrations for each site are shown by month above the 0 line. Addition of the three lowest sample concentrations by site are shown by month below the 0 line for comparison.

The pH seasonal pattern may also reflect the dilution of the WTP discharge during the high rainfall season and an increase in WTP effluent volume with lower stream flow later part in the year. The increased WTP volume in the stream contains more organic matter and acidic material that could lower the pH levels. Low pH in November and December may affect SC through increased potential for dissolved solids (Figure 4.14). Seasonal water quality trends were also examined by watershed drainage basin size to determine if there were any marked differences between seasonal high and low water quality indicators among different sized sample watersheds. Water quality parameters showed similar patterns throughout watersheds indicating that different watershed sizes did not greatly affect the basic water quality seasonal patterns.

Two notable water sampling sites that showed a sharp change in water quality throughout the sampling year were Pearson Ck (11) and Long Ck (12). Nutrient levels, especially TP, and turbidity increased dramatically in Long Creek (12) in the latter half of the sampling year from September 2005 to February 2006 (Figure 4.17). This may be attributed to major land disturbance for the construction of Highway 65 on the eastern edge of the watershed or to excessive fall manure applications entering the water. The sampling period also had several precipitation events that saw a rise in discharge levels of Long Creek (Figure 4.21) after a long dry period. Runoff carrying the built-up nutrients on the soil from lack of lush vegetation or from cattle using the stream as a drinking source during this dry period may have affected baseflow sampling at this site. Pearson Ck (11) was affected by bridge construction in September, 2005 which may have also increased the TP loading for this month (Figure 4.18). Turbidity also increased in the later part of the sampling year, possibly due to the disturbed soil from construction.

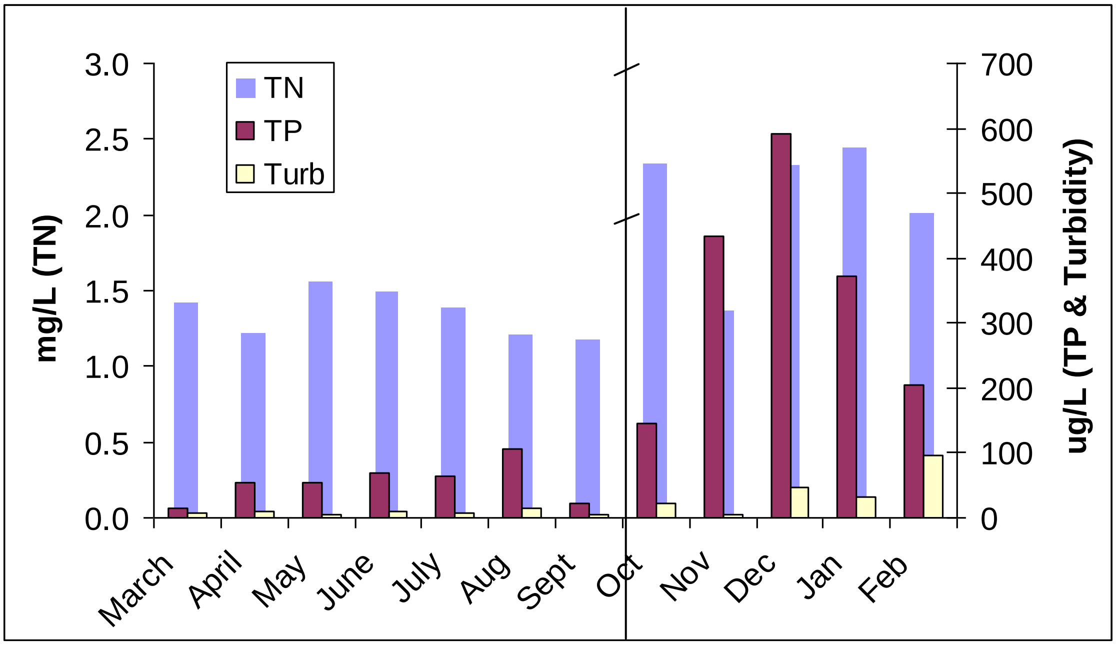


Figure 4.17: Long Ck (12) data profile. Sample TN, TP and turbidity by month showing higher concentrations after September, 2005

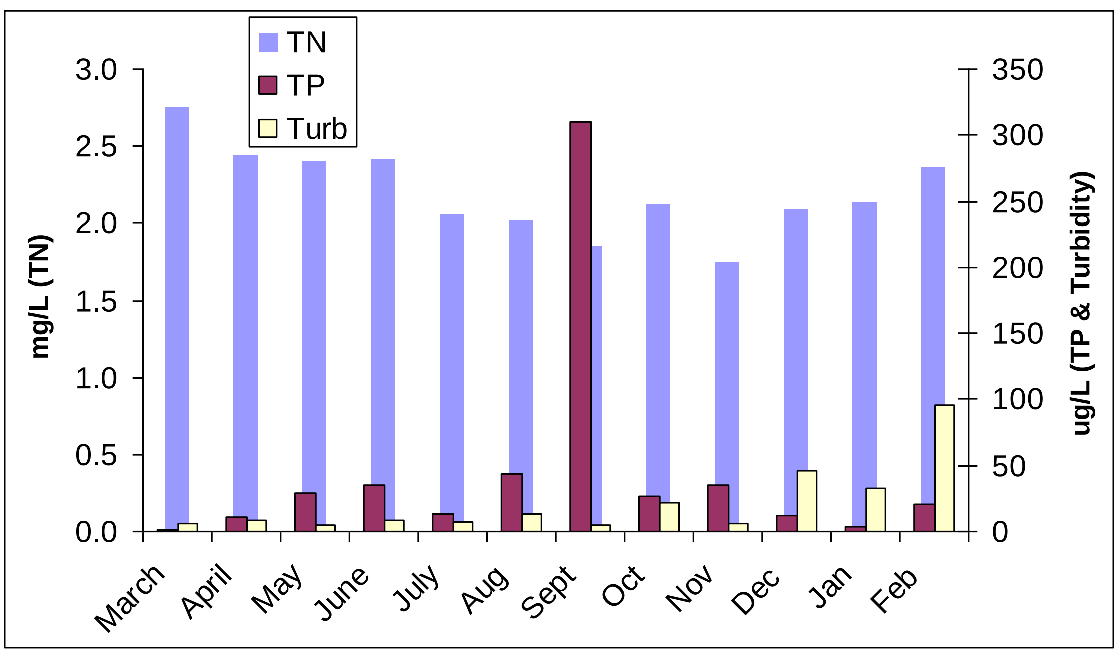


Figure 4.18: Pearson Ck (11) data profile. Sample TN, TP and turbidity by month showing a gradual decrease in TN during summer and a high TP spike in September with a gradual increase in turbidity late in the sampling year

Hydrological Influence

The sampling design for this study collected samples at only baseflow conditions for all sites and all sample dates in order to facilitate accurate comparisons among watersheds. Since hydrological conditions are known to influence water chemistry and nutrient concentrations within the watershed, this variable was examined to assess sampling consistency. Due to the large size of the URWB (15,636 km^2) and variations in climate and rainfall throughout the seasons, consistency of sampling was sometimes difficult to achieve.

The correlation of stream discharge (Q) versus drainage basin size shows that there is a (Figures 4.19 through 4.21). There are a few outliers in the graphs of mean sample Q versus A_d and max sample Q versus A_d which are caused by a few sample sites that have comparatively high maximum discharges for their drainage basin sizes or vise versa. But general trends shows a positive relationship between increased watershed size and increases in stream sample Q. Mean USGS record Q is on a scale from approximately 0 to 15 m^3/sec for long term discharge (Figure 4.19). Mean sample Q is lower than mean annual USGS gage records with a scale of only 0 to 6 m^3/sec throughout the 19 UWRB sample sites (Figure 4.20). This shows that average, long term USGS Q which includes both high and low flow measurements is overall higher than average sample Q taken at baseflow conditions. Maximum sample Q, however, ranges from 0.8 to 20 m^3/sec (Figure 4.21). High maximum sample Q may capture samples from the seasonal rise in baseflow. This is especially possible during the early spring months (March-June) when rain fall is more frequent. As shown earlier in Figure 4.16, this period contained the highest measured discharge for each sample site.

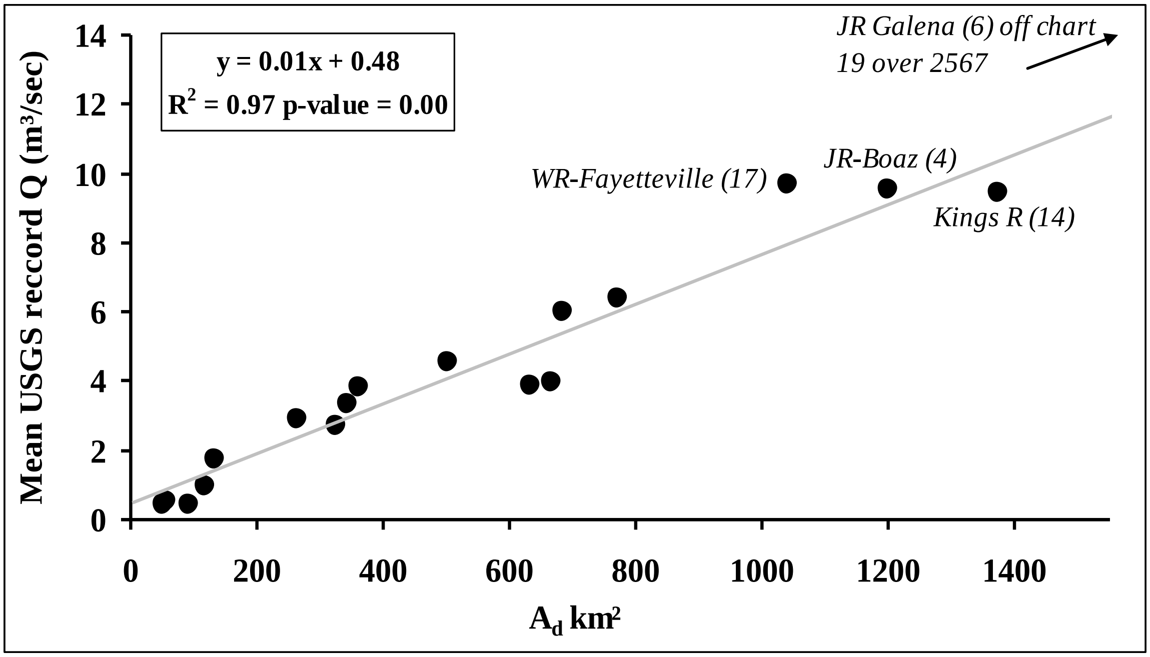


Figure 4.19: Mean USGS gage record discharge versus A_d. Table Rock Lake Dam (7) site excluded as a lake site.

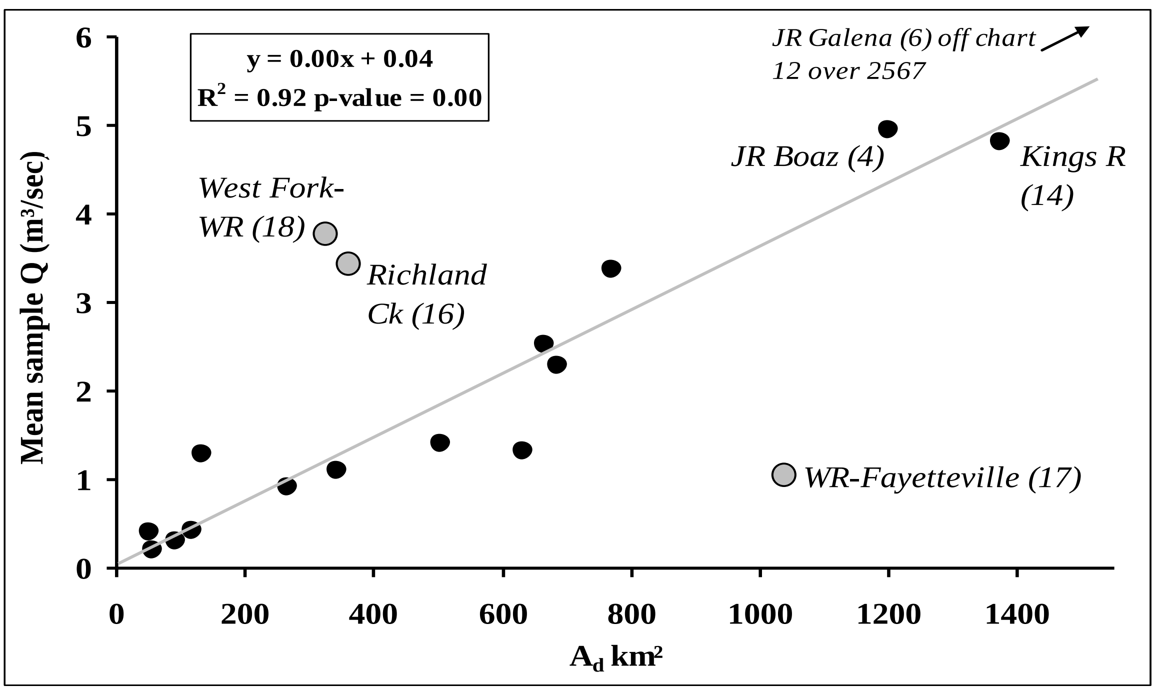


Figure 4.20: Mean sample discharge versus A_d. The general trend is shown while the outlying watersheds are labeled and indicated by lighter points. Table Rock Dam (7) was excluded as a lake site.

One condition of the few higher Q samples collected in this study is that they may contain lower concentrations of nutrients due to dilution from the higher overall stream flow, especially in watersheds that are highly affected by WTP effluent. Forested watersheds may contain higher nutrient concentrations with high-flow samples as run-off from the land carries more nutrients into the stream, compared to the spring-fed water sources during actual baseflow conditions (Miller et. al. 1997). Baseflow changes throughout the year can be seen in the hydrographs of various watersheds (Figures 4.22 through 4.27). Hydrological profiles of the WC-at Springfield (1), Long Ck (12) and West Fork-WR (18) show a high amount of variation in baseflow levels. High sample Q in March may therefore result from higher stream levels even during baseflow for this time of year.

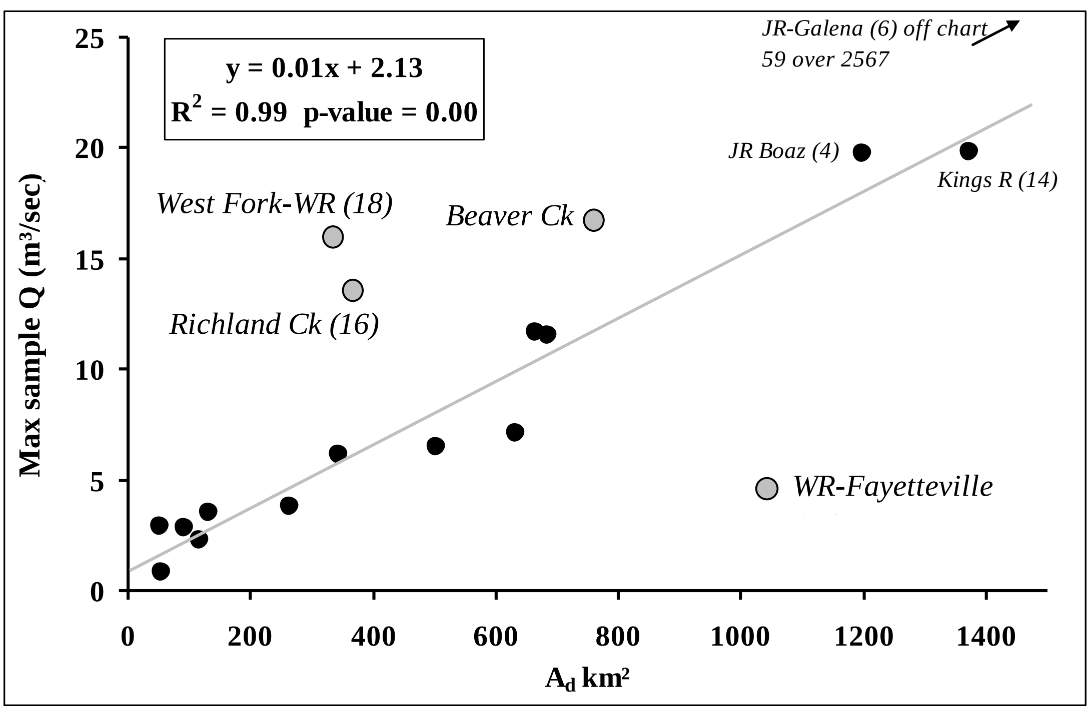


Figure 4.21: Maximum sampled discharge over A_d. The general trend is shown while the outlying watersheds are labeled and indicated by lighter points. Table Rock Dam (7) was excluded as a lake site.

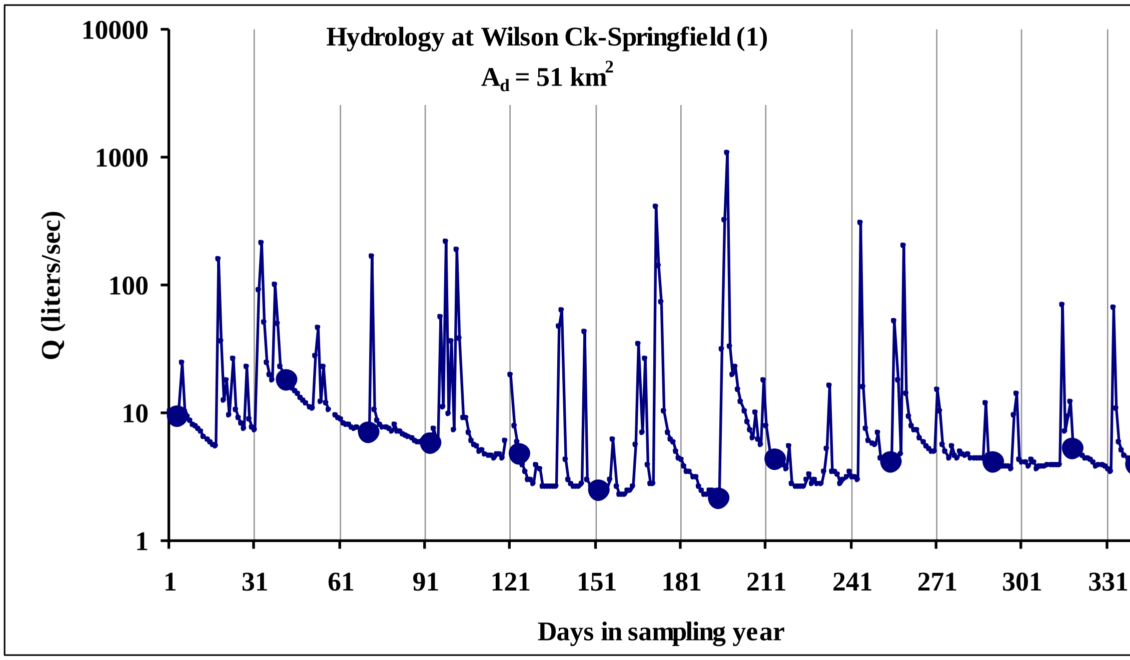


Figure 4.22: Log scale hydrological profile of WC-Springfield (1).Small dots indicate days along the profile while large dots indicate day of sample collection.

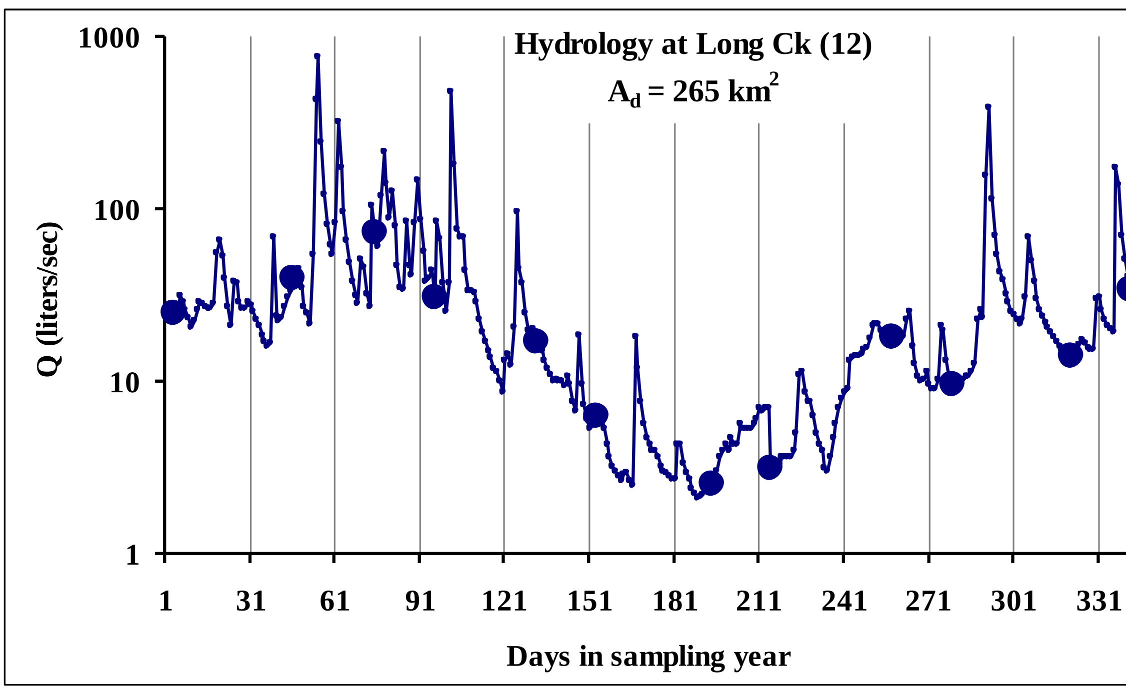


Figure 4.23: Hydrological profile of the sampling year at Long Ck (12). Small dots indicate days along the profile while large dots indicate day of sample collection.

Larger streams (> 500 km²) show slightly less short term variation in the hydrological profile than smaller streams. However, similar to smaller watersheds, high baseflow in the spring is still evident in the large streams (Figures 4.25 to 4.27). To further examine stream Q conditions, antecedent rainfall events are shown for various regions of the UWRB (Figure 4.28). This data is presented as the average number of days in a given region since rainfall occurred before each sample date. The April sample had the shortest antecedent period before a sample was taken for most watershed regions. Seasonal high nutrient concentrations, shown in the previous section in Figure 4.13, also roughly reflect the difference in antecedent days before sampling. Total N in Figure 4.13 had several high sample values during the early part of the year which generally has less antecedent days between rainfall and sampling.

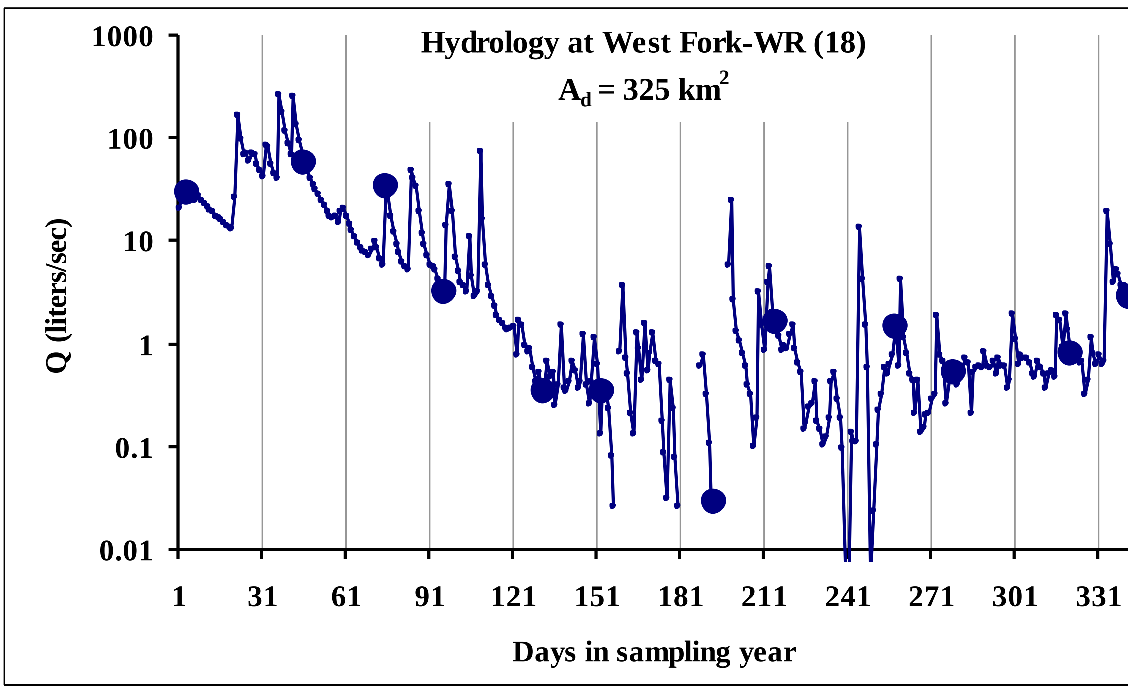


Figure 4.24: Hydrological profile of the sampling year at West Fork-WR (18). Small dots indicate days along the profile while large dots indicate day of sample collection. Breaks in the profile are where no data from the USGS gage was available.

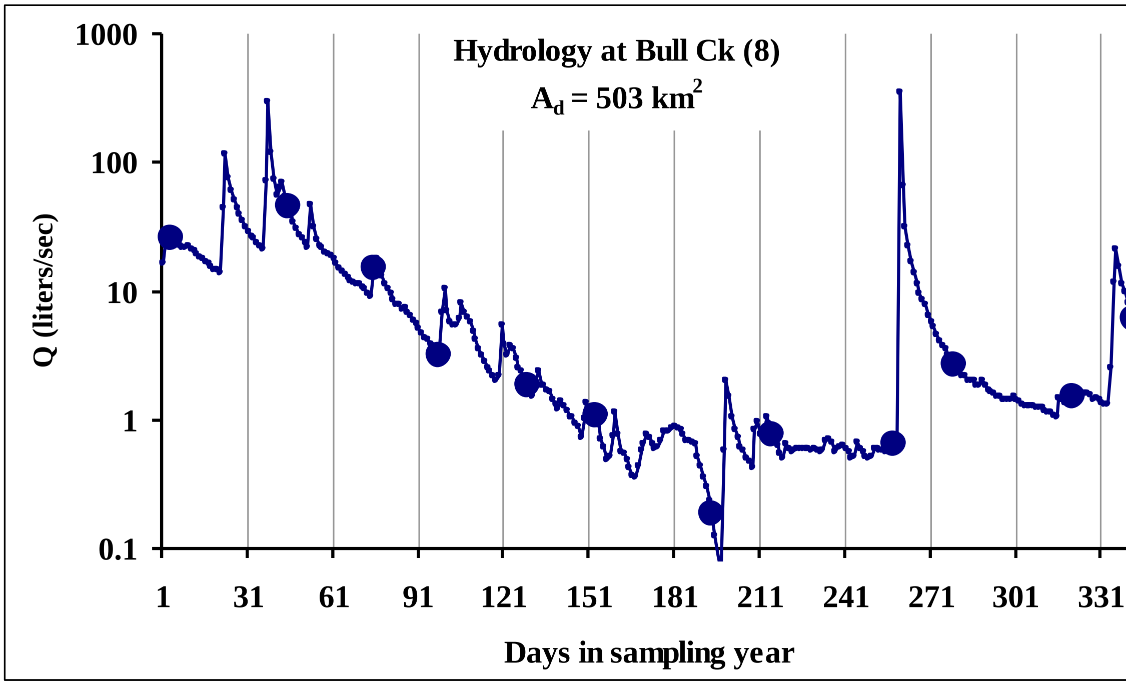


Figure 4.25: Hydrological profile of the sampling year at Bull Ck (8). Small dots indicate days along the profile while large dots indicate day of sample collection.

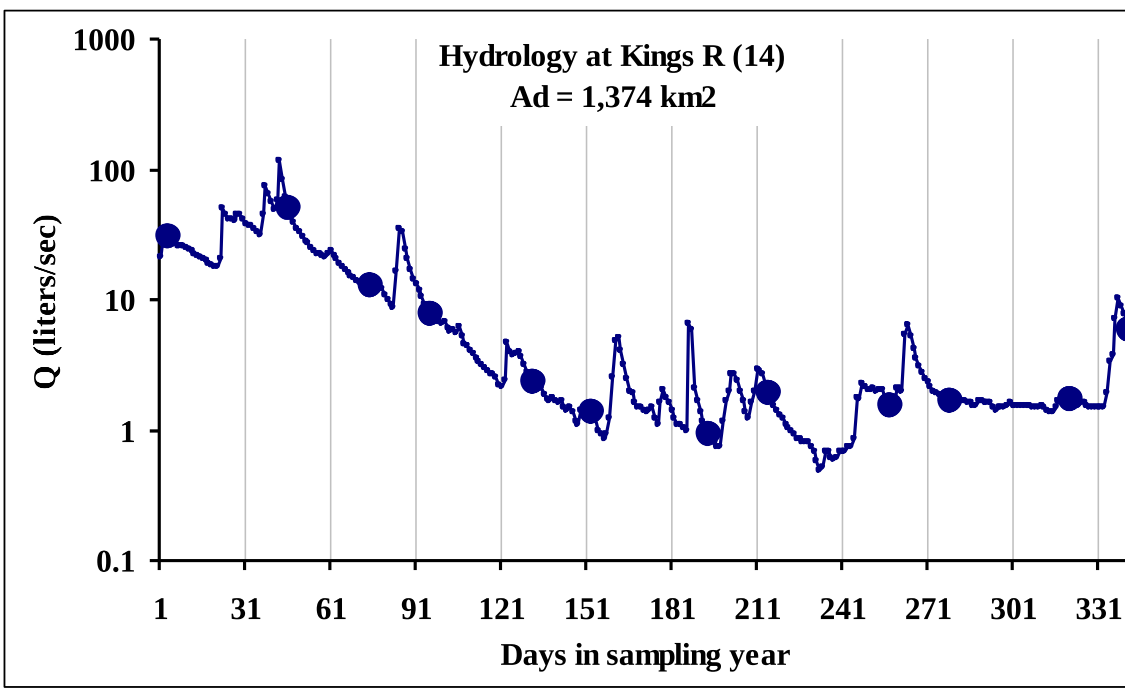


Figure 4.26: Hydrological profile of the sampling year at Kings R (14). Small dots indicate days along the profile while large dots indicate day of sample collection.

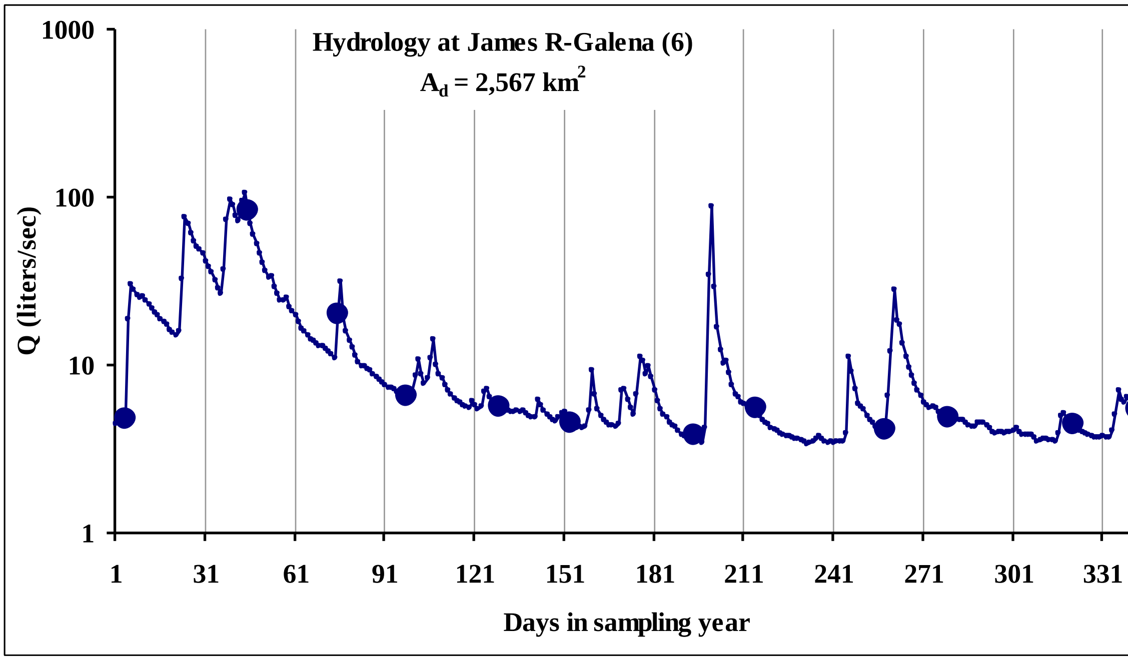


Figure 4.27: Hydrological profile of the sampling year at JR-Galena (6). Small dots indicate days along the profile while large dots indicate day of sample collection.

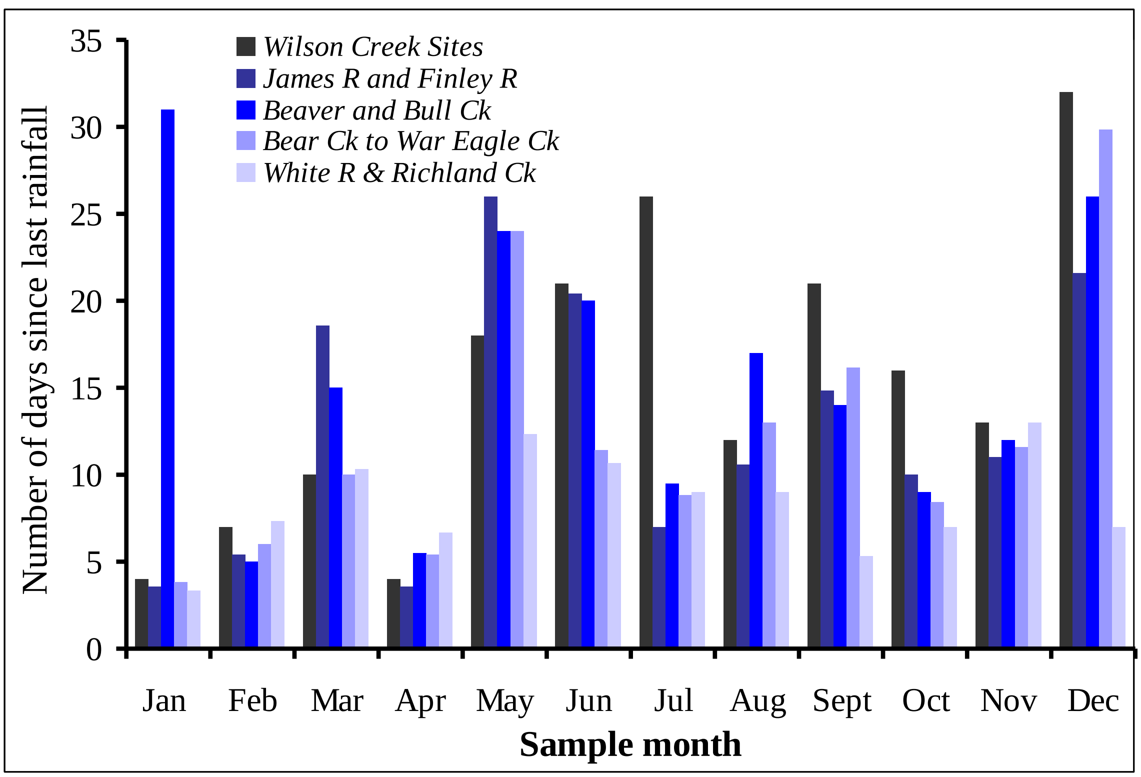


Figure 4.28: Antecedent rainfall events before sampling. Average number of days by region is shown for each sample date (1st sample March, 2005, 12th sample Feb, 2006).

Correlation Among Water Quality Indicators

Median values for water quality indicators were used in the analysis for this study instead of mean values to help reduce the effects of a few extreme high or low samples. However, to show that there is minimal difference between the mean and median sample values, the mean and median are correlated and compared to the line of equal value. The following plots, Figures 4.29 through 4.32 show the mean-to-median correlation for TP, TN, SC and turbidity. Since there is little variation among pH, water temperature and DO, these plots are not shown. Diagonal lines across the plot from the 0 point to the upper right corner indicate where the data points would fall if the mean and median values are exactly equal. The turbidity plot shows that mean values are almost all greater than median values which could be caused by the high turbidity at many sites in the fall and winter (Figure 4.32). But this should not affect correlation greatly since almost all data points, except WC-at SWTP (3) have a deviate similarly from the one-to-one line.

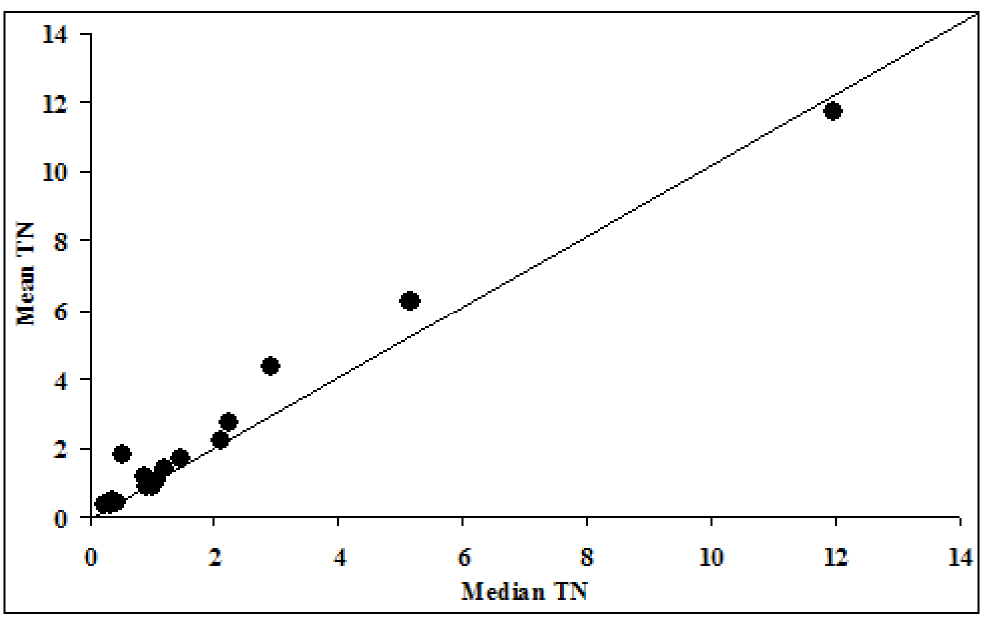


Figure 4.29: Correlation between mean and median TN values. The one-to-one line indicates where data points would fall if both mean and median were exactly the same.

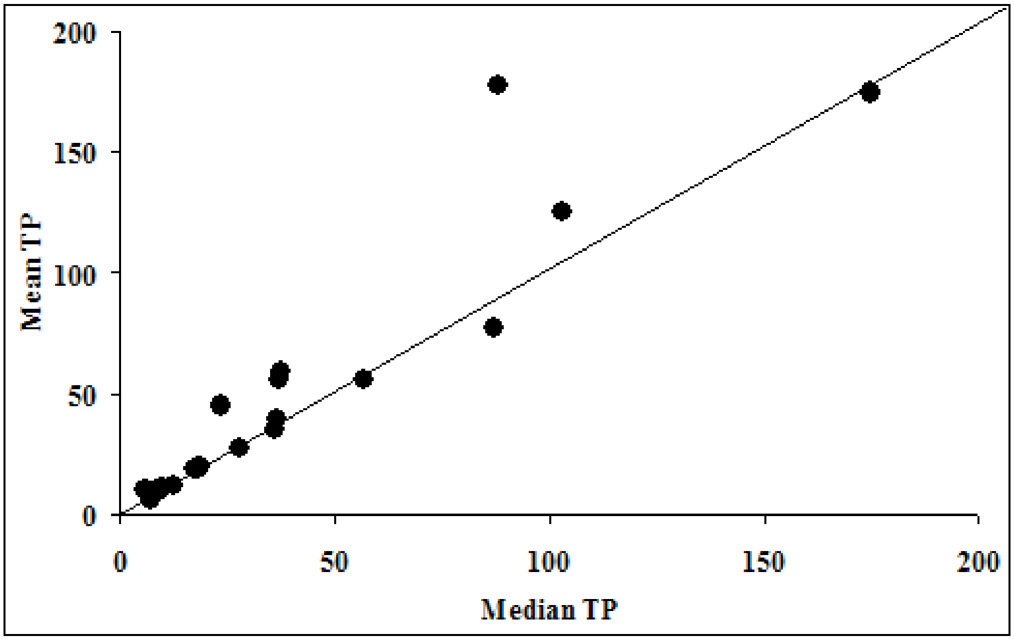


Figure 4.30: Correlation between mean and median TP values. The one-to-one line indicates where data points would fall if both mean and median were exactly the same.

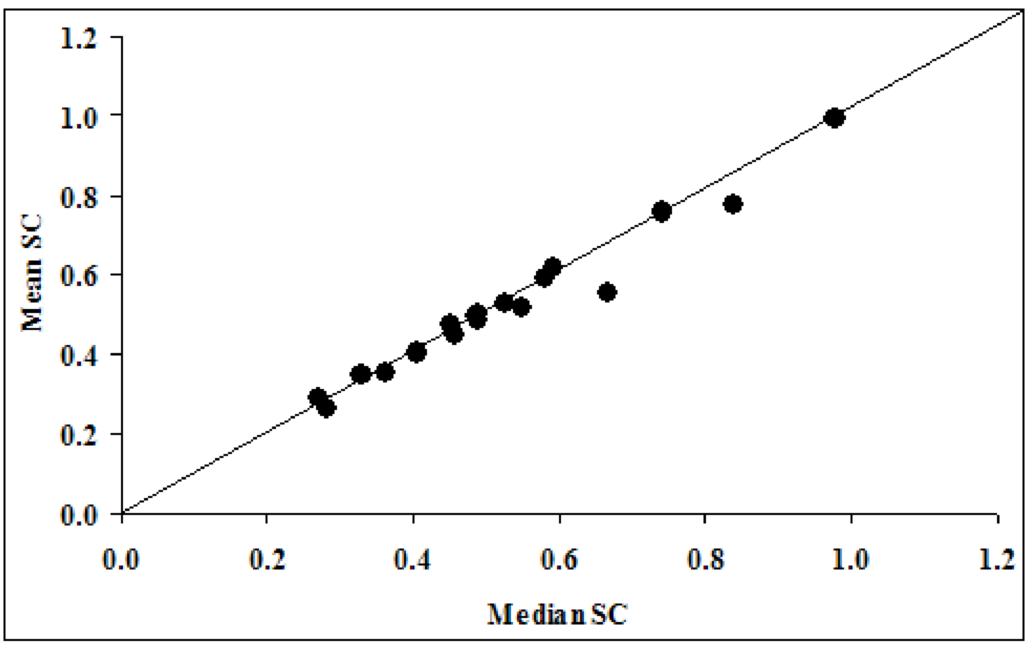


Figure 4.31: Correlation between mean and median SC values. The one-to-one line indicates where data points would fall if both mean and median were exactly the same.

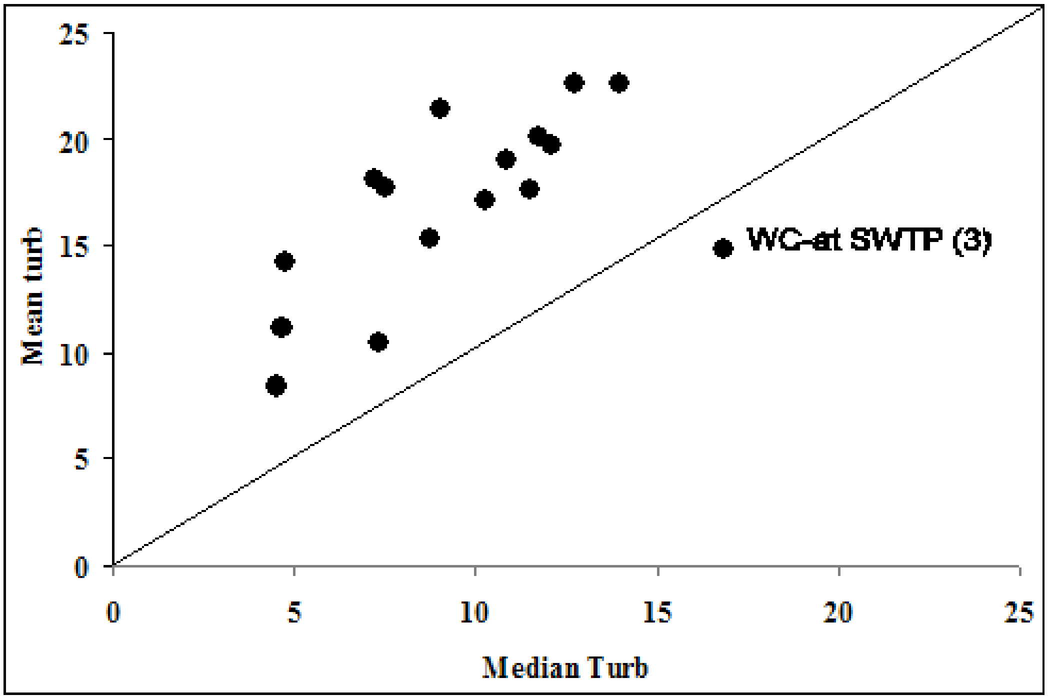


Figure 4.32: Correlation between mean and median turbidity values. The one-to-one line indicates where data points would fall if both mean and median were equal. Mean is greater for most sites as this also averages the very high values for many sites in the fall and winter seasons.

Pearson correlation matrices show the correlation among water quality variables and watershed factors including percentage of land use, SWD, carbonate bedrock, drainage basin size, and elevation at the sample site. Pearson correlation helps indicate whether there is a similarity in variations between two variables which can be investigated further to determine if it is a true cause and effect relationship or simply a similar pattern of change between unrelated data. Correlation matrices are shown for three groups of sample sites: (1) all of the sample sites (Table 4.10), (2) only sites that have WTP discharge (Table 4.11) and (3) sites with little point source influence (Table 4.12). Bold values in the matrix are those correlations that are statistically significant with a p-value of 0.05 or less, but this does not necessarily indicate a cause-and effect-relationship.

Table 4.10: Correlation matrix for all sites. Correlation between water quality and watershed variables shown as r values, an indicator of the strength and direction (positive or negative) of correlation. Bold = statistically significant (p-value is </= 0.05)

All Sites

Pearson Correlation Matrix	TN	TP	pH	SC	Turbidity	DO	Temp	SQ
TN (mg/L)	1							
TP (µ/L)	0.84	1						
pH	-0.46	-0.38	1					
SC(mS/cm)	**0.76**	**0.66**	-0.46	1				
TURB(NTU)	0.26	0.23	-0.37	-0.14	1			
DO(mg/L)	**0.83**	**0.66**	-0.13	0.44	0.27	1		
Temp	0.18	0.20	0.07	0.00	0.15	0.27	1	
SQ (liters/day/km^2)	0.33	0.22	-0.38	0.15	0.32	0.27	0.12	1
%Urban	0.45	0.39	**-0.66**	**0.71**	0.08	0.19	-0.12	0.34
% Agriculture	0.10	-0.06	0.28	0.13	-0.30	0.11	-0.28	-0.33
%Forest	-0.46	-0.24	0.43	**-0.65**	0.08	-0.20	**0.64**	-0.17
% carbonate	0.34	0.12	-0.11	**0.70**	-0.54	0.16	-0.37	-0.20
SWD gal/day/km^2	**0.93**	**0.78**	-0.42	**0.64**	0.32	**0.90**	0.25	0.42
Km² in watershed	-0.10	-0.15	0.16	-0.25	0.06	-0.12	**-0.60**	0.07
Elevation (m)	0.16	0.16	-0.46	0.17	0.46	0.12	0.18	0.17

Table 4.11: Correlation matrix for WTP influenced sites. Correlation between water quality and watershed variables shown as r values indicating the strength and direction (positive or negative) of correlation. Bold = statistically significant (p-value is </= 0.05)

WTP Sites

Pearson Correlation Matrix	**TN**	**TP**	**pH**	**SC**	**Turbidity**	**DO**	**Temp**	**SQ**
TN (mg/L)	1							
TP (µ/L)	0.90	1						
pH	-0.60	-0.38	1					
SC(mS/cm)	**0.88**	**0.81**	-0.32	1				
TURB(NTU)	0.20	0.15	-0.72	-0.18	1			
DO(mg/L)	**0.87**	**0.77**	-0.46	**0.71**	0.14	1		
Temp	0.26	0.38	-0.20	0.20	0.35	0.27	1	
SQ (liters/day/km^2)	0.43	0.32	**-0.67**	0.28	0.33	0.32	0.10	1
%Urban	**0.97**	**0.85**	**-0.69**	**0.81**	0.31	0.90	0.36	0.55
% Agriculture	-0.06	-0.14	0.42	0.33	**-0.82**	-0.11	-0.48	-0.33
%Forest	**-0.55**	-0.32	0.20	**-0.59**	0.32	-0.43	**0.60**	-0.26
% carbonate	0.43	0.31	0.13	**0.70**	**-0.66**	0.44	-0.38	-0.04
SWD gal/day/km^2	**0.96**	**0.84**	**-0.64**	**0.75**	0.30	**0.95**	0.30	0.50
Km² in watershed	-0.18	-0.27	0.15	-0.29	-0.10	-0.24	**-0.77**	0.07
Elevation (m)	0.20	0.20	-0.51	0.11	0.47	0.17	0.53	-0.01

Table 4.12: Correlation matrix for non-point influenced sites. Correlation between water quality and watershed variables, r values, an indicator of the strength and direction (positive or negative) of correlation. Bold = statistically significant (p-value is </= 0.05)

Non-point Sites *Pearson Correlation Matrix*	**TN**	**TP**	**pH**	**SC**	**Turbidity**	**DO**	**Temp**	**SQ**
TN (mg/L)	1							
TP (μ/L)	0.48	1						
pH	-0.37	-0.55	1					
SC(mS/cm)	0.31	0.19	-0.45	1				
TURB(NTU)	-0.12	-0.02	-0.22	-0.50	1			
DO(mg/L)	0.17	-0.20	**0.73**	-0.45	0.01	1		
Temp	-0.49	-0.51	0.31	**-0.73**	0.27	0.12	1	
SQ (liters/day/km^2)	-0.21	-0.07	-0.24	-0.16	0.26	-0.26	0.19	1
%Urban	0.10	0.22	**-0.59**	**0.75**	-0.05	**-0.65**	-0.62	0.19
% Agriculture	**0.65**	-0.03	0.25	0.09	-0.21	**0.66**	-0.22	-0.36
%Forest	**-0.59**	-0.21	0.45	**-0.85**	0.21	0.20	0.82	0.06
% carbonate	0.40	-0.09	-0.04	**0.83**	**-0.67**	-0.11	**-0.57**	-0.41
SWD gal/day/km^2	-0.35	-0.31	0.18	-0.10	0.14	0.13	0.24	0.20
Km² in watershed	**-0.57**	-0.41	0.48	-0.52	0.26	0.29	**0.57**	-0.34
Elevation (m)	0.22	0.17	-0.50	0.07	**0.59**	-0.09	-0.28	0.31

Nutrients appear to correlate with SC and DO for all sites and SWD sites (Tables 4.10 and 4.11). Specific conductivity and DO are also correlation with SWD which may indicate that the nutrient correlations to these water chemistry variables is being controlled by WTP effluent. Both SC and DO are highly modified by SWD effluent since it is contains high concentrations of suspended and dissolved solids, a controlling factor in SC, and is injected with DO as part of the treatment. The correlation of nutrients versus these two water quality indicators (SC and DO) does not appear in the matrix with only the non-point sites (Table 4.12) confirming the influence of WTP effluent on this apparent relationship. Nutrients correlation to SWD is further discussed in the section on WTP influence (page 127 and 128). Nutrients show a correlation with percent urban area in the SWD site matrix, a result that is again probably influenced by the WTP effluent being associated with urban areas. For non-point influenced correlations (Table 4.12) TN

is correlated with percent forest area which is a relationship often found in land use/nutrient studies (Jordan et al. 1997; Miller et al. 1997; Peterson 1998; Miller 2006). TN is also correlated with percent agricultural area. This is further discussed in the section on land use influence (pages 129 to 140). Sample pH is negatively correlated with percent urban area in all three matrices indicating a drop in pH from increased organic matter emanating from these areas or the SWD associated with them. For the non-point sites there is a positive relationship between pH and DO (Table 4.12). This correlation points to a common causative factor instead of a cause and effect relationship since DO is not directly dependent on acidity or alkalinity of the water which is measured by pH. The correlation line between these two parameters is shown in Figure 4.33. One explanation for this correlation is that increased dissolved organic matter from human or animal waste, leaf and vegetation break-down or other organic inputs can increase bacterial metabolism and respiration, decreasing DO. Organic matter also releases humic acids which can affect and lower the pH.

Specific conductivity is correlated with land use in all three matrices. It shows a positive correlation with urban land use in all matrices (Tables 4.10 through 4.12). Since SWD is associated with urban areas, the SC to percent urban correlation may again be related to WTP effects. In the correlation matrix with only the non-point sites (Table 4.12), SC has a negative correlation with percent forest where the SC value decreases with increased forest area (Figure 4.34). This may be a result of spatial autocorrelation rather than cause-and-effect. In the section on bedrock influence (pages 123 to 126), it is shown that forest is also negatively related to percentage of carbonate bedrock. All matrices show a positive relationship between SC and percent carbonate bedrock.

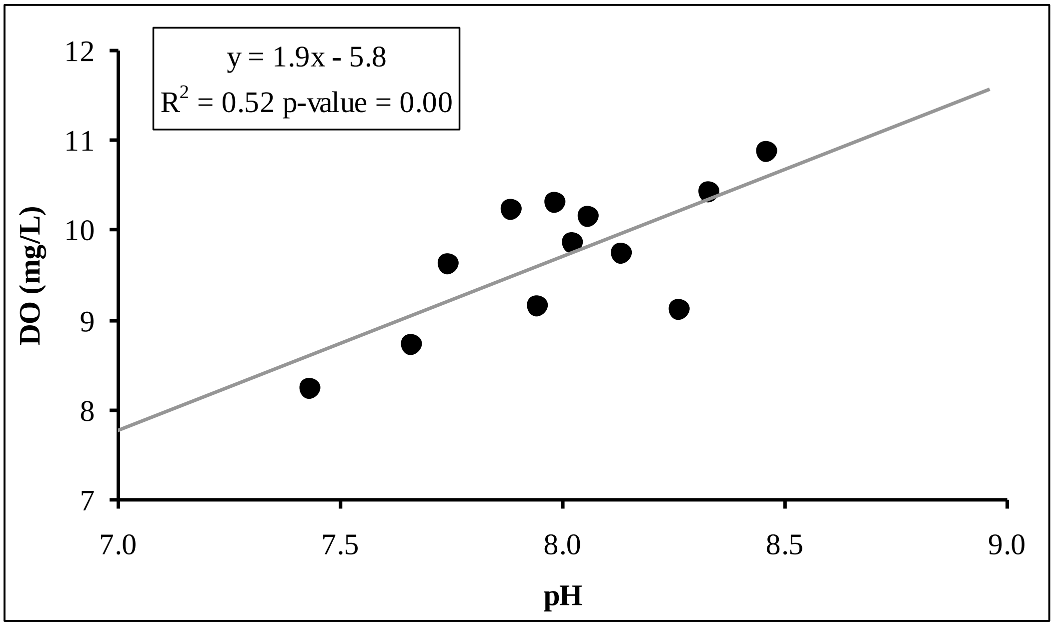


Figure 4.33: Relationship between DO and pH (non-point influenced sites only)

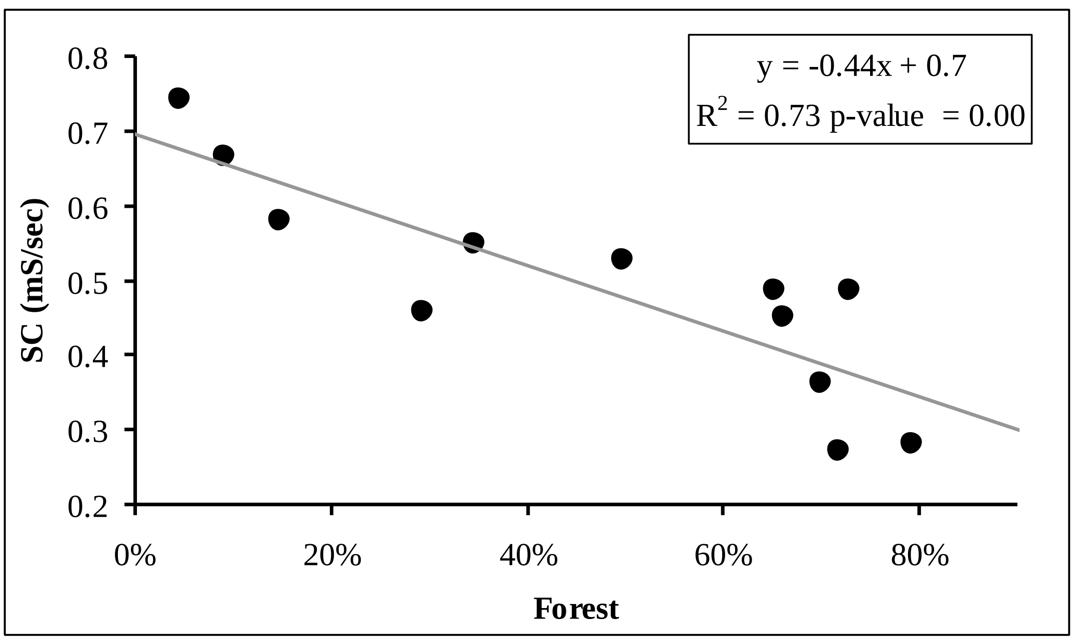


Figure 4.34: Relationship between SC and percent forest land use (non-point influenced sites only)

The relationship between SC and forest may therefore be a result of the carbonate bedrock's negative spatial relationship to percent forest area. This is probable since the least percentage of carbonate bedrock in the UWRB, the White River headwaters, are also the most forested watersheds. Turbidity also has a negative correlation with percent carbonate bedrock in the non-point watershed matrix. This is further discussed in the section on bedrock influence (pages 123 to 126).

Stream temperature has a positive relationship to forest area. As shown in the Land Use Influence section in Figure 4.42, this relationship is probably caused by cooler water in the spring-fed streams that flow through the less forested, limestone plains areas in the northern portion of the UWRB watershed rather than an actual forest effect on temperature. Average maximum and minimum temperatures in Springfield, MO are 89° F and 21.8° F respectively while the average for Fayetteville, AR are 89° F and 24.2° F. The slightly more moderate temperature in the southern portion of the UWRB may cause an apparent correlation between water temperature and the higher percent forest in these watersheds. Finally, no statistically significant trends were found for specific discharge (SQ) to nutrients or watershed variables in non-point source influenced watersheds. Correlations between nutrient and other water quality indicators are difficult to predict in baseflow samples due to the variety of factors that influence each other water chemistry variable. Baseflow samples are not amplified by higher flows so much of the regression analysis plots or Pearson Correlation matrices showed that the majority of the relationship was being defined by WTP influenced sites such as WC-at SWTP (3) and JR-Boaz (4). These high-WTP discharge sites were therefore removed from the analysis when looking at land use affects on water quality (pages 129 to 140).

Bedrock Influence

Correlations between percent carbonate bedrock in the sample watershed and water quality indicators are examined to determine the influence of bedrock types on water quality. Geology or bedrock type is known to play a role in water chemistry and nutrient loading (Spahr and Wynn 1997; Vesper and White 2003; Lunetta et. al. 2005). The Ozarks region is known for karst, carbonate bedrock which offers little or no filtration of storm run-off and wastewater. Ground water, spring discharge and WTP effluent contribute to baseflow in these regions. Karst features such as sinkholes and caves are common in the carbonate bedrocks of the UWRB closer to the main channel of the White river and throughout the James River Basin (Table 4.1). Shale, the predominant bedrock type in the Boston Mountain uplifts in the headwaters of the White River, is resistant to surface-to-ground-water interaction (MODOC 2001).

Correlation between percent carbonate bedrock and median nutrient values was not significant since bedrock does not independently affect nutrient loading, but its impact is influenced by land use and other point and non-point sources. The generalized nature of the bedrock data probably also affects its performance as a predictor of water quality. There is, however, a significant relationship between SC and bedrock type which is an expected correlation since the SC is determined by the concentration of dissolved salts or solids in the water (Figure 4.35). Dissolution of carbonate rock adds dissolved solids and ions to the water, increasing its potential conductivity. Also, more population lives on the carbonate limestone plains areas of the watershed such as Springfield, Branson, Ozark, Nixa and Berryville. More population in the carbonate areas adds salts and pollution to streams of which may increase the conductivity of the water in this area.

Given the relationship between SC and carbonate bedrock, a correlation between carbonate bedrock and turbidity was expected since turbidity may be caused by suspended solid particles in the water (Figure 4.36). The influence of WC-at SWTP (3) and Pearson Ck (11) were removed from both graphs due to these sites being influence by unique circumstances not shared by other sample watersheds. WC-at SWTP (3) is influenced by SWTP effluent and Pearson Ck (11) had construction site disturbance which both greatly affect SC and turbidity. The six sites with the lowest turbidity also have a high percentage of carbonate bedrock (Figure 4.36). Similarly, four of the sites with the highest turbidity also have a low percentage of carbonate bedrock, or high percentage of shale/sandstone bedrock. Simply by looking at these two groups of characteristics, it is clear that there is a relationship between bedrock type and turbidity.

Shale bedrock may be more erodeable than carbonate bedrock which has more tendency to become dissolved rather than erode into small suspended particles. The weaker shale bedrock is creates erodeable soils which, on the steeper slopes of the Boston Mountains, may erode and enter streams at a faster rate. The scatter or standard error (3.4) in the regression equation between carbonate bedrock versus turbidity may be accounted for by the fact that not all turbidity is a measure of the suspended solids from geological factors, but is also made up of algal cells, organic matter and chemical pollutants. Taking into account the general nature of geological data used in this study, the relationships between SC, turbidity and carbonate bedrock may be viewed as indicators of the importance of geological factors on these water quality indicators.

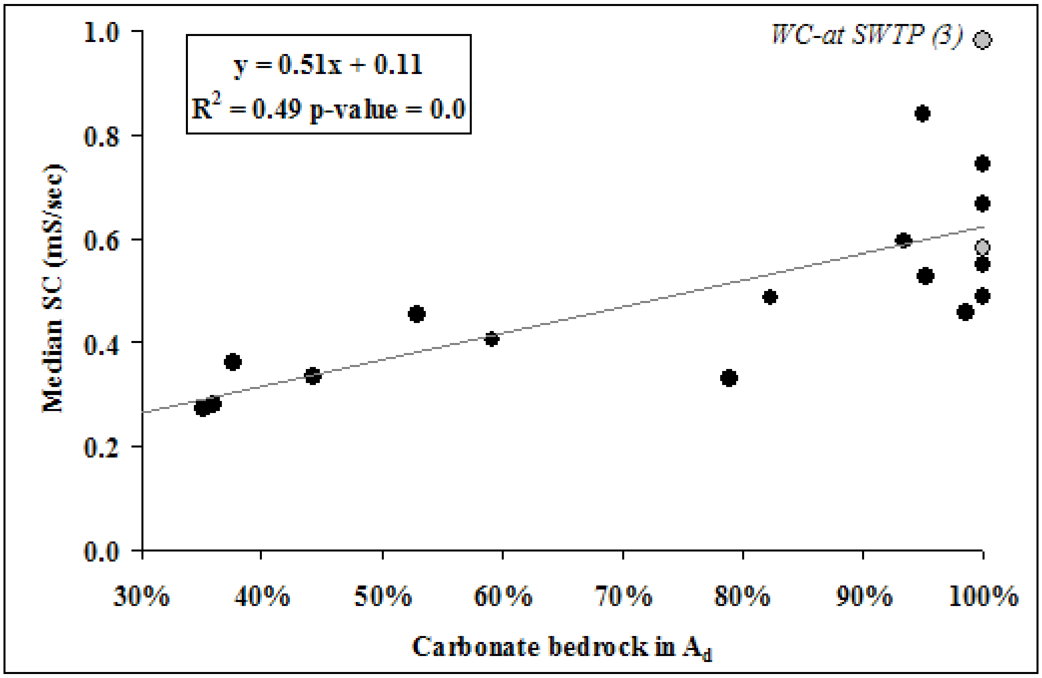


Figure 4.35: Specific conductivity versus percent carbonate bedrock. WC-at SWTP (3) and JR-Boaz (4), have high SC due to increased salts and dissolved solids from WTP effluent.

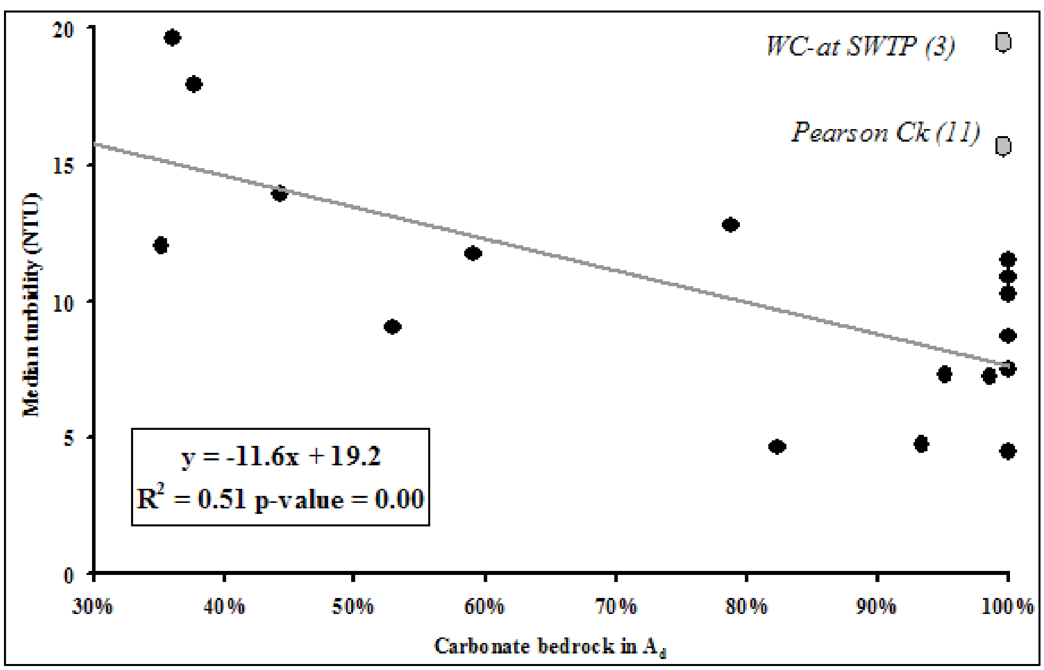


Figure 4.36: Turbidity versus percent carbonate bedrock. WC-at SWWTP (3) and Pearson Ck (11), lighter points, are excluded from the equation.

Wastewater Treatment Plant Influence

The WTP affects on nutrient loading and water quality indicators was examined by regression of SWD in gallons/day/km^2 versus these indicators. Correlation was studied for all sites that had any amount of SWD or those with a WTP in their drainage basin. Three water quality indicators, TP, TN and SC showed a positive relationship to SWD (Figure 4.37). As discussed earlier in the section on correlation among water quality indicators, other water chemistry variables including pH, DO and water temperature show correlation to SWD. Regression of these indicators versus SWD, however, confirmed that the majority of the correlation is from a single sample site (WC-below SWTP 3). However, nutrient and SC correlations show a consistent increase in concentration with increases in SWD (Figure 4.37).

The positive correlation between TP concentrations and SWD is indicated by the trend line for this variable which shows that with increases in SWD there is an increase in median TP concentrations in the streams affected by these point sources. Correlation between SWD and median TN is strongest for watersheds that have more than 10,000 gallons of effluent per km^2 per day, WC-at SWTP (3), JR-Boaz (4) and JR-Galena (6). Correlation statistics, R^2 and p-value, also indicate that the log-scale relationship is significant even with the few data points used in this correlation. Median SC versus SWD shows a positive but weaker trend line and a less significant R^2 value of 0.58. The horizontal trend lines for sites with low SWD correlated with TN and SC indicate that these water quality indicators are not strongly affected by smaller volumes of WTP effluent during baseflow conditions. Median TN, SC and TP concentrations are expected to increase with higher SWD (specific wastewater treatment plant discharge).

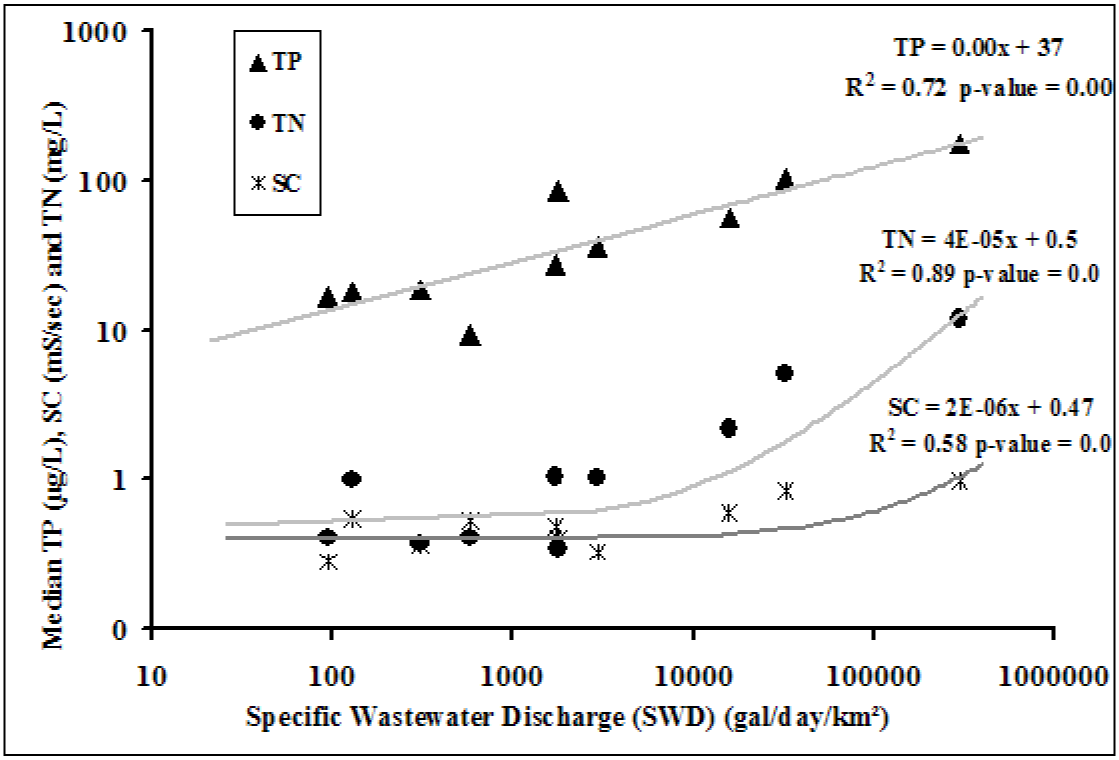


Figure 4.37: TP, TN and SC versus SWD. Correlation of median nutrient and SC values with SWD for all watersheds with wastewater point-source discharge. Relationship is log-linear for TP and log-log for TN and SC.

Land use Influence

Previous studies show that there is a link between land use and water quality in the watershed (Dupré and Robertson 2004; Jordan et. al 1997; Boyd 1996; Edwards et. al 1996). Rainfall on various land areas comes in contact with vegetation, soils, and human structures and acquires many contaminants including applied or available nutrients which are washed into the nearby streams. In examining relationships between land use and water quality, this study correlated percentages of agriculture, forest and urban land use to nutrients and the other water quality indicators for the watersheds without major WTP effluent inputs (< 600 gal/day/km^2). Sites that were ranked medium and high for SWD, shown on Table 4.7, were excluded from this analysis. WR-below Table Rock Dam (7) was also removed since this is not a stream site.

Correlation of TP versus land use indicates a negative relationship between this nutrient and percentage of forest area (Figure 4.38). Forest and vegetative areas help to hold the soil in place and prevent erosion, a major source of TP in streams. This relationship is therefore plausible. Long Ck (12) is again a far outlier in the data plot. This is may caused by the increase in non-point phosphorus loading in the Long Creek watershed from agricultural practices or the construction erosion on the U. S. highway 65 at the eastern rim of the basin (Figure 4.17). In addition, the Long Creek watershed contains the highest percentage of barren (quarry, construction site, gravel areas) at 2.5% which, while it does not encompass a large area, may have a significant impact on nutrient loading (Langer 2002). Correlation of TP to urban land use is mostly defined by a few highly urban sites including WC-Springfield (1) and WC-above SWTP (2). Again, Long Ck (12) was a far outlier while Yocum Ck (13) was a lesser outlier (Figure 4.39).

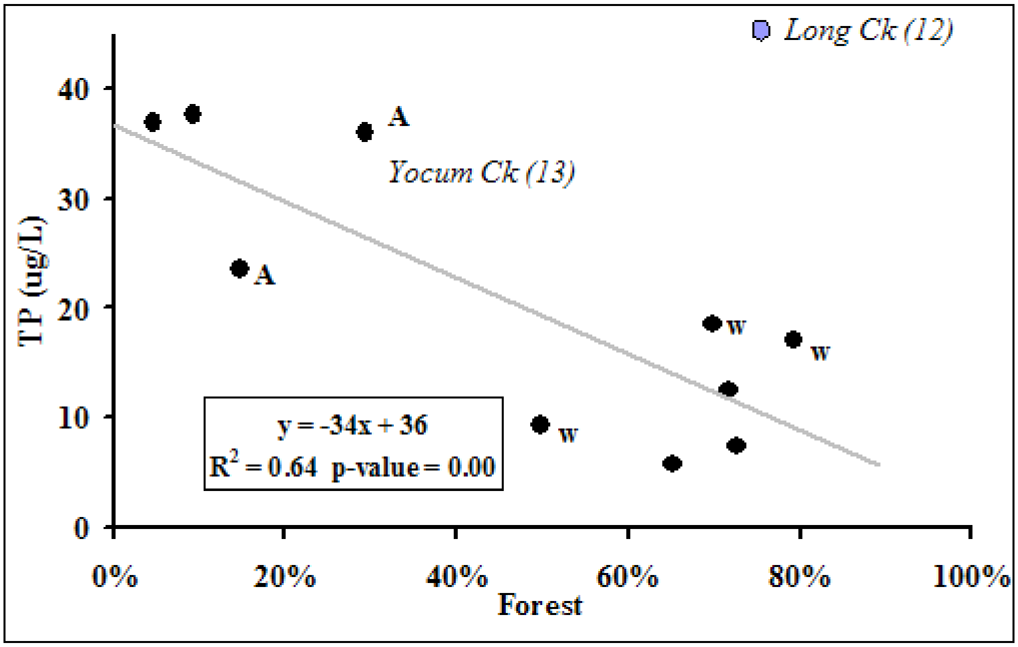


Figure 4.38: Correlation of TP and percent forest. Moderate to high SWD sites are excluded to look at land use influence. Long Ck (12) is the outlier and not included in the general trend. A = high agriculture in the watershed and W = low SWD influence.

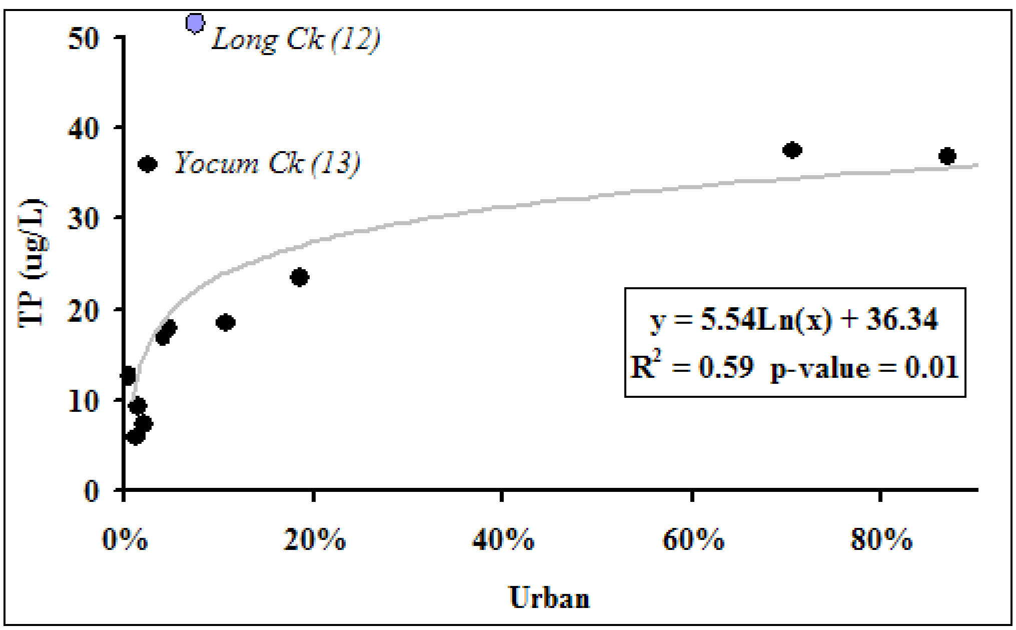


Figure 4.39: Correlation of TP and percent urban land use. Moderate to high SWD sites are excluded and Long Ck (12) is an outlier.

A correlation between percent forest versus carbonate bedrock and the relative TP concentrations for non-point watersheds are shown in Figure 4.40. This relationship can be broken into 3 distinct groups: (A) the high forest/low carbonate region, (B) the low forest/high carbonate region and group (C) the high forest/ high carbonate region. There are high TP values in group A and group C, but lower TP in group B, shown by the different sized spheres. Group A, high forest/low carbonate (high shale), may have higher TP inputs from organic matter or soil erosion due to weaker soil types. Group C, high carbonate/low forest, may also receive more TP inputs form soil erosion with less forest cover. The lowest TP values also occur in the sites with more than 50% forest area. Long Ck (12) is again the outlier having nearly equal percentages of both carbonate and shale bedrock and the highest median TP concentration.

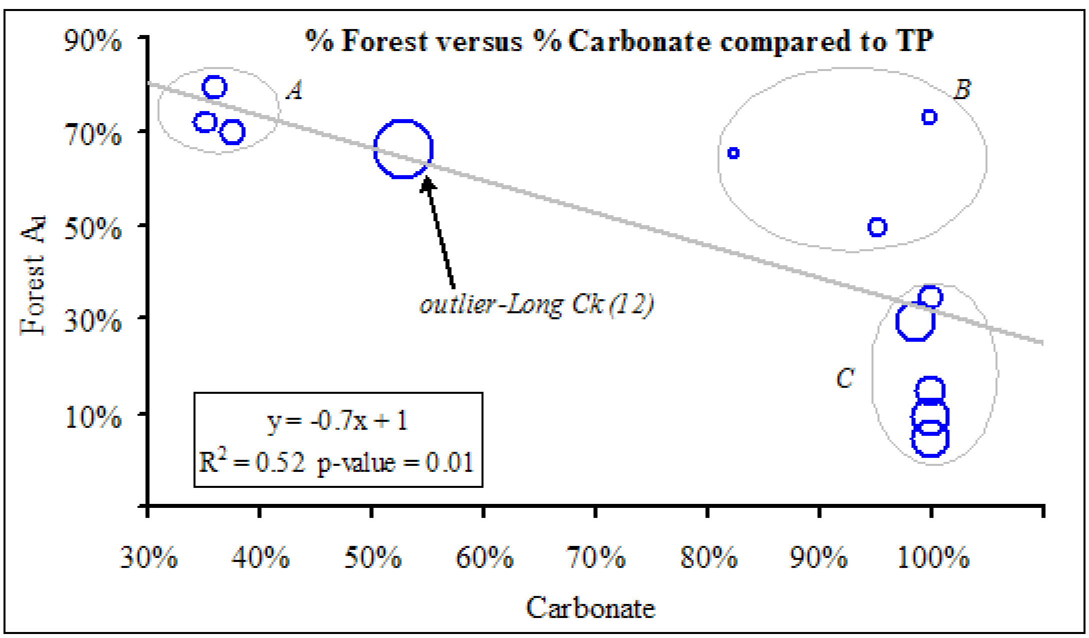


Figure 4.40: Multivariate correlation of forest, carbonate and TP. Circle sizes represent relative concentrations of median TP.

Median TN concentration showed a negative relationship to percent forest land use (Figure 4.41). However, in the initial analysis of this relationship, data from Yocum Ck (13) deviated most significantly from the general trend line. This was probably caused by the much higher TN concentrations found at this site compared to other non-point sites (Figure 4.18). In order to look at the majority of the TN-to-forest correlation trend, the influence of The Yocum Ck (13) site was removed form the TN equation. The location of Yocum Ck (13) data is shown in relation to the other data points in Figure 4.41 while not included in the equation.

A question when examining the correlation between land use and water quality is how to remove the influence of bedrock in order to accurately capture the land use influence. Since the water quality indicators such as turbidity and SC are related to carbonate bedrock (Figures 4.35 and 4.36) and bedrock varies in a similar pattern with forest land use (Figure 4.42), the relationships between land use and water quality may be capturing some of the bedrock influence through spatial autocorrelation which occurs when two unrelated variables have a similar spatial pattern causing them to show an apparent correlation. Since forest areas dominate the Boston Mountains portion of the watershed, shale bedrock is positively correlated with forest land use although shale bedrock does not cause the increased forests. The relationship between TN and forest land use may be influenced by this nutrient's correlation with carbonate bedrock. A look at the relationship between forest, carbonate bedrock and TN concentrations offers some further insight into this possibility. Figure 4.43 shows percent forest area versus carbonate bedrock with the corresponding relative TN concentrations indicated by sphere sizes for all non-point watersheds. There is not a significant difference between TN

concentrations in watersheds draining carbonate areas (group B) and those draining shale areas (group A). These groups of sites range from very low to high in overall percentage of carbonate bedrock. Both of these groups are also high in percentage of forest land use. This may be an indication that the carbonate bedrock has less influence on TN levels than suspected. Group C, with less than 50% forest area, has a definite TN increase in all sites in this region. High forest areas have an increase in uptake by vegetation as well as low nutrient input from this type of land use. A missing group of samples for more accurate comparison are those with low forest and low carbonate bedrock. However, it appears that changes in forest land use have more influence on TN than carbonate bedrock.

The positive correlation between TN and agricultural land use (Figure 4.44) is expected because TN has often been associated with agricultural land use in studies (Boyd 1996; Edwards et. al 1996; Clark et. al 2000). This association has also been shown to increase in karst areas such as the eroded limestone bedrock (Miller et. al. 1997). Among the non-point source watersheds, there was not a significant relationship or pattern found between urban land use and median TN levels. This may be due to the fact that nitrogen is a very mobile nutrient and may move long distances downstream or be quickly taken up by aquatic organisms in the few non-point sites that contain large urban areas. Nitrogen produced from the urban landscape is often quickly released from impervious areas at brief intervals during rain events. It is then flushed downstream and any remaining concentration is used up by local organisms, causing a drop in the TN concentration at baseflow conditions. Flushing of nutrients out of the upstream urban areas and subsequent increase in concentration downstream has been shown in data gathered by LMVP (2006).

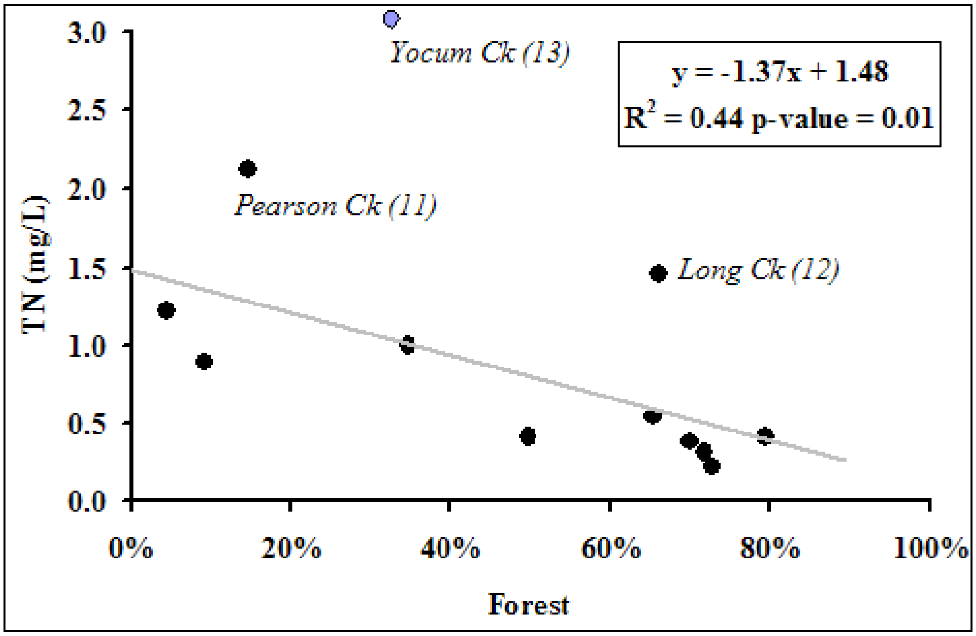


Figure 4.41: Correlation of TN and percent forest. Moderate to high SWD sites are excluded to look at non-point source relationships. Yocum Ck (13) is not included in the equation which shows a general negative trend between TN and percent forest.

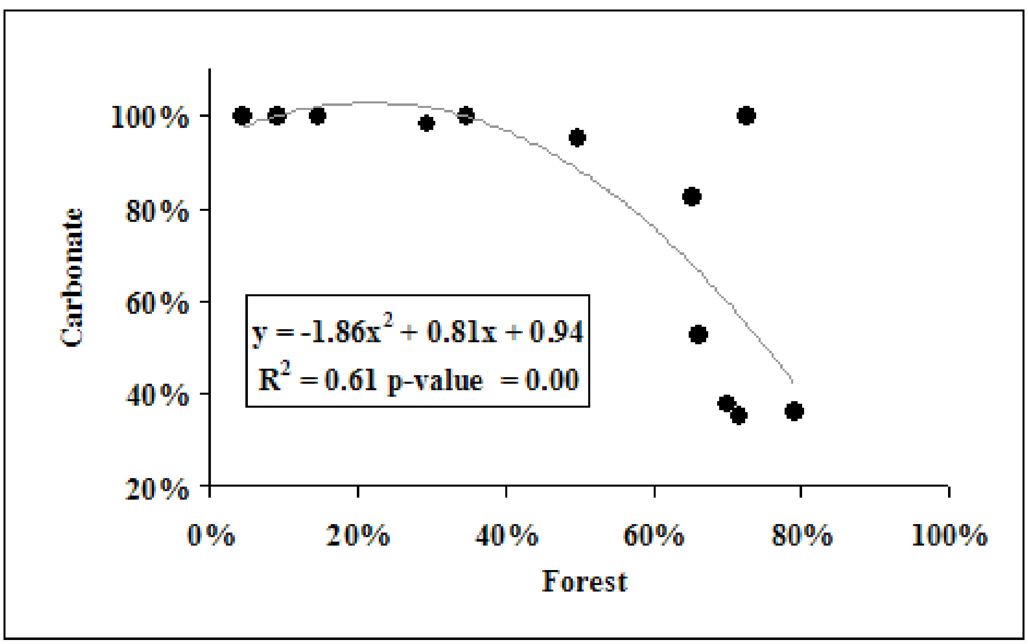


Figure 4.42: Correlation of percent carbonate bedrock and percent forest. Moderate to high SWD sites are excluded.

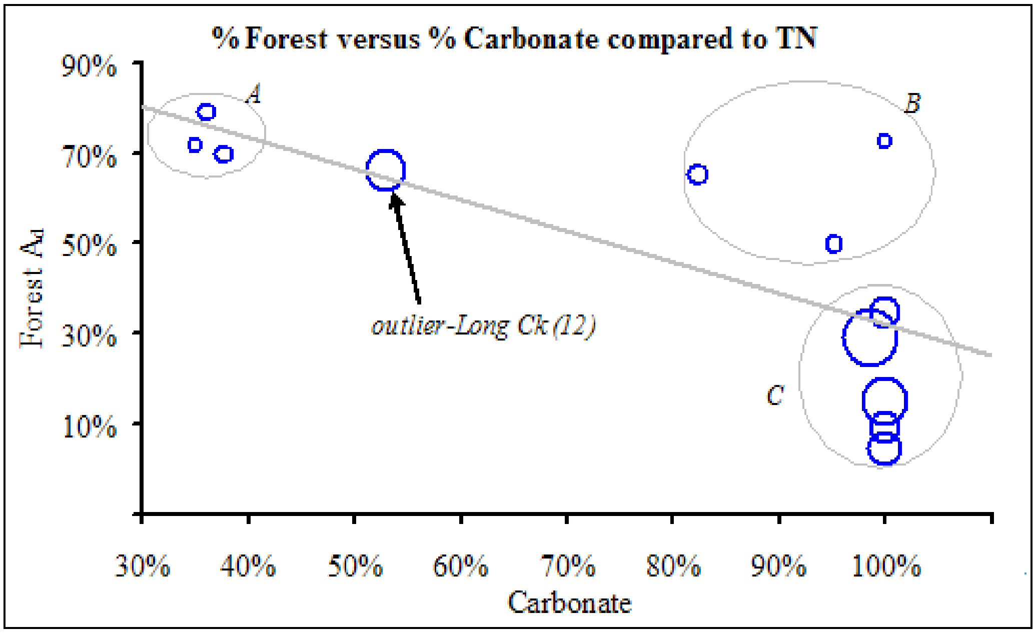


Figure 4.43: Multivariate correlation of forest, carbonate and TN. Circle sizes represent relative concentrations of median TN.

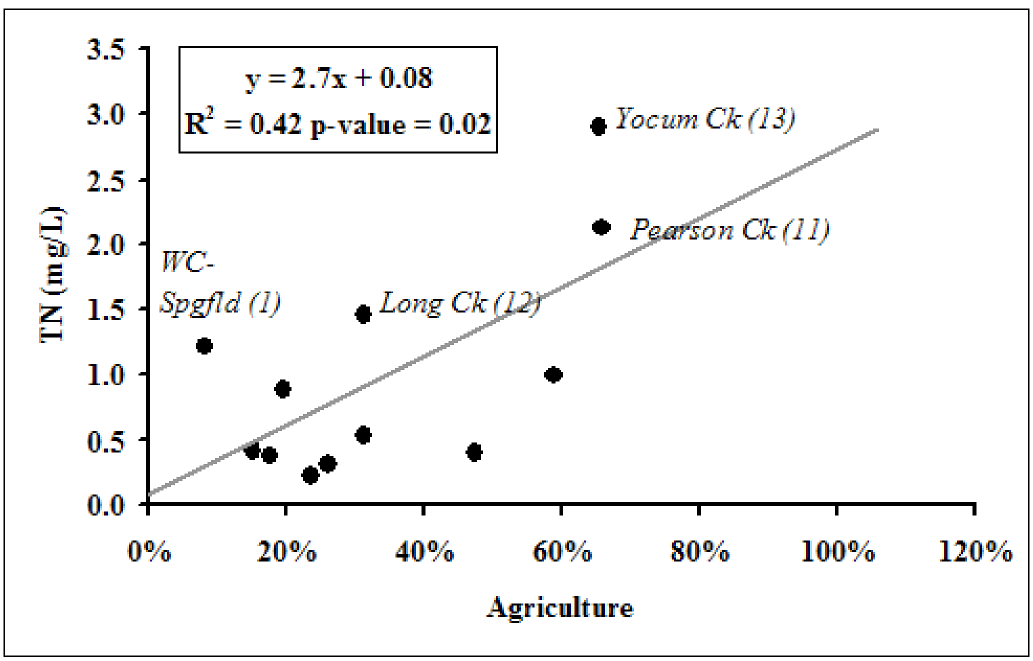


Figure 4.44: Correlation of TN and percent agriculture. Moderate to high SWD sites are excluded to look at non-point source relationships.

The correlation of stream temperature to forest land use yielded a positive relationship indicating that with increased forest area there was also an increase in temperature in the stream sample (Figure 4.45). Streams in forest areas are generally cooler in temperature than open grasslands, fields or urban areas. The positive relationship between forest area and stream temperature may be the fact that northern part of the UWRB contains more carbonate bedrock which allows circulation of cooler groundwater and surface water through sink holes and springs. The watersheds in the southern, forested portion of the UWRB are emanating from the Boston Mountain shale beds may have less groundwater interaction and more warm surface water inputs. Another cause for the positive relationship between stream temperature and forest area is that the southern, mostly forested portion of the UWRB watershed has an average warmer climate.

Specific conductivity is negatively related to percentage of forest land use (Figure 4.46). A logical explanation for this relationship is that with higher percentages of forest land use, there is less erosion of the soil, a major contributor to suspended solids and minerals in the water. With less suspended and dissolved solids, the water has less conductivity, since this property relies on the amount of dissolved and suspended mineral and salts in the water. However, as show earlier in Figure 4.35, SC is correlated to percent carbonate bedrock, so the relationship between SC and percent forest land use may be a result of heavily forested watersheds being located in the less carbonate portion of the UWRB.

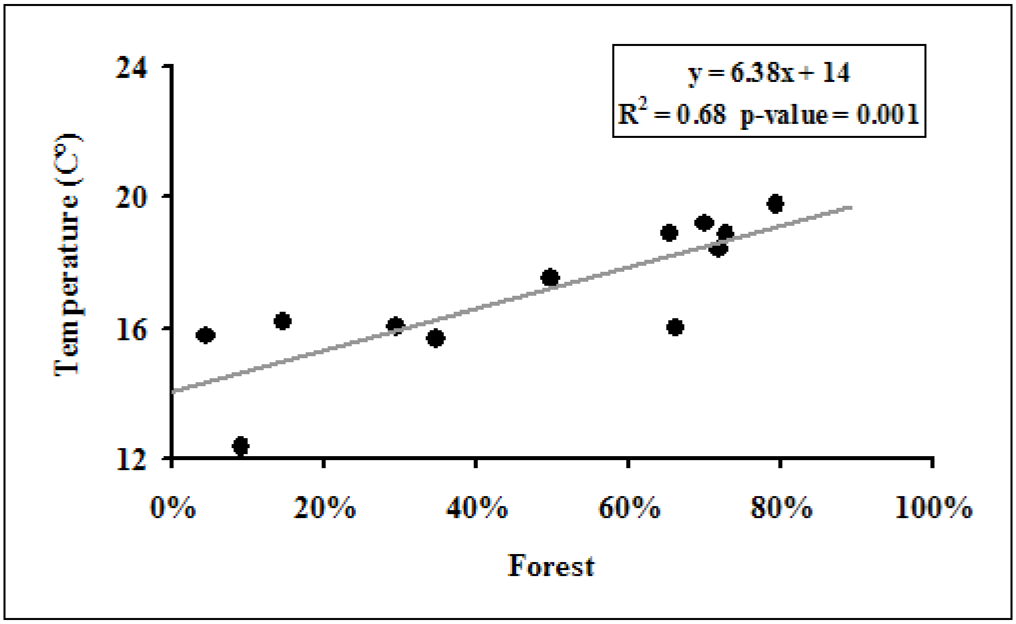


Figure 4.45: Correlation of stream temperature and percent forest. Sites on the lower left side of the graph are generally around Springfield, while sites at the upper right end of the trend line are around Fayetteville. Moderate to high SWD sites are excluded.

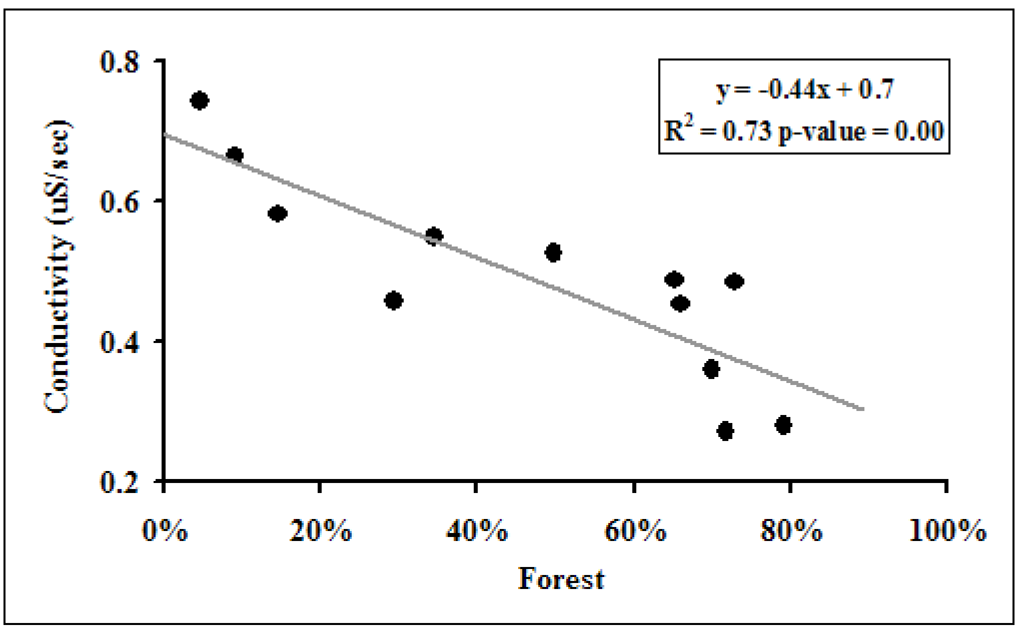


Figure 4.46: Correlation of SC and percent forest. Moderate to high SWD sites are excluded.

Figures 4.47 and 4.48 show the comparison between mean USGS stream gage SQ (specific discharge) and the sample SQ as it relates to percent forest and carbonate in the drainage area. The USGS SQ does not show much difference between the sites, probably the result of USGS values being an average of all stream discharge levels. The sample SQ, a measure of median baseflow discharge divided by A_d, shows a greater variation in stream discharge levels. The three sites with overall highest SQ are WC-Springfield (1), West Fork-WR (18) and Richland Ck (16). All of these sites has smaller drainage basins, less than 400 km^2, which may cause the SQ values to be higher even though all of these sites had very low discharge during baseflow conditions.

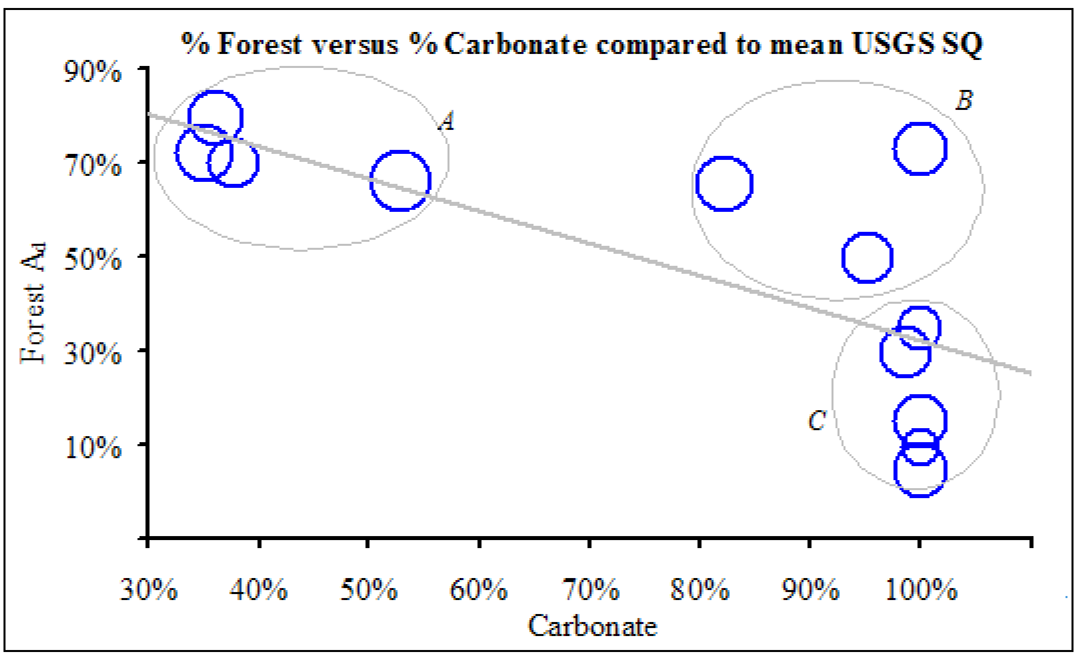


Figure 4.47: Multivariate correlation of forest, carbonate and mean USGS SQ. Circle sizes represent USGS mean specific discharge values.

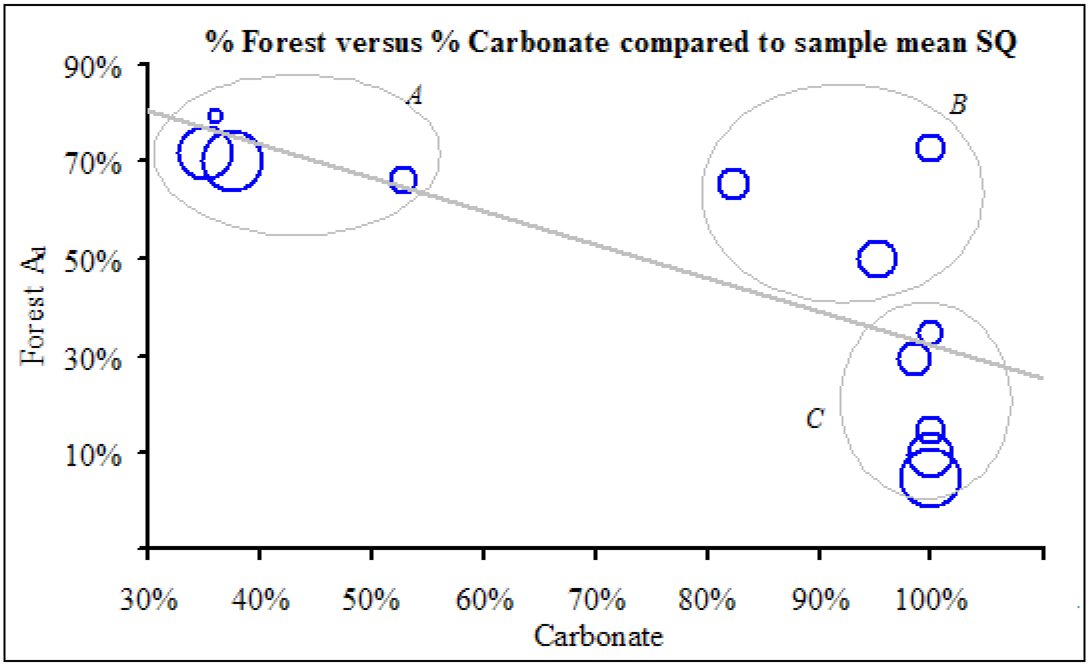


Figure 4.48: Multivariate correlation of forest, carbonate and mean sample SQ. Circle sizes represent mean sampled specific discharge values.

Water Chemistry and Nutrients in the UWRB Watershed

Nutrient concentrations during baseflow throughout the 19 sample watersheds of the UWRB are variable and may not be fully explained by watershed characteristics. This study found that there are several factors that contribute to the level of nutrient concentrations at sample sites including seasonal changes, specific wastewater discharge (SWD) and percentages of forest, agriculture and urban land use. Seasonal patterns are seen among all of the water quality parameters. Nutrient concentrations show a pattern of increased concentration in the fall and early spring months when vegetation is dormant or higher stream discharge occurs. Many high-TN samples occurred during the early spring season when many streams had higher discharge than other seasons. This was possibly due to a residual supply of non-point pollution flushed into the channel during storms.

Specific stream discharge (SQ) did not relate to nutrients directly through linear correlation, but may have been overshadowed by more baseflow sample effects such as point-source discharge from wastewater treatment plants. Besides the seasonal trends, SWD is the predominant factor controlling baseflow nutrient levels in watersheds that receive a moderate to high amount of WTP effluent (Table 4.7). These sites show a positive relationship between nutrients and SWD values (Figure 4.37). With WTP affected sites removed, percent forest and urban land use are the predominant watershed characteristics relating to TP loading. Percent forest and agricultural land use are related to TN loading in these watersheds. Sites with high percent forest and low percent carbonate bedrock have generally moderate to low nutrient levels. Sites with high forest area as well as high percentage of carbonate also have moderate to low nutrient levels while sites with low forest and high carbonate bedrock may have some of the highest

nutrient levels. The shale/sandstone bedrock areas may supply higher TP loads compared to limestone plateau areas with similar forest area, but this bedrock type does not appear to affect TN loading. The sub-watersheds that have a high percent carbonate bedrock and low forested area not only have the highest nutrient concentrations, but also contain the largest urban areas and receive the most WTP effluent throughout the UWRB watershed. These sites include the Wilson Creek sites, the James River below Springfield at JR-Boaz (4) and JR-Galena (6) and the Pearson and Finley Creeks. Another area of the UWRB watershed with high nutrient loading is the Long Creek and Yocum Creek region. Long Creek (12) had high TP levels that may have been caused by additional construction erosion during the sampling period (September 2005 to February 2006). The high TN loading in Yocum Creek may have been from large percentage of agricultural pastures in this watershed or the dairy and poultry operations along this creek.

Several factors involved in performing this study may have an affect on the results. This study was designed to take grab samples and multi-parameter samples for basic water chemistry data during baseflow conditions at the 19 sample sites. These sample sites are dispersed throughout the UWRB watershed and must be visited within the shortest possible in order to collect consistent and comparable samples. Due to driving time, collection time and placement of the sample sites across the UWRB, it was not feasible to collect all 19 samples in a single day. Rather, the samples were collected in two consecutive days, the first in the Missouri side and the other in the Arkansas side of the UWRB. In addition, samples were not collected at the same time of day since collection was performed at different watersheds at different times. This may affect water quality since water temperatures, dissolved oxygen and pH may rise and fall through the

day's progression due to solar radiation, vegetative uptake and algal photosynthesis. Grab samples were preserved with sulfuric acid and cooled to prevent metabolism or digestion of nutrient ions until analysis could be performed. This method allowed samples to be stored for up to 28 days after collection. All analysis was performed within the 28 day period, but 4 out of the 12 sample collections were delayed longer than 20 days before being analyzed. This delay, however, showed no sign of affecting nutrient concentrations when compared to other samples.

The large size of the UWRB (15,636 km^2) also has different climates and weather patterns, with generally warmer and drier conditions in the southern portion and cooler and wetter conditions in the northern areas. Consistent sampling is therefore a challenging task. Antecedent rainfall events were varied in different regions of the watershed and some falling limb sampling may have occurred in the watersheds of the James River Basin and during the earlier part of the year. The falling limb may contain a high nitrogen concentration form run-off or may dilute the nutrient concentrations from point-sources. Drought conditions, such as those in the latter part of the summer of 2005, can cause nutrient loading from WTP sources to become more prominent, while at the same time lowering the land use effects.

Grab sampling done in this study is designed to collect a sample at a particular point in the stream. The error in this method is that in different areas of the stream channel water moves at different rates and may therefore contain varying amounts of suspended or dissolved chemicals. Integrated sampling across the stream channel may therefore have more accurately captured the full spectrum of water quality conditions present at the sample site. However, grab sampling may be sufficient at baseflow

conditions which are not as affected by land run-off and are typically characterized by slow-moving water that has released most of its suspended particles through settling and sedimentation. The channel at baseflow is also much shallower, inducing mixing at the riffles and providing little room for stratification. Another problem when comparing baseflow samples to land use variables is that baseflow nutrient loading is not directly connected with land use run-off. Baseflow in the streams of the Ozarks is fed by springs and groundwater discharge or by point-source discharge. While springs and groundwater are replenished through recharge of storm water from land use areas during rain events, these sources may not directly indicated the influence of local drainage areas on water quality since the karst hydrological networks are independent of the topographical drainage basin.

Future Work

Baseflow sampling done in this study of the UWRB watersheds aims to quantify baseline water quality, particularly nutrients, in this watershed. This study, however, was performed during the short timeframe of one year, inherently limiting results to the particular weather patterns and hydrological condition of that particular period rather than painting an accurate picture of the long term stream conditions. Continued monitoring in the UWRB could provide new insight into the complex relationships between the drainage basin characteristics and water quality as well as expand upon the results of this study. In addition to long term sampling, three specific issues should be addressed in future work: (1) addition of storm event or high flow sampling, (2) improve upon the accuracy of baseflow sampling when this is the target stream condition and (3) increase

sample frequency. Addition of storm event sampling would improve the comparison of water quality to land use by sampling the direct run-off from the drainage areas. Baseflow sampling done in this study was mainly to keep sampling consistent across this large watershed. Land use effects, however, are largely dependent on precipitation run-off sampling. WTP influence therefore showed a higher impact at the baseflow levels. There are major water chemistry and nutrient loading differences between storm water samples and baseflow samples.

When baseflow samples are the target, having accurate precipitation and weather data to help determine baseflow conditions is important. Some of the sampling early in the year may have captured the falling or rising limbs of storm water run-off due to more frequent rain events and the large and varied study area. It was sometimes difficult to get an accurate weather forecast for all areas of the UWRB watershed and its scattered stream sample sites were sometimes difficult to determine as true baseflow. Finally, more frequent sampling would help pinpoint changes in water quality that may be more easily linked to land use practices or events that may not be captured in a monthly sampling. Additional data produced would also help build stronger relationships between stream characteristics and water quality variables by providing more data points. Additional sampling, frequency and accuracy would therefore help improve and extend this study to provide a clearer picture of the water quality status in the UWRB.

CHAPTER 5: CONCLUSIONS

The Upper White River Basin watershed (UWRB), which encompasses over 15,636 km², was sampled at 19 tributary sites (USGS gages) scattered throughout the basin to produce a dataset of water chemistry and nutrient concentrations. The sites were sampled once a month for one year from March 2005 to February 2006. Stream samples were taken during baseflow conditions to increase consistency and comparability of the dataset. A multi-parameter water quality sampler was use to collect water temperature, pH, dissolved oxygen (DO) specific conductivity (SC), and turbidity. Stage was measured at each site and stream discharge was obtained from the USGS Real-time water quality website (www.water.usgs.org).

A GIS database of land use, bedrock geology, drainage areas and wastewater treatment plan discharge (WTP) was used to obtain these watershed characteristics for each sample site. Laboratory analysis of grab samples resulted in 12 sets of total nitrogen (TN) and total phosphorus (TP) values for each site. Land use, geology and specific wastewater treatment plant discharge (SWD) were used to rank the 19 sites as highly disturbed, moderately disturbed and least disturbed. Seasonal influence and hydrology were also examined. Pearson's Correlation and regression analysis was performed using to examine significant relationships between land use, bedrock, SWD and water quality. Five key conclusions of this study are as follows:

1) Urban and agricultural watersheds on the karst limestone plateau such as those, draining Springfield Metropolitan areas generally have high nutrient levels. High nutrient concentrations are often associated with urban and developed areas. Nutrient levels at the James River sites below urban areas often exceeded TMDL limits

(Table 4.3) and all 4 watersheds classified as highly disturbed were located in this watershed (Table 4.7). The general public indicator of water quality, water clarity, has also been historically the lowest in the James River and the James River arm of Table Rock Lake.

2) Highest sampled TN levels were generally observed in the late winter and early spring while high TP samples were more frequent during the late fall and early winter. Late winter and early spring seasons in the Ozarks can have more precipitation than other times of the year leading to higher stream discharge (Figure 4.14 and Figures 4.22 to 4.27). This time of year vegetation is dormant and does not assimilate as many nutrients from run-off or in the streams. Combined high run-off and less nutrient uptake by vegetation may cause increased nutrient loading. The added soil erosion following the long dry summer of 2005 may have also increased the TP loading in the late fall of that year.

3) Specific wastewater discharge (SWD in gal/day/km^2) is positively correlated with nutrient concentrations for watersheds receiving WTP effluent. The positive relationship between SWD and median sample nutrient levels is expected since WTP effluent contains a high concentration of both nitrogen and phosphorus. However, the strong relationship found in this broad, basin-wide study confirms that at baseflow conditions, SWD is an important control of nutrient concentrations in the UWRB watershed.

4) Non-point source watershed correlations (< 600 gal/day/km^2 of SWD) show a negative relationship between percentage of forest and nutrient loading. Non-point influenced watersheds also show a positive relationship between TN and

percent agriculture and between TP and percent urban area. When the strong WTP influence is removed from the regression and Pearson correlation, the influence of land use becomes more visible even for the baseflow samples taken in this study.

5) James River TMDL values of 1.5 mg/L TN and 75 µg/L TP are generally exceeded in sampled watersheds with characteristics beyond the following thresholds:

> 600 (gal/day/km²) SWD

or

>10% Urban land use/drainage area
< 50% Forest land use/drainage area
> 50% Agricultural land use in drainage area

The one site that does not fit into these categories but has median nutrient loading above the James River TMDL levels is Long Creek (site 12) which also was an outlier in much of the correlation and regression analysis. This study showed that basin-wide nutrient analysis of the UWRB watershed can provide important information about water quality as it varies across this dynamic landscape. This data helps set a baseline for reference and comparisons to future water quality monitoring. In order to protect water resources, nutrient loading from wastewater discharges must be reduced to a minimum through sufficient and enforced regulations or alternative treatment options. Public education on better management practices as well as requirements by state, county and local development authorities to implement better water quality practices is essential for water quality preservation in the UWRB. As population and demands on water resources increase, information about the nutrient status and effects from human activities, is essential to provide facts for water quality conservation and management policies.

LITERATURE CITED

ADEQ 2006 NPDES Permits Arkansas Department of Environmental Quality <www.adeq.state.ar.us/water/branch_npdes/data/npdes_data.htm>

Aley T. and Thompson K. C. 2002 A Study of Septic Field Performance and Recharge Area Delineations for Twelve Spring Systems Green County, Missouri A contract report for Greene County by the Ozark Underground Laboratory

Baginska B., Prichard T. and Krogh M. 2003 Roles of Land-use Resolution and Unit-area Load Rates in Assessment of Diffuse Nutrient Emissions Journal of Environmental Management (Vol. 69 No. 1 pp 39-46)

Benfield, E. F. 1996 Methods in Stream Ecology (Chapter 27 pp 579-589)

Binkley D., Ice G. G., Kaye J. and Williams C. A. 2004 Nitrogen and Phosphorus Concentrations in Forest Streams of the United States Journal of American Water Resources Association (Vol. 40 No. 5 pp 1277-1291)

Blodgett C. 2005 Missouri Land Cover Missouri Resource Assessment Partnership <www.cerc.usgs.gov/morap/projects.asp?project_id=2>

Boyd R. A. 1996 Distribution of Nitrate and Orthophosphate in Selected Streams in Central Nebraska Water Resources Bulletin (Vol. 32 No. 6 pp 1247-1257)

Brezonik P. L. and Stadelmann T. H. 2002 Analysis and Predictive Models of Stormwater Runoff Volumes, Loads, and Pollutant Concentrations From Watersheds in the Twin Cities Metropolitan Area, Minnesota, USA Water Research (Vol. 36 No. 7 pp 1743-1757)

CAST 2005Arkansas geology Center for Advanced Spatial Technologies University of Arkansas Fayetteville <http://www.cast.uark.edu >

Chaubey I., Srivastava P., Han L., Addy S. N. and Yin X. 2000 Using GIS, remote sensing and water quality modeling to estimate animal waste pollution potential *In* P.K. Bollich (ed.) Proceedings of 23rd Annual Southern Conservation Tillage Conference for Sustainable Agriculture Monroe, LA. June 19-21 (pp136-143)

Clark G. M., Mueller D. K. and Mast A. M. 2000 Nutrient Concentrations and Yields in Undeveloped Stream Basins of the United States Journal of the American Water Resources Association (Vol. 36 No. 4 pp 849-860)

Crumpton W. G., Isenhart T. M. and Mitchel P. D. 1991 Nitrate and Organic N Analyses with Second Derivative Spectroscopy American Society of Limnology and Oceanography (Vol. 37 No. 4 pp 907-913)

Dupré D. H. and Robertson D. M. 2004 Water Quality of Nippersink Creek and Wonder Lake, McHenry County, Illinois 199 - 2001 U. S Geological Survey (Scientific Investigations Report (SIR) 2004-5085)

Edwards D. R., Daniel T. C., Scott H. D., Murdock J. F., Habiger M. J. and Burks H. M. 1996 Stream Quality Impacts of Best Management Practices in a Northwestern Arkansas Basin Water Resource Bulletin of the American Water Resources Association, (Vol. 32 No. 3 pp 499-509)

Fitzpatrick F. A., Waite I. R., D'Arconte P. J., Meador M. R., Maupin M. A. and Gurtz M. E. 1998 Revised Methods for Characterizing Stream Habitat in the National Water-Quality Assessment Program U. S. Geological Survey (Water-Resources Investigations Report 98-4052)

Fox J. 1997 Applied Regression analysis, Linear Models and Related Methods (Chapter 1 pp 1-13)

Gorham B. 2005 Statewide Land Use / Land Cover of Arkansas University of Arkansas' Center for Advanced Spatial Technologies, Arkansas Natural Resource Conservation Commission <www.cast.uark.edu/cast/research/lulc/index.html>

Graca M. A. S., Ferriera R. C. F. and Coimbra C. N. 2001 Litter Processing Along a Stream Gradient: The Role of Invertebrates and Decomposers Journal of the American Benthological Society (Vol. 20 No 3 pp 408-420)

Greene R. G. and Cruise J. F. 1995 Urban Watershed Modeling Using Geographic Information System Journal of Water Resources Planning and Management (Vol. 121 No. 4 pp 318-325)

Huang Y. F., Cheng X., Huang G. H., Bing Chen., Zeng G. M., Li J. B., and Xia J. 2003 GIS-based Distributed Model for Simulating Runoff and Sediment Load in the Malian River Basin Hydrobiologia (Vol. 494 No 1-3 pp 127-134)

Jordan T. E., Correll D. L. and Weller D. E. 1997 Non-point Source Discharge of Nutrients From Piedmont Watersheds of Chesapeake Bay Journal of American Water Resources Association (Vol. 33 No. 3 pp 631-635)

Langer W. H. 2002 Potential Environmental Impacts of Quarrying Stone in Karst- A Literature Review U. S. Geological Survey Open-File Report OF-01-0484 <http://geology.cr.usgs.gov/pub/ofrs/OFR-01-0484/>

Lent R. M., Waldron M. C. and Rader J. C. 1998 Multivariate Classification of Small Order Watersheds in the Quabbin Reservoir Basin, Massachusetts Journal of American Water Resources Association (Vol. 34 No. 2 pp 439-450)

Lopez R. D., Nash M. S., Heggem D. T., Bice L. A., Evanson E. J., Woods L.V. Remortel R., Jackson M. A., Ebert D. W., Harris T. 2006 Water Quality Vulnerability in the Ozarks using Landscape Ecology Metrics U. S. Environmental Protection Agency EPA/600/C-06/017

Lunetta R. S., Greene R. G. and Lyon J. G. 2005 Modeling the Distribution of Diffuse Nitrogen Sources and Sinks in the Neuse River Basin of North Carolina, USA Journal of the American Water Resources Association (Vol. 41 No. 5 pp 1129-1147)

Mallarino A. P., Stewart B. M., Baker J. L., Downing J. D. and. Sawyer J. E. 2004 Phosphorus indexing for cropland: Overview and basic concepts of the Iowa phosphorus index Journal of Soil and Water Conservation (Vol. 57 No. 6 pp 440-447)

Matějíček L., Benešová L., Tonika J. 2003 Ecological Modeling of Nitrate Pollution in Small River Basins by Spreadsheets and GIS Ecological Modeling (Vol. 170 No. 2-3 pp 245-263)

McNair S. A. and Chow-Fraser P. 2003 Change in Biomass and Planctonic Algae along a Disturbance Gradient for 24 Great Lakes Coastal Wetlands Canada Journal of Fish and Aquatic Science (Vol. 60 No. 6 pp 676-689)

Meals D.W. and Budd L.F. 1998 Lake Champlain Basin Nonpoint Source Phosphorus Assessment Journal of American Water Resources Association (Vol. 34 No. 2 pp 251-256)

Miller C. V., Davis J. M., Ator S. W. and Brakebill J. W. 1997 Nutrients in Streams During Baseflow in Selected Environmental Settings of the Potomac River Basin Journal of American Water Resources Association (Vol. 33 No.6 pp 1155-1171)

Miller R. B. 2006 Nutrient Loads in an Urban Ozark Watershed: Jordan, Fassnight and Upper Wilson Creeks, Springfield, Missouri A thesis study presented to Missouri State University

MODNR 2001 Total Maximum Daily Load (TMDL) for James River, Webster, Green, Christian, and Stone Counties, Missouri Missouri Department of Natural Resources <www.dnr.mo.gov/wpscd/wpcp/tmdl/wpc-tmdl-EPA-Appr.htm>

MODNR 2004 National Pollutant Discharge Elimination System (NPDES) Facilities Missouri Department of Natural Resources Water Protection and Soil Conservation Division, Water Protection Program <http://msdis.missouri.edu>

MODOC 2001 White River Watershed Inventory and Assessment Missouri Department of Conservation <http://www.mdc.mo.gov/fish/watershed/whriver/contents/390cotxt.htm>
MORAP 2004 Land Use Classification Dataset Missouri Spatial Data Information Service (MSDIS) University of Missouri-Columbia <http://msdisweb.missouri.edu/datasearch/ThemeList.jsp>

Mýtýk N. R. and Delfino J. J. 2004 Evaluation of Nitrate Data in Ocklawaha River Basin, Florida (1953-2002) Journal of American Water Resources Association (Vol. 40 No. 4 pp 913-924)

NED 1999 National Elevation Dataset U.S. Geological Survey (USGS), EROS Data Center <http://ned.usgs.gov/>

NOAA 2006 National Oceanic and Atmospheric Administration <http://www.noaa.gov/climate.html>

Olson K.C., Larson R., Pierce V., Randle R., Horner J., Berg E., Lorenzen C., Milhollin R., Ricketts R. and Weaber R. 2004 An Analysis of Missouri's Competitive Position in the Beef Industry and a Resource for Potential Investors University of Missouri Commercial Agriculture Program <http://agebb.missouri.edu/commag/beef/audit/audit.pdf>

Ourso R. T. and Frenzel S. A. 2002. Identification of Linear and Threshold Responses in Streams Along a Gradient of Urbanization in Anchorage, Alaska Hydrobiologia (Vol. 501 No. 1-3 pp 117-131)

Panfil M. S. and Jacobson R. B. 2001 Relations Among Geology, Physiography, Land Use, and Stream Habitat Conditions in the Buffalo and Current River Systems, Missouri and Arkansas (USGS 2001-0005 p 111)

Patton C. J. and Kryskalla J. R. 2003 Methods of Analysis by the U. S. Geological Survey National Water Quality Laboratory – Evaluation of Alkaline Persulfate Digestion as an Alternative to Kjeldahl Digestion for Determination of Total and Dissolved Nitrogen and Phosphorus in Water U. S. Geological Survey (Water-Resources Investigations Report 03-4174)

Petersen J. C., Adamski J. C., Bell R. W., Davis J. V., Femmer S. R., Friewald D. A. and Joseph R. L. 1998 Water Quality in the Ozarks Plateaus, Arkansas,Kansas, Missouri, and Oklahoma, 1992-1995 U. S. Geological Survey (Circular Report 1158)

Schueler T. R. and Holland H. K. 2000 The Practice of Watershed Protection Center for Watershed Protection (Chapter 2 pp 133-144)

Segarra-Garcia R. and Loganathan V. G. 1992 Storm-water Detention Storage Design Under Random Pollutant Loading Journal of Water Resources Planning and Management (Vol. 118 No. 5 pp 475-491)

Spahr N. E. and Wynn K. H. 1997 Nitrogen and Phosphorus in the Surface Waters of the Colorado River Basin Journal of American Water Resources Association (Vol. 33 No. 3 pp 547-560)

SWTP 2006 Springfield Southwest Wastewater Treatment Plant <http://www.ci.springfield.mo.us/egov/publicworks/sanitary/index.html>

Stark S. L., Nuckols J. R., Rada J. 1999 Using GIS to Investigate Septic System Sites and Nitrate Pollution Potential Environmental Health (Vol. 61 No. 8 pp 15-20)

Thorpe A. P., Obrecht D. V. and Jones J. R. 2006 Missouri Department of Natural Resources The Lakes of Missouri Volunteers Program 2005 Data Report (pp 101-121 <www.lmvp.org>)

Turner E. R. and Rabalais N. N. 2003 Linking Landscape and Water Quality in the Mississippi River Basin for 200 Years Bioscience (Vol. 53 No. 6 pp 563-571)

USDA (a) 2004 U. S. Department of Agriculture National Agricultural Statistics Service Arkansas Field Office <http://www.nass.usda.gov/ar/>

USDA (b) 2004 U. S. Department of Agriculture National Agricultural Statistics Service <http://www.nass.usda.gov/QuickStats/PullData_US.jsp>

USDA/NRCS 2005 U. S. Department of Agriculture/Natural Resources Conservation Service Geospatial Data Gateway <http://datagateway.nrcs.usda.gov/ >

USEPA 2004 Guidance for Geospatial Data Quality Assurance Project Plans Office of Environmental Information (Report Reference QA/G-5G)

USEPA 2007 Polluted Runoff (Nonpoint Source Pollution) U. S. Environmental Protection Agency <http://www.epa.gov/owow/nps/sec319cwa.html>

USEPA 2004 Water Quality and Biological Assessment of Selected Segments in the Illinois River Basin and Kings River Basin, Arkansas Prepared by: PARSONS and University of Arkansas Ecological Engineering Group (Volume 1)

USEPA 1999 Protocol for Developing Nutrient TMDLs U. S. Environmental Protection Agency Office of Water, Washington D. C (p135 EPA 841-B-99-007).

USGS 1993 United States Geological Survey National Hydrology Dataset Missouri Spatial Data Information Service <http://msdisweb.missouri.edu/datasearch/ThemeList.jsp>

USGS 2005 Water Resources Investigations Report 94-4022 (Circular 1158) <http://ar.water.usgs.gov/nawqa/ozark/setting.html>

Vesper D. J. and White W. B. 2003 Spring and Conduit Sediments as Storage Reservoirs for Heavy Metals in Karst Aquifers Environmental Geology International Journal of Geosciences (Vol. 45 pp 481-493)

Vannote R. L., Minshall G. W., Cummins K. W., Sedell J. R. and Gushing E. 1980 The River Continuum Concept Canadian Journal of Fisheries Aquatic Science (Vol. 37 No. 1 pp 130-137)

Wernick B.G., Cook K. E. and Schrier H. 1998 Land Use and Streamwater Nitrate-N Dynamics in an Urban-Rural Fringe Watershed 1998 Journal of American Water Resources Association (Vol. 34 No. 3 pp 639-650)

Winter J. G., Dillon P. J. 2005 Effects of golf course construction and operation on water chemistry of headwaters streams on Precambrian Shield Environmental Pollution (Vol. 133 No. 2 pp 243-253)

APPENDIX A

Water Quality Data

Wilson Creek (1): Baseflow water quality data sampled at Scenic Avenue Springfield, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m^3/s	Ant Days
3/5/2005	11:03:32	2.45	16.83	7.41	0.73	7.20	13.05	9.17	0.07	0.18	10.00
4/15/2005	11:46:54	1.95	23.29	7.72	0.76	7.80	11.97	15.05	0.12	0.31	4.00
5/14/2005	13:46:14	0.98	60.24	7.79	0.31	12.00	8.71	19.47	1.14	2.92	18.00
6/4/2005	13:31:50	1.21	29.63	7.96	1.08	17.70	13.67	23.12	0.50	0.10	21.00
7/9/2005	10:36:36	1.12	97.33	7.77	0.76	5.50	6.14	22.33	0.39	0.05	26.00
8/1/2005	10:12:38	1.10	42.79	7.44	0.68	7.10	4.51	22.86	0.40	0.04	5.00
9/9/2005	11:29:12	0.91	79.15	7.61	0.70	6.80	6.01	21.40	0.40	0.04	19.00
10/1/2005	12:00:50	1.76	194.19	7.38	0.72	31.30	7.65	16.39	0.50	0.07	16.00
11/12/2005	10:25:14	0.82	30.96	7.43	0.87	5.80	5.19	11.87	0.46	0.91	13.00
12/17/2005	10:33:50	1.27	74.75	6.50	0.99	6.20	11.51	2.51	0.39	0.06	32.00
1/14/2006	11:25:58	1.23	0.00	7.10	0.70	44.50	7.75	3.94	0.49	0.08	4.00
2/4/2006	11:11:58	1.54	21.63	7.03	0.78	61.10	8.90	4.10	0.32	0.06	7.00
	Mean	1.36	55.88	7.43	0.76	17.75	8.76	14.35	0.43	0.40	14.58
	Min	0.82	0.00	6.50	0.31	5.50	4.51	2.51	0.07	0.04	4.00
	Max	2.45	194.19	7.96	1.08	61.10	13.67	23.12	1.14	2.92	32.00
	Median	1.22	36.88	7.44	0.74	7.50	8.23	15.72	0.40	0.08	14.50
	Std-dev	0.48	52.36	0.40	0.19	18.29	3.13	7.86	0.26	0.83	9.07
	CV%	35	94	5	25	103	36	55	61	206	62

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Wilson Creek above SWTP (2): Baseflow water quality data sampled at Farm Road 156 near Brookline, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/5/2005	11:29:00	2.30	13.03	8.03	0.67	6.10	13.64	9.72	0.22	0.00	10.00
4/15/2005	11:29:16	1.87	17.57	8.17	0.70	7.80	13.65	14.04	0.41	0.20	4.00
5/14/2005	13:28:12	0.96	71.97	7.88	0.27	15.30	8.76	19.55	0.85	2.83	18.00
6/4/2005	14:18:06	0.56	94.07	8.24	0.86	11.70	9.72	25.50	0.15	0.00	21.00
7/9/2005	10:51:52	2.26	61.08	7.98	0.35	15.30	8.12	21.68	0.16	0.00	8.00
8/1/2005	10:32:52	0.83	105.29	7.91	0.35	8.80	6.67	22.84	0.18	0.00	12.00
9/9/2005	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
10/1/2005	12:24:06	0.55	31.22	8.19	0.66	19.50	9.54	19.21	0.15	0.00	16.00
11/12/2005	10:48:28	0.68	185.96	7.34	0.90	6.70	0.00	10.62	0.01	0.31	13.00
12/17/2005	10:50:16	0.77	37.61	6.60	0.90	6.40	17.59	3.87	0.10	0.00	32.00
1/14/2006	11:43:20	1.12	1.54	7.91	0.72	30.30	7.75	4.35	0.13	0.00	4.00
2/4/2006	11:32:42	0.88	31.97	8.22	0.30	77.90	11.09	4.12	0.12	0.00	7.00
	Mean	1.16	59.21	7.86	0.61	18.71	9.68	14.14	0.23	0.30	13.18
	Min	0.55	1.54	6.60	0.27	6.10	0.00	3.87	0.01	0.00	4.00
	Max	2.30	185.96	8.24	0.90	77.90	17.59	25.50	0.85	2.83	32.00
	Median	0.88	37.61	7.98	0.67	11.70	9.54	14.04	0.15	0.00	12.00
	Std-dev	0.66	53.62	0.49	0.25	20.94	4.54	8.06	0.23	0.84	8.32
	CV%	57	91	6	41	112	47	57	101	277	63

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Wilson Creek below SWTP (3): Baseflow water quality data sampled at W Farm Road 168 near Battlefield, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m^3/s	Ant Days
3/5/2005	11:52:50	12.40	123.72	7.40	0.96	4.00	21.68	13.44	0.49	1.33	6.00
4/15/2005	11:05:02	2.49	80.07	7.40	0.84	18.40	16.97	15.18	0.51	1.87	3.00
5/14/2005	13:04:24	12.93	250.59	7.34	0.56	25.10	18.50	18.81	0.62	3.54	18.00
6/4/2005	14:49:16	7.47	325.19	8.18	0.47	18.50	10.07	25.13	0.48	1.10	21.00
7/9/2005	11:11:58	21.30	206.08	7.59	1.15	4.90	14.25	22.63	0.45	1.02	32.00
8/1/2005	11:01:40	17.67	223.86	7.49	0.96	16.90	15.26	23.23	0.42	1.05	12.00
9/9/2005	12:47:04	10.67	156.15	8.10	1.00	12.20	16.06	23.30	0.45	1.08	25.00
10/1/2005	12:42:48	13.98	193.44	7.85	1.10	16.80	14.04	23.18	0.48	0.91	16.00
11/12/2005	11:16:42	6.81	264.89	7.51	1.52	0.00	15.06	20.27	0.48	0.96	13.00
12/17/2005	11:03:26	8.00	137.96	6.70	1.23	0.30	19.99	15.06	0.47	0.93	32.00
1/14/2006	11:56:22	11.50	34.75	7.65	1.25	31.80	15.89	14.76	0.48	0.71	4.00
2/4/2006	11:48:26	15.90	99.97	7.27	0.90	29.00	16.26	14.75	0.46	0.91	7.00
	Mean	11.76	174.72	7.54	0.99	14.83	16.17	19.15	0.48	1.28	15.75
	Min	2.49	34.75	6.70	0.47	0.00	10.07	13.44	0.42	0.71	3.00
	Max	21.30	325.19	8.18	1.52	31.80	21.68	25.13	0.62	3.54	32.00
	Median	11.95	174.80	7.50	0.98	16.85	15.98	19.54	0.48	1.03	14.50
	Std-dev	5.17	84.59	0.39	0.29	10.80	2.99	4.30	0.05	0.77	10.18
	CV%	44	48	5	29	73	19	22	10	60	65

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

James River –Boaz (4): Baseflow water quality data sampled at West Big Bend Road near Boaz, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/5/2005	13:02:22	2.37	35	8.42	0.60	5.60	16.97	13.33	0.54	9.94	9.00
4/15/2005	10:20:20	1.61	43	7.79	0.50	19.00	9.76	15.25	0.95	19.74	3.00
5/14/2005	11:14:48	4.21	172	7.88	0.61	31.20	8.70	20.41	0.52	9.37	32.00
6/4/2005	15:28:46	4.45	202	8.40	0.56	11.30	10.61	26.88	0.41	2.61	21.00
7/9/2005	18:19:30	14.58	327	8.24	0.92	9.30	9.03	28.06	0.36	2.04	6.00
8/1/2005	11:49:16	5.23	237	7.87	0.95	11.70	7.78	25.54	0.34	1.44	12.00
9/9/2005	13:23:04	4.12	185	8.10	0.50	2.80	9.23	24.07	0.35	1.64	18.00
10/1/2005	13:36:28	5.10	116	8.22	0.83	23.70	9.15	18.52	0.49	2.41	3.00
11/12/2005	12:09:26	9.37	90	7.91	1.11	6.90	9.24	12.87	0.38	2.24	11.00
12/17/2005	11:35:56	8.75	33	7.90	0.90	10.50	15.62	3.39	0.37	1.87	32.00
1/14/2006	12:35:22	7.35	12	8.20	1.00	23.70	9.76	5.56	0.41	2.86	4.00
2/4/2006	12:25:06	7.84	51	7.42	0.85	55.20	10.75	6.74	0.47	3.14	7.00
	Mean	6.25	125	8.03	0.78	17.58	10.55	16.72	0.47	4.94	13.17
	Min	1.61	12	7.42	0.50	2.80	7.78	3.39	0.34	1.44	3.00
	Max	14.58	327	8.42	1.11	55.20	16.97	28.06	0.95	19.74	32.00
	Median	5.16	103	8.01	0.84	11.50	9.50	16.89	0.41	2.51	10.00
	Std-dev	3.57	99	0.29	0.21	14.61	2.81	8.59	0.17	5.49	10.43
	CV%	57	79	4	27	83	27	51	36	111	79

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Finley Creek (5): Baseflow water quality data sampled at Riverdale Road near Nixa, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m^3/s	Ant Days
3/5/2005	13:30:02	1.50	8.21	8.33	0.41	3.10	16.11	10.75	0.79	6.46	21.00
4/15/2005	9:48:34	1.07	14.00	7.98	0.38	11.20	10.71	12.56	0.87	11.67	3.00
5/14/2005	10:40:02	1.05	47.48	7.86	0.39	12.60	8.60	18.07	0.78	6.32	18.00
6/4/2005	16:16:02	0.56	36.67	7.94	0.32	93.10	11.64	8.54	0.32	1.23	21.00
7/9/2005	18:45:18	1.02	25.67	8.02	0.50	6.50	9.15	27.11	0.25	0.49	6.00
8/1/2005	12:30:26	1.09	29.57	7.87	0.49	10.50	9.58	26.20	0.25	0.54	12.00
9/9/2005	14:00:28	0.69	50.65	8.61	0.68	0.00	10.57	26.32	0.23	0.50	18.00
10/1/2005	14:32:28	0.97	39.37	8.20	0.48	17.90	8.86	19.73	0.30	0.86	3.00
11/12/2005	13:05:58	1.24	43.82	7.69	0.61	2.70	9.01	13.31	0.27	0.81	11.00
12/17/2005	12:11:24	1.01	17.61	8.30	0.69	2.20	16.21	3.10	0.23	0.51	32.00
1/14/2006	13:03:50	1.37	-2.04	8.29	0.58	24.80	10.42	4.43	0.28	0.48	4.00
2/4/2006	12:55:00	1.08	21.97	8.08	0.49	44.10	11.22	5.47	0.25	0.47	7.00
	Mean	1.05	27.75	8.10	0.50	19.06	11.01	14.63	0.40	2.53	13.00
	Min	0.56	-2.04	7.69	0.32	0.00	8.60	3.10	0.23	0.47	3.00
	Max	1.50	50.65	8.61	0.69	93.10	16.21	27.11	0.87	11.67	32.00
	Median	1.06	27.62	8.05	0.49	10.85	10.50	12.94	0.28	0.68	11.50
	Std-dev	0.26	16.48	0.26	0.12	26.37	2.59	8.76	0.25	3.64	9.10
	CV%	24	59	3	23	138	24	60	62	144	70

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

James River-Galena (6): Baseflow water quality data sampled at the Old Galena Bridge, Galena, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/5/2005	14:09:56	2.02	10.97	8.62	0.46	5.30	16.28	12.09	1.40	27.92	21.00
4/15/2005	9:13:46	1.50	35.43	7.94	0.43	13.60	8.57	13.64	1.68	59.18	2.00
5/14/2005	9:58:10	2.38	62.66	7.79	0.49	3.90	6.52	20.62	1.15	17.36	31.00
6/4/2005	18:33:24	1.40	91.11	8.31	0.53	6.70	8.85	25.59	0.43	5.83	20.00
7/9/2005	19:19:10	2.09	91.08	8.38	0.59	2.70	10.72	28.91	0.20	4.59	7.00
8/1/2005	13:07:50	4.72	124.57	8.36	0.73	2.70	10.05	28.27	0.13	3.71	3.00
9/9/2005	14:44:42	2.57	93.15	7.88	0.33	62.90	9.83	26.54	0.13	3.31	16.00
10/1/2005	15:56:40	2.93	81.59	8.53	0.61	18.10	9.76	20.71	0.16	4.73	15.00
11/12/2005	13:46:54	2.02	50.25	8.22	0.80	2.60	11.59	12.79	0.11	3.45	11.00
12/17/2005	12:43:14	1.06	6.89	8.70	0.97	2.10	16.86	2.24	0.12	3.37	32.00
1/14/2006	13:39:16	6.57	4.04	8.71	0.88	4.20	11.82	5.22	0.10	3.85	4.00
2/4/2006	13:37:06	3.89	20.63	8.64	0.60	46.20	12.09	6.75	0.13	5.10	5.00
	Mean	2.76	56.03	8.34	0.62	14.25	11.08	16.95	0.48	11.87	13.92
	Min	1.06	4.04	7.79	0.33	2.10	6.52	2.24	0.10	3.31	2.00
	Max	6.57	124.57	8.71	0.97	62.90	16.86	28.91	1.68	59.18	32.00
	Median	2.23	56.45	8.37	0.59	4.75	10.39	17.13	0.15	4.66	13.00
	Std-dev	1.59	40.56	0.33	0.19	19.77	3.00	9.42	0.58	16.68	10.47
	CV%	57	72	4	31	139	27	56	121	141	75

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

White River below Table Rock Dam (7): Water quality data sampled at the White River near Branson, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s
3/5/2005	15:12:58	0.76	9.24	8.03	0.32	20.50	14.57	7.44	1.54	117.77
4/15/2005	8:26:20	0.69	7.21	7.90	0.32	11.40	8.57	8.21	1.67	121.14
5/14/2005	9:09:40	0.99	12.31	7.23	0.32	8.40	9.23	8.50	1.30	100.24
6/4/2005	19:16:56	0.67	7.04	8.22	0.44	4.60	8.75	7.32	0.62	86.17
7/9/2005	20:00:38	1.13	14.00	8.02	0.35	71.80	12.78	9.38	0.54	79.52
8/1/2005	14:08:32	1.13	13.14	7.81	0.32	71.60	9.54	9.17	0.54	62.31
9/9/2005	15:56:50	1.03	10.15	8.04	0.44	3.30	8.73	9.46	0.42	61.20
10/1/2005	16:50:24	0.99	8.63	7.83	0.32	25.50	7.85	10.51	0.43	52.12
11/12/2005	14:49:00	0.82	12.04	7.59	0.36	4.20	5.00	10.40	0.40	46.23
12/17/2005	13:45:54	0.48	8.32	8.50	0.41	3.10	12.13	9.48	0.37	26.22
1/14/2006	14:32:06	0.53	4.39	8.56	0.34	14.10	12.09	10.10	0.38	25.57
2/4/2006	14:45:26	1.00	24.63	8.56	0.29	32.80	12.29	9.70	0.36	26.51
	Mean	0.85	10.93	8.02	0.35	22.61	10.13	9.14	0.71	67.08
	Min	0.48	4.39	7.23	0.29	3.10	5.00	7.32	0.36	25.57
	Max	1.13	24.63	8.56	0.44	71.80	14.57	10.51	1.67	121.14
	Median	0.91	9.70	8.03	0.33	12.75	9.39	9.42	0.49	61.76
	Std-dev	0.23	5.16	0.40	0.05	24.78	2.67	1.06	0.49	34.20
	CV%	27	47	5	15	110	26	12	68	51

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Bull Creek (8): Baseflow water quality data sampled at State Highway F near Walnut Shade, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/5/2005	15:45:48	0.60	2.34	8.27	0.43	4.40	13.88	11.33	1.15	4.16	9.00
4/15/2005	15:39:56	0.14	0.43	8.35	0.45	10.60	13.91	15.60	1.22	6.51	8.00
5/14/2005	17:10:28	0.48	10.93	8.26	0.42	4.40	9.46	22.60	1.04	2.55	26.00
6/4/2005	10:49:44	0.11	0.00	7.93	0.49	11.00	6.44	22.05	0.64	0.62	20.00
7/10/2005	10:29:08	0.64	8.17	7.94	0.49	4.60	8.12	25.42	0.65	0.26	11.00
8/1/2005	14:39:28	0.31	10.64	7.94	0.43	3.40	7.86	28.27	0.83	0.15	21.00
9/9/2005	16:48:30	0.16	11.15	8.35	0.49	8.00	8.74	26.73	0.87	0.04	12.00
10/1/2005	17:27:00	0.22	3.07	8.24	0.46	15.40	8.64	22.93	0.71	0.13	2.00
11/12/2005	15:37:00	0.15	7.39	7.91	0.57	0.10	8.41	12.64	0.71	0.25	13.00
12/17/2005	14:12:10	0.23	7.25	8.50	0.69	2.00	14.70	2.96	0.70	0.25	32.00
1/14/2006	15:13:16	0.17	0.82	8.52	0.52	2.70	10.41	6.24	0.67	0.31	4.00
2/4/2006	15:15:38	1.09	11.30	8.30	0.51	33.90	11.54	6.82	0.75	1.64	5.00
	Mean	0.36	6.13	8.21	0.49	8.38	10.18	16.97	0.83	1.41	13.58
	Min	0.11	0.00	7.91	0.42	0.10	6.44	2.96	0.64	0.04	2.00
	Max	1.09	11.30	8.52	0.69	33.90	14.70	28.27	1.22	6.51	32.00
	Median	0.22	7.32	8.27	0.49	4.50	9.10	18.83	0.73	0.28	11.50
	Std-dev	0.29	4.52	0.22	0.07	9.17	2.72	8.81	0.20	2.04	9.30
	CV%	82	74	3	15	109	27	52	24	145	68

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Beaver Creek (9): Baseflow water quality data sampled at State Highway 76 near Bradleyville, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m^3/s	Ant Days
3/5/2005	16:32:04	0.62	4.76	8.44	0.49	3.00	14.58	12.05	0.81	6.99	21.00
4/15/2005	14:49:54	0.69	9.00	8.28	0.47	7.30	13.37	15.54	1.22	17.61	3.00
5/14/2005	16:09:24	0.32	11.28	8.44	0.49	2.00	10.76	22.37	0.67	4.45	22.00
6/4/2005	10:33:34	0.40	8.89	8.05	0.58	22.10	8.84	19.45	0.28	2.01	20.00
7/10/2005	9:46:02	0.66	6.92	8.17	0.54	1.40	9.57	24.67	0.52	1.39	8.00
8/1/2005	15:29:50	0.22	14.57	8.37	0.49	5.70	9.78	29.32	0.39	0.82	13.00
9/9/2005	18:15:36	0.11	24.65	7.89	0.53	13.70	8.62	23.01	0.45	0.71	16.00
10/1/2005	18:21:42	0.24	3.44	8.32	0.48	20.00	8.58	20.56	0.31	1.27	16.00
11/12/2005	16:29:48	0.15	10.61	8.12	0.57	7.30	10.08	14.00	0.24	0.79	11.00
12/17/2005	14:52:20	0.42	9.39	8.60	0.66	1.00	15.73	4.28	0.31	1.25	20.00
1/14/2006	15:54:10	0.45	0.00	8.58	0.57	16.00	10.95	6.95	0.30	1.02	58.00
2/4/2006	15:58:04	0.88	13.63	8.34	0.53	25.20	12.01	7.64	0.44	2.21	5.00
	Mean	0.43	9.76	8.30	0.53	10.39	11.07	16.65	0.50	3.38	17.75
	Min	0.11	0.00	7.89	0.47	1.00	8.58	4.28	0.24	0.71	3.00
	Max	0.88	24.65	8.60	0.66	25.20	15.73	29.32	1.22	17.61	58.00
	Median	0.41	9.20	8.33	0.53	7.30	10.42	17.50	0.42	1.33	16.00
	Std-dev	0.24	6.27	0.21	0.06	8.67	2.38	7.86	0.29	4.85	14.17
	CV%	56	64	3	10	83	22	47	58	144	80

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

James River-Springfield (10): Baseflow water quality data sampled at South Farm Road 193 east of Springfield, MO.

Sampling DATE	Collection Time	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/5/2005	17:36:18	0.56	6.14	8.31	0.42	7.10	15.33	10.35	1.37	3.26	21.00
4/15/2005	13:28:38	1.01	12.93	8.06	0.40	9.00	13.18	13.92	1.51	7.08	3.00
5/14/2005	15:04:12	1.00	24.38	7.93	0.45	8.40	9.14	19.55	1.28	2.12	31.00
6/4/2005	13:08:14	1.09	24.44	8.96	0.32	68.40	16.10	23.86	0.62	0.76	20.00
7/9/2005	9:59:08	1.08	35.67	7.82	0.53	6.90	7.33	23.26	0.55	0.42	8.00
8/1/2005	16:34:12	1.03	13.86	7.89	0.57	19.40	9.41	25.30	0.36	0.16	13.00
9/9/2005	18:31:36	0.83	33.15	8.06	0.60	17.10	10.59	21.24	0.46	0.17	5.00
10/2/2005	9:12:48	1.14	21.59	7.94	0.61	20.60	7.96	17.31	0.45	0.45	13.00
11/12/2005	17:39:28	0.45	20.25	7.60	0.59	7.60	6.58	12.58	0.51	0.19	11.00
12/17/2005	15:52:14	0.69	8.68	8.50	0.67	3.80	15.72	3.91	0.51	0.23	6.00
1/14/2006	16:55:34	0.78	1.89	8.23	0.57	1.30	9.70	6.65	0.50	0.17	3.00
2/4/2006	17:03:20	1.00	15.63	8.12	0.49	14.10	11.31	5.72	0.61	0.76	4.00
	Mean	0.89	18.22	8.12	0.52	15.31	11.03	15.30	0.73	1.32	11.50
	Min	0.45	1.89	7.60	0.32	1.30	6.58	3.91	0.36	0.16	3.00
	Max	1.14	35.67	8.96	0.67	68.40	16.10	25.30	1.51	7.08	31.00
	Median	1.00	17.94	8.06	0.55	8.70	10.15	15.62	0.53	0.44	9.50
	Std-dev	0.22	10.34	0.36	0.10	17.79	3.33	7.53	0.41	2.05	8.70
	CV%	25	57	4	20	116	30	49	56	156	76

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Pearson Creek (11): Baseflow water quality data sampled at Old State Highway D near Springfield, MO.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m^3/s	Ant Days
3/5/2005	17:52:54	2.75	0.97	7.98	0.54	5.00	14.34	11.59	0.88	0.51	21.00
4/15/2005	13:09:24	2.44	10.79	7.82	0.58	16.30	14.08	13.86	0.93	0.82	7.00
5/14/2005	14:45:02	2.40	29.21	7.88	0.58	6.00	10.16	17.81	0.88	0.45	18.00
6/4/2005	11:22:42	2.41	35.56	7.89	0.74	6.70	7.20	21.75	0.60	0.12	20.00
7/9/2005	9:40:26	2.05	13.17	7.41	0.61	13.20	8.06	19.07	0.68	0.10	8.00
8/1/2005	16:48:20	2.02	43.14	8.03	0.58	25.10	10.28	23.74	0.64	0.07	13.00
9/10/2005	11:46:30	1.85	310.15	7.65	0.46	8.10	7.05	20.76	0.44	0.12	17.00
10/2/2005	9:31:22	2.12	26.41	7.74	0.52	22.60	7.45	18.33	0.51	0.12	16.00
11/12/2005	18:00:32	1.74	34.54	7.81	0.42	155.00	8.35	14.54	0.24	0.06	11.00
12/17/2005	16:07:04	2.09	12.25	8.50	0.77	98.00	16.68	7.12	0.25	0.05	6.00
1/14/2006	17:10:50	2.13	3.68	8.46	0.65	0.00	10.73	9.18	0.30	0.03	3.00
2/4/2006	17:17:54	2.35	20.63	8.28	0.62	14.70	11.89	8.08	0.32	0.04	4.00
	Mean	2.20	45.04	7.95	0.59	30.89	10.52	15.49	0.56	0.21	12.00
	Min	1.74	0.97	7.41	0.42	0.00	7.05	7.12	0.24	0.03	3.00
	Max	2.75	310.15	8.50	0.77	155.00	16.68	23.74	0.93	0.82	21.00
	Median	2.12	23.52	7.89	0.58	13.95	10.22	16.18	0.56	0.11	12.00
	Std-dev	0.28	84.53	0.32	0.10	46.85	3.17	5.60	0.25	0.25	6.37
	CV%	13	188	4	17	152	30	36	46	120	53

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Long Creek (12): Baseflow water quality data at County Road 90 near Denver, AR.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/6/2005	11:55:12	1.42	14.07	8.12	0.45	6.50	14.96	11.43	0.71	2.07	10.00
4/16/2005	10:19:44	1.21	53.29	8.23	0.43	9.00	13.62	13.65	0.79	3.79	10.00
5/15/2005	10:44:28	1.56	53.34	7.77	0.41	5.20	9.29	17.78	0.73	1.16	39.00
6/5/2005	10:42:04	1.49	69.63	7.69	0.42	9.00	8.39	21.39	0.69	0.51	12.00
7/10/2005	11:37:32	1.39	63.17	7.71	0.45	6.80	10.00	23.18	0.61	0.40	9.00
8/2/2005	11:27:04	1.20	106.36	7.62	0.47	13.90	9.54	22.06	0.61	0.37	22.00
9/10/2005	12:13:44	1.18	22.65	8.02	0.44	4.90	9.14	22.77	0.63	0.71	34.00
10/2/2005	11:01:10	2.33	146.41	7.72	0.40	21.30	7.35	19.85	0.69	0.48	7.00
11/13/2005	10:37:30	1.36	433.11	7.28	0.58	6.00	6.40	14.15	0.70	0.45	12.00
12/18/2005	12:50:02	2.33	591.89	7.50	0.54	45.90	10.48	7.30	0.68	0.31	34.00
1/15/2006	10:54:24	2.45	373.32	7.77	0.59	32.10	9.68	7.78	0.68	0.36	5.00
2/5/2006	11:32:48	2.01	205.63	7.85	0.51	96.00	9.93	6.15	0.69	0.39	8.00
	Mean	1.66	177.74	7.77	0.47	21.38	9.90	15.62	0.68	0.92	16.83
	Min	1.18	14.07	7.28	0.40	4.90	6.40	6.15	0.61	0.31	5.00
	Max	2.45	591.89	8.23	0.59	96.00	14.96	23.18	0.79	3.79	39.00
	Median	1.45	87.99	7.75	0.45	9.00	9.61	15.97	0.69	0.47	11.00
	Std-dev	0.48	187.92	0.26	0.07	26.72	2.37	6.39	0.05	1.04	12.15
	CV%	29	106	3	14	125	24	41	7	113	72

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Yocum Creek (13): Baseflow water quality data sampled at County Road 618 near Oak Grove, AR.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m^3/s	Ant Days
3/6/2005	11:04:48	5.59	24.07	7.81	0.37	6.50	14.68	10.57	1.08	1.08	10.00
4/16/2005	9:51:34	17.43	16.50	7.91	0.33	11.00	12.92	13.75	1.13	2.27	4.00
5/15/2005	11:08:02	4.09	65.41	7.98	0.46	4.70	9.92	17.46	1.00	0.37	33.00
6/5/2005	11:11:18	4.06	55.93	8.01	0.46	6.50	9.56	20.47	1.10	0.11	12.00
7/10/2005	12:00:52	3.21	34.42	7.99	0.49	4.50	10.34	22.81	1.05	0.24	9.00
8/2/2005	11:53:08	2.72	46.71	7.91	0.45	8.00	10.27	24.12	1.15	0.34	17.00
9/10/2005	13:02:00	2.12	52.15	8.62	0.43	5.90	9.40	28.18	1.03	0.11	17.00
10/2/2005	11:31:20	1.28	37.52	7.97	0.44	20.60	8.14	21.13	1.08	0.11	7.00
11/13/2005	11:07:52	2.52	45.25	7.77	0.51	2.50	10.21	14.61	1.04	0.11	12.00
12/18/2005	13:36:58	2.78	12.25	8.35	0.52	56.00	12.03	4.31	1.05	0.10	34.00
1/15/2006	11:17:02	2.82	-0.25	8.18	0.51	8.30	11.63	7.47	1.11	0.11	5.00
2/5/2006	12:02:18	2.99	29.30	8.19	0.46	82.40	12.32	6.77	1.06	0.11	8.00
	Mean	4.30	34.94	8.06	0.45	18.08	10.95	15.97	1.07	0.42	14.00
	Min	1.28	-0.25	7.77	0.33	2.50	8.14	4.31	1.00	0.10	4.00
	Max	17.43	65.41	8.62	0.52	82.40	14.68	28.18	1.15	2.27	34.00
	Median	2.90	35.97	7.99	0.46	7.25	10.31	16.04	1.07	0.11	11.00
	Std-dev	4.28	19.45	0.24	0.06	24.96	1.81	7.63	0.04	0.64	9.97
	CV%	99	56	3	13	138	17	48	4	154	71

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Kings River (14): Baseflow water quality data sampled at State Highway 143 near Berryville, AR.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/6/2005	18:12:40	0.57	2.34	8.80	0.30	17.70	17.15	11.37	1.15	12.52	10.00
4/16/2005	11:48:54	0.35	23.64	8.39	0.28	12.40	13.38	14.85	1.32	19.85	5.00
5/15/2005	11:58:16	0.73	144.38	8.26	0.34	3.00	9.63	21.27	1.17	13.42	16.00
6/5/2005	11:59:46	0.47	122.59	8.33	0.34	10.20	8.79	24.97	0.35	3.43	12.00
7/10/2005	13:34:14	0.30	0.67	8.47	0.40	4.80	9.42	28.13	0.32	1.19	9.00
8/2/2005	13:09:24	0.44	144.57	8.46	0.49	10.70	10.21	31.01	0.24	0.54	7.00
9/10/2005	13:52:32	0.22	160.65	8.13	0.41	13.40	8.91	25.48	0.28	0.51	7.00
10/2/2005	13:18:58	0.34	118.26	8.38	0.41	20.50	8.23	23.90	0.30	1.27	4.00
11/13/2005	11:56:04	0.22	108.82	7.97	0.53	8.00	9.86	14.76	0.33	0.96	10.00
12/18/2005	14:27:24	0.07	29.75	8.31	0.47	46.90	12.00	3.92	0.27	0.88	31.00
1/15/2006	12:01:14	0.14	2.25	8.51	0.51	11.00	10.74	6.16	0.36	0.68	3.00
2/5/2006	12:45:44	0.76	65.30	8.37	0.36	83.00	11.35	5.28	0.47	2.61	5.00
	Mean	0.38	76.94	8.37	0.40	20.13	10.81	17.59	0.55	4.82	9.92
	Min	0.07	0.67	7.97	0.28	3.00	8.23	3.92	0.24	0.51	3.00
	Max	0.76	160.65	8.80	0.53	83.00	17.15	31.01	1.32	19.85	31.00
	Median	0.34	87.06	8.38	0.40	11.70	10.04	18.06	0.34	1.23	8.00
	Std-dev	0.22	62.60	0.20	0.08	22.82	2.48	9.46	0.41	6.58	7.60
	CV%	57	81	2	21	113	23	54	75	136	77

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

War Eagle Creek (15): Baseflow water quality data sampled at State Highway 45 near Highlandville, AR.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/6/2005	13:22:46	0.96	1.66	8.27	0.21	13.10	15.55	10.17	0.68	6.71	10.00
4/16/2005	13:09:46	0.55	22.57	8.02	0.18	22.20	12.92	15.64	0.82	11.52	4.00
5/15/2005	12:52:16	1.25	53.34	7.88	0.27	6.00	9.68	19.81	0.60	4.53	16.00
6/5/2005	12:53:42	1.13	48.15	7.66	0.30	14.80	7.43	23.01	0.20	1.42	11.00
7/10/2005	14:28:26	1.08	13.58	7.95	0.40	26.70	8.66	26.04	0.10	0.62	8.00
8/2/2005	14:00:20	0.84	14.57	8.12	0.37	9.60	9.85	27.64	0.12	0.34	14.00
9/10/2005	14:19:58	0.38	24.15	8.64	0.28	9.40	9.00	27.09	0.14	0.31	7.00
10/2/2005	14:14:00	0.94	31.59	7.88	0.45	36.10	7.97	21.25	0.12	0.31	17.00
11/13/2005	12:45:58	0.97	67.75	7.69	0.56	11.50	9.40	13.91	0.12	0.54	12.00
12/18/2005	14:53:18	1.06	41.18	8.17	0.38	24.90	10.17	6.22	0.15	0.31	30.00
1/15/2006	12:51:28	1.40	56.89	8.45	0.54	9.00	11.26	5.42	0.15	0.31	4.00
2/5/2006	13:36:24	1.17	98.63	7.93	0.28	88.40	10.93	4.75	0.19	0.54	3.00
	Mean	0.98	39.51	8.06	0.35	22.64	10.24	16.75	0.28	2.29	11.33
	Min	0.38	1.66	7.66	0.18	6.00	7.43	4.75	0.10	0.31	3.00
	Max	1.40	98.63	8.64	0.56	88.40	15.55	27.64	0.82	11.52	30.00
	Median	1.02	36.39	7.99	0.33	13.95	9.77	17.73	0.15	0.54	10.50
	Std-dev	0.29	27.26	0.29	0.12	22.59	2.24	8.62	0.26	3.55	7.50
	CV%	29	69	4	34	100	22	51	91	155	66

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Richland Creek (16): Baseflow water quality data sampled at State Highway 45 near Goshen, AR.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/6/2005	14:51:34	0.65	0.97	9.14	0.17	5.00	17.59	13.07	0.69	10.11	10.00
4/16/2005	13:46:16	0.36	7.21	8.61	0.15	15.30	13.40	17.44	0.76	16.32	5.00
5/15/2005	13:23:42	0.89	14.38	8.32	0.24	7.50	11.71	19.33	0.66	6.59	16.00
6/5/2005	13:25:44	0.57	3.70	8.30	0.24	8.30	9.97	25.21	0.24	3.29	12.00
7/10/2005	15:05:18	0.20	17.33	8.44	0.31	10.60	10.86	29.94	0.20	1.40	9.00
8/2/2005	14:28:06	0.50	12.79	8.52	0.27	11.60	10.89	32.23	0.05	0.65	9.00
9/10/2005	14:40:30	0.19	23.65	8.79	0.25	23.10	9.05	25.71	0.13	0.60	6.00
10/2/2005	15:30:24	0.21	12.33	8.59	0.28	23.40	9.55	26.67	0.11	0.20	15.00
11/13/2005	13:20:30	0.25	15.61	7.91	0.39	2.80	10.43	16.99	0.11	0.30	13.00
12/18/2005	15:16:14	0.07	10.11	8.08	0.45	38.50	9.85	4.56	0.12	0.40	8.00
1/15/2006	13:15:58	0.08	4.75	8.48	0.38	12.50	11.05	8.63	0.07	0.03	5.00
2/5/2006	14:03:22	0.96	15.97	8.00	0.36	78.10	11.00	6.00	0.15	0.78	8.00
	Mean	0.41	11.57	8.43	0.29	19.73	11.28	18.82	0.27	3.39	9.67
	Min	0.07	0.97	7.91	0.15	2.80	9.05	4.56	0.05	0.03	5.00
	Max	0.96	23.65	9.14	0.45	78.10	17.59	32.23	0.76	16.32	16.00
	Median	0.30	12.56	8.46	0.27	12.05	10.88	18.39	0.14	0.72	9.00
	Std-dev	0.30	6.51	0.34	0.09	20.87	2.28	9.36	0.26	5.12	3.68
	CV%	74	56	4	31	106	20	50	97	151	38

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

White River (17): baseflow water quality data sampled at Highway 90 near Fayetteville, AR.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/6/2005	15:13:56	0.43	2.34	8.15	0.14	16.80	14.69	11.20	1.04	2.29	11.00
4/16/2005	14:11:50	0.36	7.21	7.92	0.12	19.10	12.08	16.87	1.15	5.18	10.00
5/15/2005	13:43:28	0.42	16.79	7.89	0.14	10.50	8.98	22.71	1.07	3.09	16.00
6/5/2005	13:47:40	0.22	3.33	7.94	0.20	23.90	8.62	25.28	0.70	1.50	7.00
7/10/2005	15:39:24	0.41	31.50	8.34	0.26	13.10	10.41	27.86	0.14	0.04	9.00
8/2/2005	14:59:00	0.56	19.57	8.23	0.30	20.20	9.82	29.08	0.45	0.14	9.00
9/10/2005	14:51:44	0.12	31.15	7.69	0.33	13.60	6.77	30.49	0.45	0.16	5.00
10/2/2005	15:53:48	0.54	15.67	7.97	0.30	38.00	8.38	24.02	0.40	0.11	3.00
11/13/2005	13:45:42	0.41	24.18	7.41	0.37	12.10	5.43	15.12	0.60	0.16	13.00
12/18/2005	15:24:18	0.35	17.25	8.08	0.49	28.40	10.34	4.19	0.61	0.08	10.00
1/15/2006	13:36:08	0.31	13.32	8.33	0.38	21.00	9.87	7.16	0.60	0.08	3.00
2/5/2006	14:28:18	0.87	38.97	8.13	0.14	101.00	10.87	7.15	0.68	0.51	7.00
	Mean	0.42	18.44	8.01	0.26	26.48	9.69	18.43	0.66	1.11	8.58
	Min	0.12	2.34	7.41	0.12	10.50	5.43	4.19	0.14	0.04	3.00
	Max	0.87	38.97	8.34	0.49	101.00	14.69	30.49	1.15	5.18	16.00
	Median	0.41	17.02	8.03	0.28	19.65	9.85	19.79	0.61	0.16	9.00
	Std-dev	0.19	11.44	0.27	0.12	24.72	2.40	9.38	0.30	1.64	3.87
	CV%	45	62	3	45	93	25	51	46	147	45

Std-dev = Standard deviation

CV= coefficient of variation (the standard deviation divided by the mean)

Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event

Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

West Fork of the White River near Fayetteville (18). Baseflow water quality data.

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m³/s	Ant Days
3/6/2005	15:33:10	0.64	0.62	7.92	0.22	14.50	14.62	11.44	1.01	9.00	10.00
4/16/2005	14:24:48	0.35	9.00	7.96	0.21	24.90	12.21	17.08	1.26	19.14	5.00
5/15/2005	13:52:40	0.92	17.48	7.70	0.22	17.80	8.88	21.31	1.09	11.89	5.00
6/5/2005	13:59:06	0.23	13.70	7.82	0.26	35.60	7.86	24.60	0.30	3.51	13.00
7/10/2005	15:49:48	0.54	28.58	7.62	0.40	8.60	8.18	27.85	0.11	0.16	9.00
8/2/2005	15:09:30	0.38	19.57	7.61	0.44	13.80	8.54	29.89	0.18	0.12	9.00
9/10/2005	15:20:14	0.37	48.15	7.46	0.24	12.30	6.48	32.41	0.08	0.14	5.00
10/2/2005	16:06:02	0.60	20.48	7.49	0.32	32.30	5.42	23.32	0.24	0.03	3.00
11/13/2005	14:03:54	0.25	26.68	7.17	0.40	9.40	4.53	14.84	0.25	0.25	13.00
12/18/2005	10:21:26	0.19	12.96	6.56	0.65	87.00	9.68	5.07	0.25	0.14	3.00
1/15/2006	13:51:42	0.23	13.68	8.28	0.50	18.10	9.85	6.61	0.23	0.20	2.00
2/5/2006	14:39:54	0.89	25.63	7.88	0.40	95.90	10.99	5.60	0.26	0.28	7.00
	Mean	0.47	19.71	7.62	0.36	30.85	8.94	18.34	0.44	3.74	7.00
	Min	0.19	0.62	6.56	0.21	8.60	4.53	5.07	0.08	0.03	2.00
	Max	0.92	48.15	8.28	0.65	95.90	14.62	32.41	1.26	19.14	13.00
	Median	0.38	18.53	7.66	0.36	17.95	8.71	19.20	0.25	0.23	6.00
	Std-dev	0.25	11.96	0.44	0.14	29.60	2.83	9.69	0.42	6.28	3.79
	CV%	54	61	6	38	96	32	53	96	168	54

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Bear Creek (19). At State Highway 14 near Omaha, AR. Baseflow Water Quality Data

Sampling DATE	Collection TIME	TN (mg/L)	TP (µg/L)	pH	COND (mS/cm)	TURB (NTU)	DO (mg/L)	Temp (C°)	Stage (m)	Q m^3/s	Ant Days
3/6/2005	19:32:04	0.98	0.28	8.24	0.49	4.70	13.48	12.08	0.42	2.80	10.00
4/16/2005	16:27:08	0.89	3.64	8.27	0.49	6.30	12.14	17.99	0.54	6.12	4.00
5/15/2005	19:01:20	0.70	5.76	8.28	0.46	2.70	9.92	20.02	0.37	1.95	16.00
6/5/2005	14:54:09	2.84	25.93	7.67	0.53	10.20	7.41	19.74	0.42	0.62	10.00
7/10/2005	17:38:56	0.38	14.00	8.14	0.46	1.90	8.77	27.09	0.28	0.24	9.00
8/2/2005	16:55:04	0.33	5.29	8.13	0.42	3.60	9.51	30.13	0.22	0.34	5.00
9/10/2005	18:46:08	0.08	35.65	7.94	0.43	4.60	8.53	26.95	0.20	0.11	16.00
10/2/2005	17:57:26	0.26	3.81	8.23	0.43	17.00	8.81	24.63	0.30	0.12	7.00
11/13/2005	17:23:14	13.84	12.04	8.01	0.51	1.60	10.00	16.19	0.29	0.28	12.00
12/18/2005	12:23:22	0.23	5.82	6.84	0.61	52.00	9.56	7.76	0.31	0.18	20.00
1/15/2006	16:54:04	0.20	1.54	8.46	0.52	0.00	11.50	8.23	0.32	0.23	2.00
2/5/2006	18:02:34	0.93	11.63	8.13	0.49	29.00	11.30	6.81	0.32	0.28	6.00
	Mean	1.80	10.45	8.03	0.49	11.13	10.08	18.14	0.33	1.11	9.75
	Min	0.08	0.28	6.84	0.42	0.00	7.41	6.81	0.20	0.11	2.00
	Max	13.84	35.65	8.46	0.61	52.00	13.48	30.13	0.54	6.12	20.00
	Median	0.54	5.79	8.14	0.49	4.65	9.74	18.87	0.32	0.28	9.50
	Std-dev	3.86	10.59	0.42	0.05	15.26	1.73	8.12	0.09	1.79	5.45
	CV/%	214	101	5	11	137	17	45	28	162	56

Std-dev = Standard deviation
CV= coefficient of variation (the standard deviation divided by the mean)
Ant Days = Days since the last peak in discharge or Q usually associated with the last rainfall event
Q = Discharge of stream (on dates Q was unavailable from the USGS real-time, it was estimated using stage data)

Total Nitrogen (mg/L)

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	2.5	2.0	1.0	1.2	1.1	1.1	0.9	1.8	0.8	1.3	1.2	1.5	1.4	0.8	2.5	1.2	0.5	35.0
WC-above SWTP (2)	2.3	1.9	1.0	0.6	2.3	0.8	NS	0.6	0.7	0.8	1.1	0.9	1.2	0.6	2.3	0.9	0.7	57.0
WC-at SWTP (3)	12.4	2.5	12.9	12.3	15.9	17.7	10.7	14.0	6.8	8.0	11.5	15.9	11.7	2.5	17.7	12.4	4.3	37.0
JR-Boaz (4)	2.4	1.6	4.2	4.5	14.6	5.2	4.1	5.1	9.4	8.8	7.4	7.8	6.3	1.6	14.6	5.2	3.6	57.0
Finley R (5)	1.5	1.1	1.1	0.6	1.0	1.1	0.7	1.0	1.2	1.0	1.4	1.1	1.1	0.6	1.5	1.1	0.3	24.0
JR-Galena (6)	2.0	1.5	2.4	1.4	2.1	4.7	2.6	2.9	2.0	1.1	6.6	3.9	2.8	1.1	6.6	2.2	1.6	57.0
WR-below TR Dam (7)	0.8	0.7	1.0	0.7	1.1	1.1	1.0	1.0	0.8	0.5	0.5	1.0	0.9	0.5	1.1	0.9	0.2	27.0
Bull Ck (8)	0.6	0.1	0.5	0.1	0.6	0.3	0.2	0.2	0.2	0.2	0.2	1.1	0.4	0.1	1.1	0.2	0.3	82.0
Beaver Ck (9)	0.6	0.7	0.3	0.4	0.7	0.2	0.1	0.2	0.2	0.4	0.5	0.9	0.4	0.1	0.9	0.4	0.2	56.0
JR-above Springfield (10)	0.6	1.0	1.0	1.1	1.1	1.0	0.8	1.1	0.5	0.7	0.8	1.0	0.9	0.5	1.1	1.0	0.2	25.0
Pearson Ck (11)	2.8	2.4	2.4	2.4	2.1	2.0	1.9	2.1	1.7	2.1	2.1	2.4	2.2	1.7	2.8	2.1	0.3	13.0
Long Ck (12)	1.4	1.2	1.6	1.5	1.4	1.2	1.2	2.3	1.4	2.3	2.5	2.0	1.7	1.2	2.5	1.5	0.5	29.0
Yocum Ck (13)	5.6	17.4	4.1	4.1	3.2	2.7	2.1	1.3	2.5	2.8	2.8	3.0	4.3	1.3	17.4	2.9	4.3	99.0
Kings R (14)	0.6	0.4	0.7	0.5	0.3	0.4	0.2	0.3	0.2	0.1	0.1	0.8	0.4	0.1	0.8	0.3	0.2	57.0
War Eagle Ck (15)	1.0	0.6	1.3	1.1	1.1	0.8	0.4	0.9	1.0	1.1	1.4	1.2	1.0	0.4	1.4	1.0	0.3	29.0
Richland Ck (16)	0.7	0.4	0.9	0.6	0.2	0.5	0.2	0.2	0.3	0.1	0.1	1.0	0.4	0.1	1.0	0.3	0.3	74.0
White R-Fayetteville (17)	0.4	0.4	0.4	0.2	0.4	0.6	0.1	0.5	0.4	0.4	0.3	0.9	0.4	0.1	0.9	0.4	0.2	45.0
West Fork White (18)	0.6	0.4	0.9	0.2	0.5	0.4	0.4	0.6	0.3	0.2	0.2	0.9	0.5	0.2	0.9	0.4	0.3	54.0
Bear Ck (19)	1.0	0.9	0.7	2.8	0.4	0.3	0.1	0.3	13.8	0.2	0.2	0.9	1.8	0.1	13.8	0.5	3.9	214.0

Total Phosphorus (ug/L)

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	17	23	60	30	97	43	79	194	31	75	0	22	56	0	194	37	52	94
WC-above SWTP (2)	13	18	72	94	61	105	NS	31	186	38	2	32	59	2	186	38	54	91
WC-at SWTP (3)	124	80	251	325	206	224	156	193	265	138	35	100	175	35	325	175	85	48
JR-Boaz (4)	35	43	172	202	327	237	185	116	90	33	12	51	125	12	327	103	99	79
Finley R (5)	8	14	47	37	26	30	51	39	44	18	0	22	28	0	51	28	16	58
JR-Galena (6)	11	35	63	91	91	125	93	82	50	7	4	21	56	4	125	56	41	72
WR-below TR Dam (7)	9	7	12	7	14	13	10	9	12	8	4	25	11	4	25	10	5	48
Bull Ck (8)	2	0	11	-3	8	11	11	3	7	7	1	11	6	-3	11	7	5	82
Beaver Ck (9)	5	9	11	9	7	15	25	3	11	9	0	14	10	0	25	9	6	64
JR-above Springfield (10)	6	13	24	24	36	14	33	22	20	9	2	16	18	2	36	18	10	57
Pearson Ck (11)	1	11	29	36	13	43	310	26	35	12	4	21	45	1	310	24	84	188
Long Ck (12)	14	53	53	70	63	106	23	146	433	592	373	206	178	14	592	88	188	106
Yocum Ck (13)	24	17	65	56	34	47	52	38	45	12	0	29	35	0	65	36	19	56
Kings R (14)	2	24	144	123	1	145	161	118	109	30	2	65	77	1	161	87	63	81
War Eagle Ck (15)	2	23	53	48	14	15	24	32	68	41	57	99	40	2	99	36	27	69
Richland Ck (16)	1	7	14	4	17	13	24	12	16	10	5	16	12	1	24	13	7	56
White R-Fayetteville (17)	2	7	17	3	32	20	31	16	24	17	13	39	18	2	39	17	11	62
West Fork White (18)	1	9	17	14	29	20	48	20	27	13	14	26	20	1	48	19	12	61
Bear Ck (19)	0	4	6	26	14	5	36	4	12	6	2	12	10	0	36	6	11	101

pH

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	7.4	7.7	7.8	7.9	7.8	7.4	7.6	7.4	7.4	6.5	7.1	7.0	7.4	6.5	7.9	7.4	0.4	5.0
WC-above SWTP (2)	8.0	8.2	7.9	9.0	8.0	7.9	7.7	8.2	7.3	6.6	7.9	8.2	7.9	6.6	9.0	8.0	0.6	7.0
WC-at SWTP (3)	7.4	7.4	7.3	8.0	7.6	7.5	8.1	7.9	7.5	6.7	7.7	7.3	7.5	6.7	8.1	7.5	0.4	5.0
JR-Boaz (4)	8.4	7.8	7.9	8.2	8.2	7.9	8.1	8.2	7.9	7.9	8.2	7.4	8.0	7.4	8.4	8.0	0.3	3.0
Finley R (5)	8.3	8.0	7.9	8.2	8.0	7.9	8.6	8.2	7.7	8.3	8.3	8.1	8.1	7.7	8.6	8.1	0.3	3.0
JR-Galena (6)	8.6	7.9	7.8	8.4	8.4	8.4	7.9	8.5	8.2	8.7	8.7	8.6	8.4	7.8	8.7	8.4	0.3	4.0
WR-below TR Dam (7)	8.0	7.9	7.2	7.9	8.0	7.8	8.0	7.8	7.6	8.5	8.6	8.6	8.0	7.2	8.6	8.0	0.4	5.0
Bull Ck (8)	8.3	8.4	8.3	8.3	7.9	7.9	8.4	8.2	7.9	8.5	8.5	8.3	8.2	7.9	8.5	8.3	0.2	3.0
Beaver Ck (9)	8.4	8.3	8.4	8.2	8.2	8.4	7.9	8.3	8.1	8.6	8.6	8.3	8.3	7.9	8.6	8.3	0.2	2.0
JR-above Springfield (10)	8.3	8.1	7.9	7.9	7.8	7.9	8.1	7.9	7.6	8.5	8.2	8.1	8.0	7.6	8.5	8.0	0.2	3.0
Pearson Ck (11)	8.0	7.8	7.9	8.1	7.4	8.0	7.7	7.7	7.8	8.5	8.5	8.3	8.0	7.4	8.5	7.9	0.3	4.0
Long Ck (12)	7.8	7.9	7.8	7.7	7.7	7.6	8.0	7.7	7.3	7.5	7.8	7.9	7.7	7.3	8.0	7.8	0.2	2.0
Yocum Ck (13)	8.1	8.2	8.0	8.0	8.0	7.9	8.6	8.0	7.8	8.4	8.2	8.2	8.1	7.8	8.6	8.1	0.2	3.0
Kings R (14)	8.3	8.4	8.3	8.3	8.5	8.5	8.1	8.4	8.0	8.3	8.5	8.4	8.3	8.0	8.5	8.4	0.2	2.0
War Eagle Ck (15)	9.1	8.0	7.9	7.7	8.0	8.1	8.6	7.9	7.7	8.2	8.5	7.9	8.1	7.7	9.1	8.0	0.4	5.0
Richland Ck (16)	8.2	8.6	8.3	8.3	8.4	8.5	8.8	8.6	7.9	8.1	8.5	8.0	8.4	7.9	8.8	8.4	0.3	3.0
White R-Fayetteville (17)	7.9	7.9	7.9	7.9	8.3	8.2	7.7	8.0	7.4	8.1	8.3	8.1	8.0	7.4	8.3	8.0	0.3	3.0
West Fork White (18)	8.8	8.0	7.7	7.8	7.6	7.6	7.5	7.5	7.2	6.6	8.3	7.9	7.7	6.6	8.8	7.7	0.6	7.0
Bear Ck (19)	8.2	8.3	8.3	7.7	8.1	8.1	7.9	8.2	8.0	6.8	8.5	8.1	8.0	6.8	8.5	8.1	0.4	5.0

Specific Conductivity (mS/cm)

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	0.73	0.76	0.31	0.74	0.76	0.68	0.70	0.72	0.87	1.00	0.70	0.78	0.73	0.31	1.00	0.74	0.16	22
WC-above SWTP (2)	0.67	0.70	0.27	0.32	0.35	0.35	1.15	0.66	0.90	0.90	0.72	0.30	0.61	0.27	1.15	0.67	0.29	48
WC-at SWTP (3)	0.96	0.84	0.56	1.08	1.15	0.96	1.00	1.10	1.52	1.23	1.25	0.90	1.05	0.56	1.52	1.04	0.24	23
JR-Boaz (4)	0.60	0.50	0.61	0.86	0.92	0.95	0.50	0.83	1.11	0.90	1.00	0.85	0.80	0.50	1.11	0.85	0.20	25
Finley R (5)	0.41	0.38	0.39	0.47	0.50	0.49	0.68	0.48	0.61	0.69	0.58	0.49	0.51	0.38	0.69	0.49	0.10	20
JR-Galena (6)	0.46	0.43	0.49	0.56	0.59	0.73	0.33	0.61	0.80	0.97	0.88	0.60	0.62	0.33	0.97	0.59	0.19	31
WR-below TR Dam (7)	0.32	0.32	0.32	0.32	0.35	0.32	0.44	0.32	0.36	0.41	0.34	0.29	0.34	0.29	0.44	0.32	0.04	13
Bull Ck (8)	0.43	0.45	0.42	0.53	0.49	0.43	0.49	0.46	0.57	0.69	0.52	0.51	0.50	0.42	0.69	0.49	0.07	15
Beaver Ck (9)	0.49	0.47	0.49	0.44	0.54	0.49	0.53	0.48	0.57	0.66	0.57	0.53	0.52	0.44	0.66	0.51	0.06	11
JR-above Springfield (10)	0.42	0.40	0.45	0.49	0.53	0.57	0.60	0.61	0.59	0.67	0.57	0.49	0.53	0.40	0.67	0.55	0.08	16
Pearson Ck (11)	0.54	0.58	0.58	0.58	0.61	0.58	0.46	0.52	0.42	0.77	0.65	0.62	0.58	0.42	0.77	0.58	0.09	16
Long Ck (12)	0.37	0.33	0.41	0.42	0.45	0.47	0.44	0.40	0.58	0.54	0.59	0.51	0.46	0.33	0.59	0.45	0.08	18
Yocum Ck (13)	0.45	0.43	0.46	0.46	0.49	0.45	0.43	0.44	0.51	0.52	0.51	0.45	0.47	0.43	0.52	0.46	0.03	7
Kings R (14)	0.21	0.28	0.34	0.34	0.40	0.49	0.41	0.41	0.53	0.47	0.51	0.36	0.40	0.21	0.53	0.40	0.10	25
War Eagle Ck (15)	0.17	0.18	0.27	0.30	0.40	0.37	0.28	0.45	0.56	0.38	0.54	0.28	0.35	0.17	0.56	0.33	0.12	36
Richland Ck (16)	0.14	0.15	0.24	0.24	0.31	0.27	0.25	0.28	0.39	0.45	0.38	0.36	0.29	0.14	0.45	0.27	0.09	33
White R-Fayetteville (17)	0.22	0.12	0.14	0.20	0.26	0.30	0.33	0.30	0.37	0.49	0.38	0.14	0.27	0.12	0.49	0.28	0.11	41
West Fork White (18)	0.30	0.21	0.22	0.26	0.40	0.44	0.24	0.32	0.40	0.65	0.50	0.40	0.36	0.21	0.65	0.36	0.13	36
Bear Ck (19)	0.49	0.49	0.46	0.53	0.46	0.42	0.43	0.43	0.51	0.61	0.52	0.49	0.49	0.42	0.61	0.49	0.05	11

Turbidity (NTU)

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	7	8	12	7	6	7	7	31	6	6	45	61	17	6	61	7	19	110
WC-above SWTP (2)	6	8	15	68	15	9	7	20	7	6	30	78	22	6	78	12	25	111
WC-at SWTP (3)	4	9	25	18	5	17	12	17	0	0	32	29	14	0	32	15	11	77
JR-Boaz (4)	6	19	31	12	9	12	3	24	7	11	24	55	18	3	55	12	15	83
Finley R (5)	3	11	13	14	7	11	0	18	3	2	25	46	13	0	46	11	13	102
JR-Galena (6)	5	14	4	11	3	3	63	18	3	2	4	46	15	2	63	5	20	134
WR-below TR Dam (7)	21	11	8	93	72	72	3	26	4	3	14	33	30	3	93	17	31	104
Bull Ck (8)	4	11	4	7	5	3	8	15	0	2	3	34	8	0	34	5	9	114
Beaver Ck (9)	3	7	2	5	1	6	14	20	7	1	16	25	9	1	25	7	8	89
JR-above Springfield (10)	7	9	8	11	7	19	17	21	8	4	1	14	11	1	21	9	6	58
Pearson Ck (11)	5	16	6	22	13	25	8	23	155	98	0	15	32	0	155	16	46	144
Long Ck (12)	7	11	5	9	7	14	5	21	6	46	32	96	22	5	96	10	27	124
Yocum Ck (13)	7	9	5	7	5	8	6	21	3	56	8	82	18	3	82	7	25	140
Kings R (14)	13	12	3	10	5	11	13	21	8	47	11	83	20	3	83	12	23	116
War Eagle Ck (15)	5	22	6	15	27	10	9	36	12	25	9	88	22	5	88	13	23	105
Richland Ck (16)	17	15	8	8	11	12	23	23	3	39	13	78	21	3	78	14	20	98
White R-Fayetteville (17)	15	19	11	24	13	20	14	38	12	28	21	101	26	11	101	20	25	94
West Fork White (18)	18	25	18	36	9	14	12	32	9	87	18	96	31	9	96	18	29	95
Bear Ck (19)	5	6	3	10	2	4	5	17	2	52	0	29	11	0	52	5	15	137

Dissolved Oxygen (mg/L)

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	13	12	9	14	6	5	6	8	5	12	8	9	9	5	14	8	3	36
WC-above SWTP (2)	14	14	9	10	8	7	0	10	0	18	8	11	9	0	18	9	5	58
WC-at SWTP (3)	22	17	19	10	14	15	16	14	15	20	16	16	16	10	22	16	3	19
JR-Boaz (4)	17	10	9	11	9	8	9	9	9	16	10	11	11	8	17	10	3	27
Finley R (5)	16	11	9	12	9	10	11	9	9	16	10	11	11	9	16	11	3	24
JR-Galena (6)	16	9	7	9	11	10	10	10	12	17	12	12	11	7	17	10	3	27
WR-below TR Dam (7)	15	9	9	9	13	10	9	8	5	12	12	12	10	5	15	9	3	26
Bull Ck (8)	14	14	9	6	8	8	9	9	8	15	10	12	10	6	15	9	3	27
Beaver Ck (9)	15	13	11	9	10	10	9	9	10	16	11	12	11	9	16	10	2	22
JR-above Springfield (10)	15	13	9	16	7	9	11	8	7	16	10	11	11	7	16	10	3	30
Pearson Ck (11)	14	14	10	7	8	10	7	7	8	17	11	12	11	7	17	10	3	30
Long Ck (12)	15	14	9	8	10	10	9	7	6	10	10	10	10	6	15	10	2	24
Yocum Ck (13)	15	13	10	10	10	10	9	8	10	12	12	13	11	8	15	10	2	17
Kings R (14)	17	13	10	9	9	10	9	8	10	12	11	11	11	8	17	10	2	23
War Eagle Ck (15)	16	13	10	7	9	10	9	8	9	10	11	11	10	7	16	10	2	22
Richland Ck (16)	18	13	12	10	11	11	9	10	10	10	11	11	11	9	18	11	2	20
White R-Fayetteville (17)	15	12	9	9	10	10	7	8	5	10	10	11	10	5	15	10	2	25
West Fork White (18)	15	12	9	8	8	9	6	5	5	10	10	11	9	5	15	9	3	32
Bear Ck (19)	13	12	10	7	9	10	9	9	10	10	12	11	10	7	13	10	2	17

Water Temperature (C°)

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	9	15	19	22	22	23	21	16	12	3	4	4	14	3	23	16	8	54
WC-above SWTP (2)	10	14	20	24	22	23	24	19	11	4	4	4	15	4	24	17	8	54
WC-at SWTP (3)	13	15	19	23	23	23	23	23	20	15	15	15	19	13	23	20	4	21
JR-Boaz (4)	13	15	20	26	28	26	24	19	13	3	6	7	17	3	28	17	8	51
Finley R (5)	11	13	18	25	27	26	26	20	13	3	4	5	16	3	27	16	9	56
JR-Galena (6)	12	14	21	27	29	28	10	21	13	2	5	7	16	2	29	13	9	59
WR-below TR Dam (7)	7	8	9	9	9	9	27	11	10	9	10	10	11	7	27	9	5	48
Bull Ck (8)	11	16	23	26	25	28	27	23	13	3	6	7	17	3	28	19	9	52
Beaver Ck (9)	12	16	22	27	25	29	23	21	14	4	7	8	17	4	29	18	8	49
JR-above Springfield (10)	10	14	20	22	23	25	21	17	13	4	7	6	15	4	25	16	7	49
Pearson Ck (11)	12	14	18	19	19	24	21	18	15	7	9	8	15	7	24	16	5	35
Long Ck (12)	11	14	18	21	23	22	23	20	14	7	8	6	16	6	23	16	6	41
Yocum Ck (13)	11	14	17	20	23	24	28	21	15	4	7	7	16	4	28	16	8	47
Kings R (14)	10	15	21	25	28	31	25	24	15	4	6	5	17	4	31	18	10	55
War Eagle Ck (15)	13	16	20	23	26	28	27	21	14	6	5	5	17	5	28	18	8	50
Richland Ck (16)	11	17	19	25	30	32	26	27	17	5	9	6	19	5	32	18	9	51
White R-Fayetteville (17)	11	17	23	25	28	29	30	24	15	4	7	7	18	4	30	20	9	51
West Fork White (18)	11	17	21	25	28	30	32	23	15	5	7	6	18	5	32	19	10	53
Bear Ck (19)	12	18	20	20	27	30	27	25	16	8	8	7	18	7	30	19	8	45

Stage (Meters)

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	0.07	0.12	1.14	0.50	0.39	0.40	0.40	0.50	0.46	0.39	0.49	0.32	0.43	0.07	1.14	0.40	0.26	61
WC-above SWTP (2)	0.22	0.41	0.85	0.15	0.16	0.18	NS	0.15	0.01	0.10	0.13	0.12	0.23	0.01	0.85	0.15	0.23	101
WC-at SWTP (3)	0.49	0.51	0.62	0.48	0.45	0.42	0.45	0.48	0.48	0.47	0.48	0.46	0.48	0.42	0.62	0.48	0.05	10
JR-Boaz (4)	0.54	0.95	0.52	0.41	0.36	0.34	0.35	0.49	0.38	0.37	0.41	0.47	0.47	0.34	0.95	0.41	0.17	36
Finley R (5)	0.79	0.87	0.78	0.32	0.25	0.25	0.23	0.30	0.27	0.23	0.28	0.25	0.40	0.23	0.87	0.28	0.25	62
JR-Galena (6)	1.40	1.68	1.15	0.43	0.20	0.13	0.13	0.16	0.11	0.12	0.1	0.13	0.48	0.10	1.68	0.15	0.58	121
WR-below TR Dam (7)	1.54	1.67	1.30	0.62	0.54	0.54	0.42	0.43	0.40	0.37	0.38	0.36	0.71	0.36	1.67	0.49	0.49	68
Bull Ck (8)	1.15	1.22	1.04	0.64	0.65	0.83	0.87	0.71	0.71	0.70	0.67	0.75	0.83	0.64	1.22	0.73	0.20	24
Beaver Ck (9)	0.81	1.22	0.67	0.28	0.52	0.39	0.45	0.31	0.24	0.31	0.3	0.44	0.50	0.24	1.22	0.42	0.29	58
JR-above Springfield (10)	1.37	1.51	1.28	0.62	0.55	0.36	0.46	0.45	0.51	0.51	0.5	0.61	0.73	0.36	1.51	0.53	0.41	56
Pearson Ck (11)	0.88	0.93	0.88	0.60	0.68	0.64	0.44	0.51	0.24	0.25	0.3	0.32	0.56	0.24	0.93	0.56	0.25	46
Long Ck (12)	0.71	0.79	0.73	0.69	0.61	0.61	0.63	0.69	0.70	0.68	0.68	0.69	0.68	0.61	0.79	0.69	0.05	7
Yocum Ck (13)	1.08	1.13	1.00	1.10	1.05	1.15	1.03	1.08	1.04	1.05	1.11	1.06	1.07	1.00	1.15	1.07	0.04	4
Kings R (14)	1.15	1.32	1.17	0.35	0.32	0.24	0.28	0.30	0.33	0.27	0.36	0.47	0.55	0.24	1.32	0.34	0.41	75
War Eagle Ck (15)	0.68	0.82	0.60	0.20	0.10	0.12	0.14	0.12	0.12	0.15	0.15	0.19	0.28	0.10	0.82	0.15	0.26	91
Richland Ck (16)	0.69	0.76	0.66	0.24	0.20	0.05	0.13	0.11	0.11	0.12	0.07	0.15	0.27	0.05	0.76	0.14	0.26	97
White R-Fayetteville (17)	1.04	1.15	1.07	0.70	0.14	0.45	0.45	0.40	0.60	0.61	0.6	0.68	0.66	0.14	1.15	0.61	0.30	46
West Fork White (18)	1.01	1.26	1.09	0.30	0.11	0.18	0.08	0.24	0.25	0.25	0.23	0.26	0.44	0.08	1.26	0.25	0.42	96
Bear Ck (19)	0.42	0.54	0.37	0.42	0.28	0.22	0.20	0.30	0.29	0.31	0.32	0.32	0.33	0.20	0.54	0.32	0.09	28

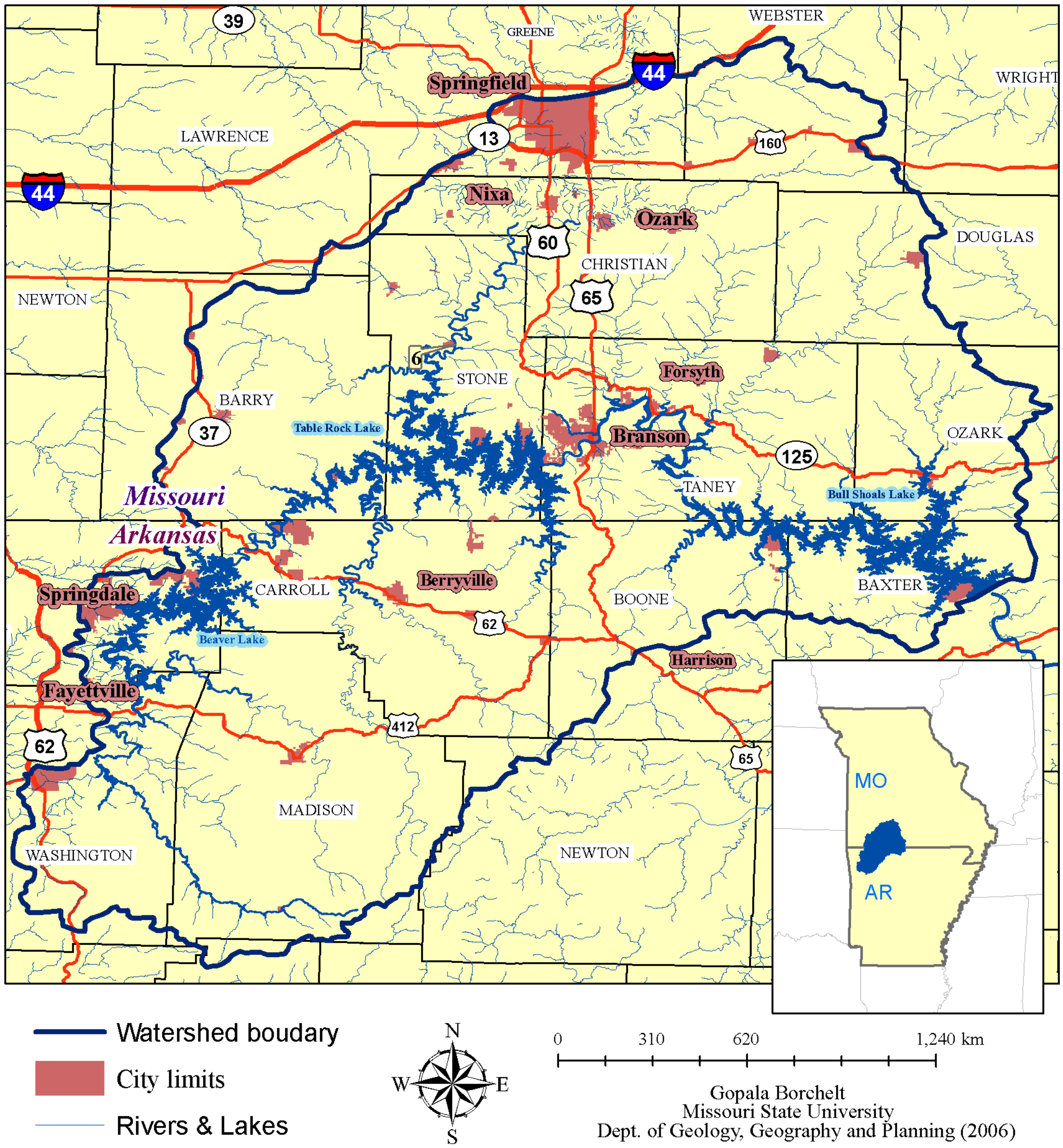
Discharge (Q) m³/sec

Sites	March	April	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mean	Min	Max	Median	Std-dev	CV%
WC-Springfield (1)	0.18	0.31	2.92	0.10	0.05	0.04	0.04	0.07	0.91	0.06	0.08	0.06	0.40	0.04	2.92	0.08	0.83	206
WC-above SWTP (2)	0.00	0.20	2.83	0.00	0.00	0.00	NS	0.00	0.31	0.00	0.00	0.00	0.30	0.00	2.83	0.00	0.84	277
WC-at SWTP (3)	1.33	1.87	3.54	1.10	1.02	1.05	1.08	0.91	0.96	0.93	0.71	0.91	1.28	0.71	3.54	1.03	0.77	60
JR-Boaz (4)	9.94	19.74	9.37	2.61	2.04	1.44	1.64	2.41	2.24	1.87	2.86	3.14	4.94	1.44	19.74	2.51	5.49	111
Finley R (5)	6.46	11.67	6.32	1.23	0.49	0.54	0.50	0.86	0.81	0.51	0.48	0.47	2.53	0.47	11.67	0.68	3.64	144
JR-Galena (6)	27.92	59.18	17.36	5.83	4.59	3.71	3.31	4.73	3.45	3.37	3.85	5.10	11.87	3.31	59.18	4.66	16.68	141
WR-below TR Dam (7)	118	121	100	86	80	62	61	52	46	26	26	27	67	25	121	61	34	51
Bull Ck (8)	4.16	6.51	2.55	0.62	0.26	0.15	0.04	0.13	0.25	0.25	0.31	1.64	1.41	0.04	6.51	0.28	2.04	145
Beaver Ck (9)	6.99	17.61	4.45	2.01	1.39	0.82	0.71	1.27	0.79	1.25	1.02	2.21	3.38	0.71	17.61	1.33	4.85	144
JR-above Sprgfld (10)	3.26	7.08	2.12	0.76	0.42	0.16	0.17	0.45	0.19	0.23	0.17	0.76	1.32	0.16	7.08	0.44	2.05	156
Pearson Ck (11)	0.51	0.82	0.45	0.12	0.10	0.07	0.12	0.12	0.06	0.05	0.03	0.04	0.21	0.03	0.82	0.11	0.25	120
Long Ck (12)	2.07	3.79	1.16	0.51	0.40	0.37	0.71	0.48	0.45	0.31	0.36	0.39	0.92	0.31	3.79	0.47	1.04	113
Yocum Ck (13)	1.08	2.27	0.37	0.11	0.24	0.34	0.11	0.11	0.11	0.10	0.11	0.11	0.42	0.10	2.27	0.11	0.64	154
Kings R (14)	12.52	19.85	13.42	3.43	1.19	0.54	0.51	1.27	0.96	0.88	0.68	2.61	4.82	0.51	19.85	1.23	6.58	136
War Eagle Ck (15)	6.71	11.52	4.53	1.42	0.62	0.34	0.31	0.31	0.54	0.31	0.31	0.54	2.29	0.31	11.52	0.54	3.55	155
Richland Ck (16)	10.11	16.32	6.59	3.29	1.40	0.65	0.60	0.20	0.30	0.40	0.03	0.78	3.39	0.03	16.32	0.72	5.12	151
WR-Fayetteville (17)	2.29	5.18	3.09	1.50	0.04	0.14	0.16	0.11	0.16	0.08	0.08	0.51	1.11	0.04	5.18	0.16	1.64	147
West Fork White (18)	9.00	19.14	11.89	3.51	0.16	0.12	0.14	0.03	0.25	0.14	0.20	0.28	3.74	0.03	19.14	0.23	6.28	168
Bear Ck (19)	2.80	6.12	1.95	0.62	0.24	0.34	0.11	0.12	0.28	0.18	0.23	0.28	1.11	0.11	6.12	0.28	1.79	162

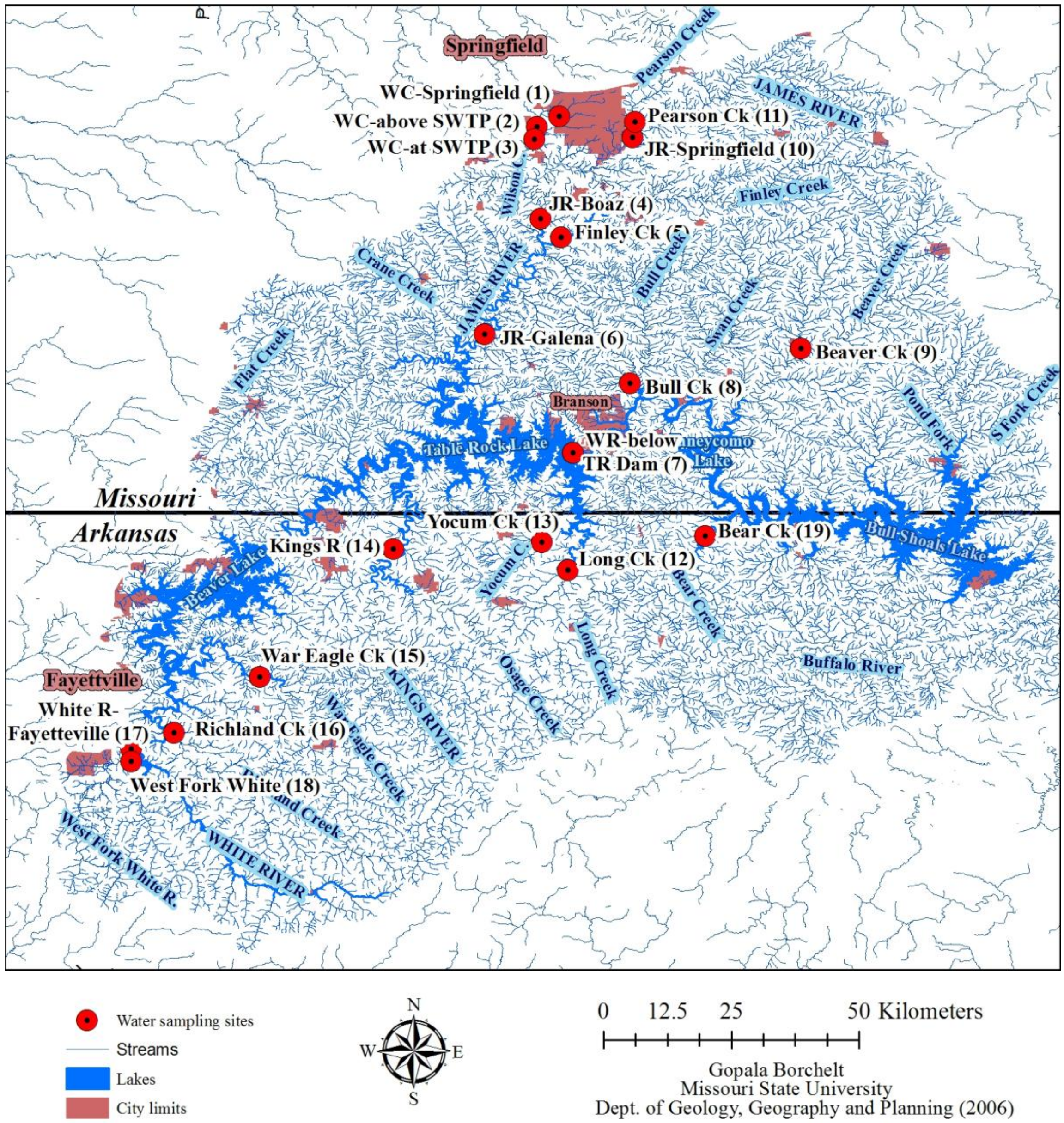
APPENDIX B

GIS Data Layers and Maps

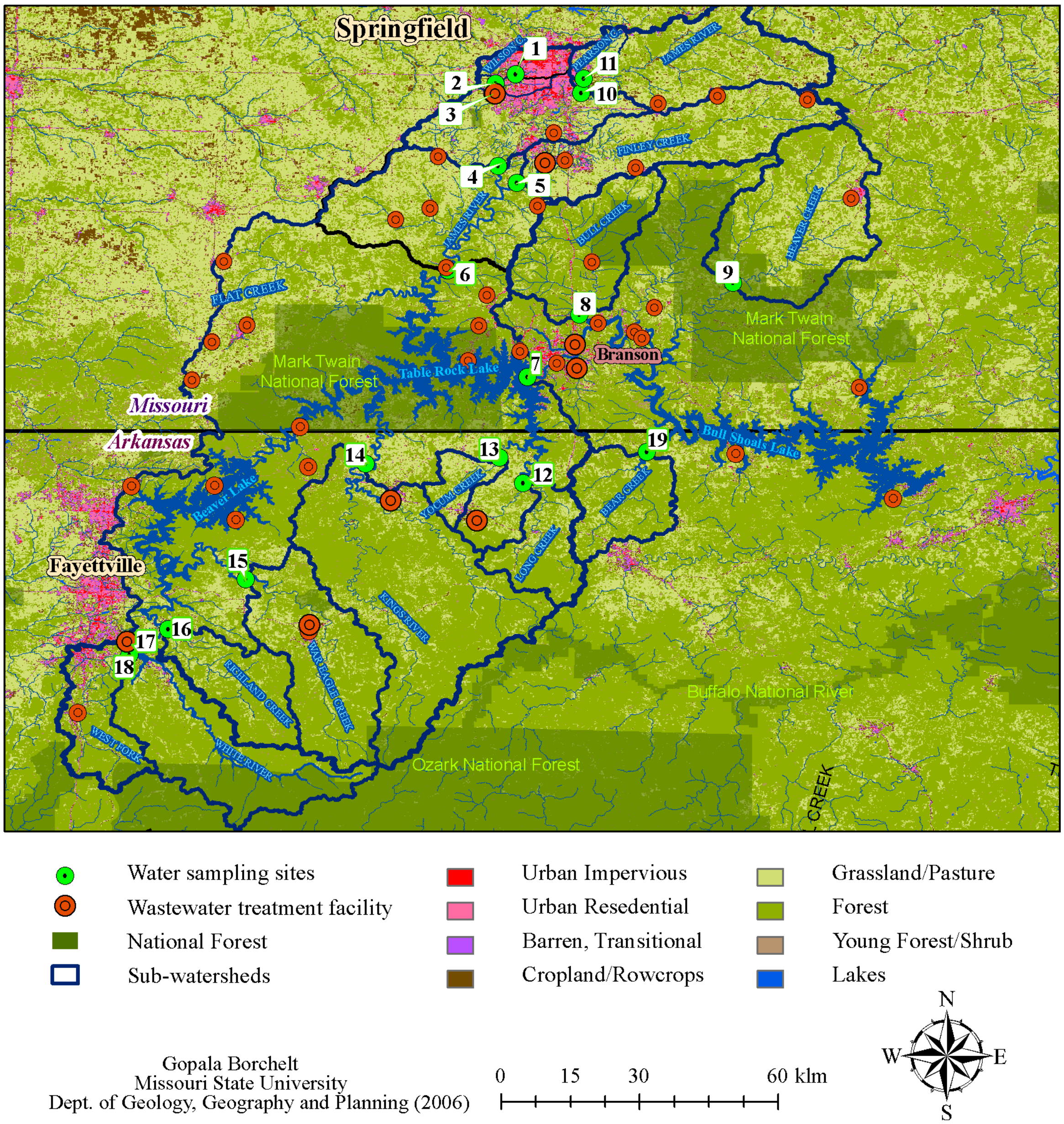
Upper White River Basin Watershed



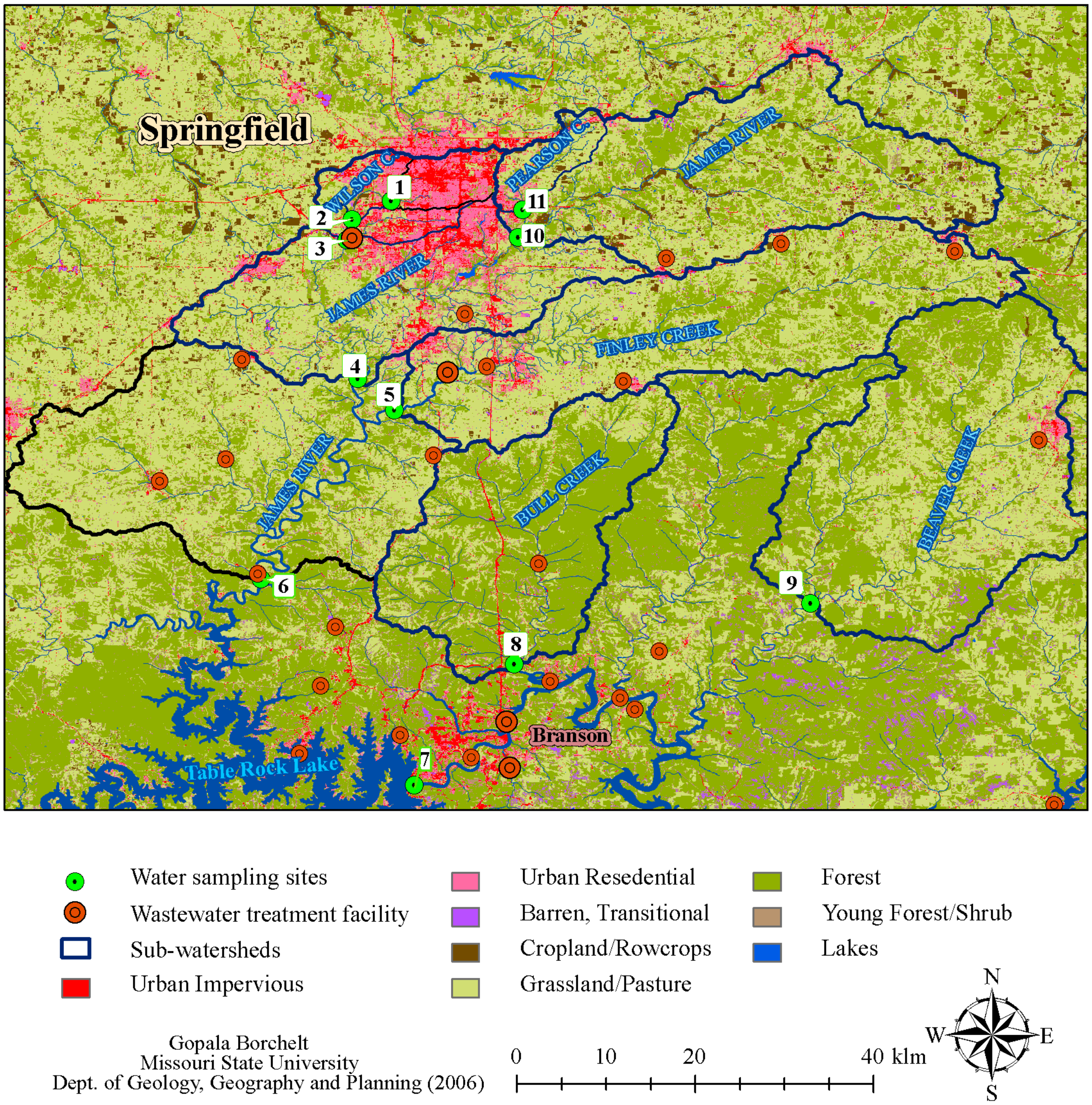
Hydrology and Sampling Sites in the Upper White River Basin



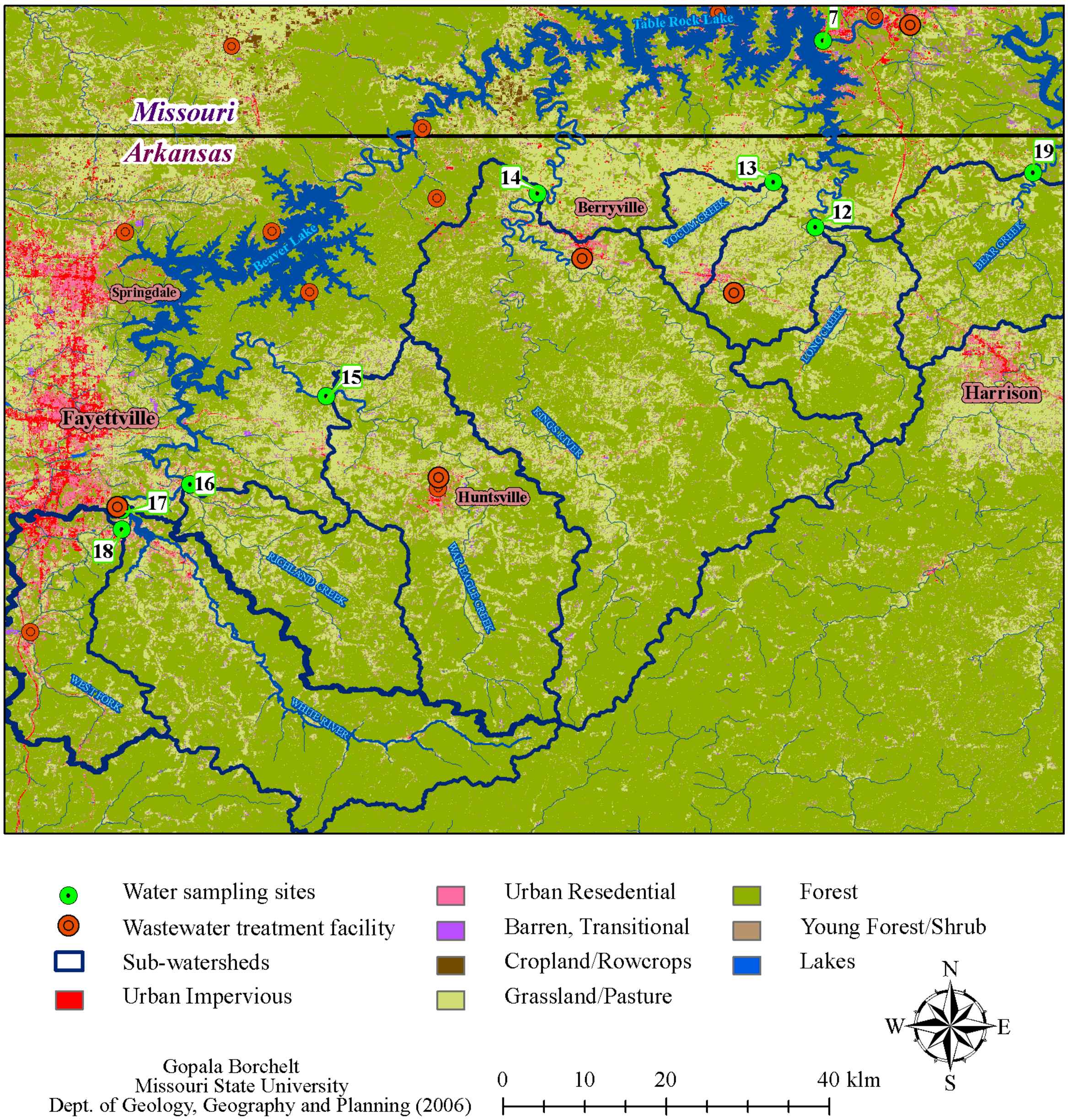
Wilson Creek Waterhseds with Land Use areas and Hydrology



James River, Bull Creek and Beaver Creek Waterhseds with Land Use areas and Hydrology



Arkansas Sub-waterhseds of the Upper White River Basin



APPENDIX-C

Standard Operating Procedures

Standard Operating Procedures
For Water Sampling

Missouri State University

Prepared by: ______________________________________ Date: ____________
Graduate Student Geospatial Sciences

Approved by: _____________________________________ Date: ____________
Quality Assurance Coordinator

Table of Contents

1. Scope and Applicability

This procedure is intended to serve as a field reference guide for the collection of water quality samples from the sites of the Upper White River Basin project. Water samples will be collected manually as grab samples on a bi-monthly basis and during base flow when possible.

2. Summary of Method

2.1 Water samples will be collected at a wade able depth. A sample bottle is inserted into the water at 1/3 of the depth of the water. The bottle is orientated into the water flow, submerged, and a sample taken. Care is taken not to collect stirred up sediments that have been disturbed by the sampling personnel while entering the stream. The bottle is held in the water until approximately 80% of the bottle is full and then quickly removed and capped. This will prevent sediment and dissolved solids from accumulating in the bottle.

3. Health and Safety

3.1 When wading in streams where water depths may be 1 meter deep or more, wear a life preserver and/or remove hip boots or chest waders. Currents can force wading field workers into deep water and water-filled boots can make swimming difficult.

3.2 When walking through densely vegetated areas along streams, be sure to look for and avoid toxic plants like poison ivy. Be sure to wear appropriate insect repellent and protective clothing for protection from mosquitoes, chiggers, and ticks. In addition, probe areas in your path with a walking stick to warn and disperse poisonous snakes like the cottonmouth and copperhead, which may inhabit riparian areas.

3.3 Be sure to clean up with bacteria disinfectant soap and water after wading in streams. This is particularly important for streams that drain livestock areas, sewage treatment plant effluents, and other obvious pollution sources. Under no circumstances should you drink the water from any stream.

3.4 The concentrated hydrochloric acid is highly corrosive. Use protective gloves during handling.

4. Personnel Qualifications

Water samples will be collected by Missouri State University (MSU) graduate students who have received appropriate training, prior coursework, and field experience regarding the collection of grab samples, and who are familiar with all of MSU’s sample handling and tagging procedures.

5. Equipment and Supplies

5.1 500 mL plastic sampling bottles and lids

5.2 Field Book, Pen, and Permanent Marker

5.3 Global Positioning System (GPS)

5.4 Cooler with ice and bottle rack

5.5 Concentrated H_2SO_4 in dropper bottle (Caution: highly corrosive. Handle with gloves.)

5.6 Protective Gloves

5.7 Narrow range pH paper (i.e. pH 0 6 3)

5.8 Glass or plastic stirring rods.

6. Procedure

6.1 Pre-sampling Activities

Sample collection equipment and sample containers must be decontaminated.

- Wash each sample container with a 2% (V:V) HCl wash (2ml hydrochloric acid and 100ml deionized water) prior to field work

6.2 Planning

The selection of the location for sampling is based on the locations of the USGS gage stations in the Upper White River watershed area. The sampling sites are all pre-selected before field sampling is started.

6.3 Water Sampling Activities

1. Label all sample bottles with the project name and site numbers allowing two for duplicates and two for field blanks.

2. Select the appropriately labeled bottle for a particular site and proceed to enter the water.

3. Rinse the sample bottle in the stream 2-3 times. Submerge bottle to 1/3 of depth of stream.

4. All samples should be taken from the flowing portion of the stream or if in a pool

at least one foot from shore and at least 6 inches below the surface. Since the sample bottle fills with water as a result of the hydrostatic pressure, it will continue to collect more suspended solids in the bottle than would normally be present if the sample bottle is held in the water after it is full. This sample will not be a representative sample and should be discarded. Rinse the bottle out and try again. A proper sample should occupy approximately 80% of the sample bottle.

5. To preserve the water sample for TN and TP analyses, add concentrated H_2SO_4 (4 drops for each 500 mL water sample). Check the pH of the water sample using narrow range pH paper. The pH should be ≤ 2.0. Continue to add H_2SO_4 if the pH remains > 2.0. Sample preservation and holding times are illustrated in Appendix II.

6. Each sample should be immediately sealed and appropriately labeled with the sample #
(i.e. UWRB-1-06/20/05-NP). Refer to the Data Records and Management section of this SOP for further information. Field notes should be recorded in a field book and copied to the standard data sheet located and stored in the geomorphology laboratory. Place each sample bottle into a cooler. Each sample should be kept above the ice, so that the sample is not submerged or altered in any way.

7. Do not forget to sample for a Field Duplicate for each sample run. Label these samples with the appropriate sample # (i.e. UWRB-1-06/20/05-1FD). See below in the Data and Records Management section of this SOP for further information.

6.4 Storage Activities

1. Once back at the geomorphology laboratory (Temple Hall room 125), transfer the sample bottles to the refrigerator. Note any necessary information on the standard data sheet.

2. Transfer the samples to the refrigerator in the chemistry laboratory (located between rooms 422 and 432 of Temple Hall) when chemistry laboratory personnel are available to receive the samples. Sign off on the samples on the Chain of Custody Records.

7. Data and Records Management

1. The sample number consists of the site ID, the date, analyses abbreviation, duplicate, and filter number if applicable. The Site ID is illustrated below.

Site ID	Site Description
WC-Springfield (1)	Wilson Creek, Springfield 7052000
WC-above SWTP (2)	Wilson Creek, Springfield 7052100
WC-at SWTP (3)	Wilson Creek, Battlefield 7052160
JR-Boaz (4)	James River, Boaz 7052250
Finley R (5)	Finley Creek, Riverdale 7052345
JR-Galena (6)	James River, Galena 7052500
WR-below TR Dam (7)	Table Rock Dam, Branson 7053400
Bull Ck (8)	Bull Creek, Walnut Shade 7053810
Beaver Ck (9)	Beaver Creek, Bradleyville 7054080
JR-above Springfield (10)	James River, Springfield 7050700
Pearson Ck (11)	Pearson Creek, Springfield 7050690
Long Ck (12)	Long Creek, Denver 7053207
Yocum Ck (13)	Yocum Creek, Oak Grove 7053250
Kings R (14)	Kings River, Berryville 7050500
War Eagle Ck (15)	War Eagle Creek, Hindsville 7049000
Richland Ck (16)	Richland Creek, Goshen 7048800
White R-Fayetteville (17)	White River, Fayetteville 7048600
West Fork White (18)	West Fork W.R., Fayetteville 7648550
Bear Ck (19)	Bear Creek, Omaha 7054410

2. The date should be that of when the sample was collected (mm/dd/yy). The analyses abbreviations are NP = Nitrogen and Phosphorus. The Field Duplicate and Field Blank will be indicated by either an “fd” or “fb”. Definitions of the types of samples required in this study are available in the Standard Operating Procedure for Quality Assurance / Quality Control with General Environmental Sample Collection, Handling, and Analyses (SOP Ref:QA/QCE-D-1).

Sample #
WC-Springfield (1) 1/20/05-NPfd
WC-Springfield (1) 1/20/05-NPfb

8. QA/QC

1. All sample bottles must be thoroughly cleaned in the laboratory prior to use. The samples bottles used have been approved by the Environmental Protection Agency in past studies, but those bottles must be clean to obtain meaningful results. The analysis of the Field Blanks will discover any problems associated with the decontaminating procedures.

2. Samples must be acidified for the nitrogen (N) and phosphorus (P) analyses. The pH must be ≤ 2.0.

3. Samples must be cooled immediately after collection to preserve and to retard chemical and biological activity.

4. The sample bottles should be labeled using the correct sample #. The standard data sheet includes the sample #, site ID, date, and any other necessary information.

5. Holding times are the maximum times that samples may be held before analysis is completed and still be considered valid. The sample collector must make sure that samples reach the laboratory as soon as possible after sampling so they can be analyzed before the holding time is exceeded. The holding time for TN and TP analyses is 28 days.

6. Trip blanks are not necessary for the water-sampling portion of this project. Two field blanks for each sample run is adequate. Label the field blanks with the appropriate sample # (fb). Remember that a field blank is an aliquot of deionized water treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all pre-analysis treatments.

7. A field duplicate is required to determine the precision of the water-sampling portion of this project. Two field duplicates, for the TN, TP (NP) for each sample run is adequate. The field duplicate bottle should be labeled with the appropriate sample # (i.e. UWRB-1-01/20/05-Nfd). Two samples are taken at the same time and placed under identical circumstances which are treated identically throughout the field and laboratory procedures.

9. References

MDNR, Required/Recommended Containers, Volumes, Preservatives, Holding Times, and Special Sampling Considerations, SOP # MDNR-FSS-001, February 2, 1998.

Scientific Instruments, Inc., Model 5200, DH-48 Sediment Sampler User Instructions and Parts List, http://www.scientif.com, June 1, 2001.

Appendix I. Standard Data Sheet for Water Sampling

Sample #	Site Name	Stage (m)

Appendix II. Parameters, Detection Limits, Accuracy, Precision Table

Parameter	# of Analyses	SOP Reference	Sample Preservation	Holding Time	Detection Limits	Accuracy	Precision
					Req'd	Req'd.	Req'd.
Total Nitrogen	216	W-D-1and TN-D-1	cool, H2SO4 to pH≤2.0	28 days	0.1 mg TN/L	20%	20%
Total Phosphorus	216	W-D-1 and P-D-1	cool, H2SO4 to pH≤2.0	28 days	0.1 mg TN/L	20%	20%

Standard Operating Procedures
For Total Phosphorus

Version 1

Missouri State University

Prepared by: ____ Date: _______________
Ph.D. Chemistry

Approved by: ____ Date: _______________
Quality Assurance Coordinator

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1. SCOPE AND APPLICABILITY

This Standard Operating Procedure provides the MSU laboratory personnel with guidance on the procedure for determining total phosphorus (TP) in surface water samples. TP is a measure of the all forms of phosphorus, including organic phosphorus. This method is not applicable to samples preserved with $HgCl_2$. The detection limit is # 0.005 mg TP/L and the upper range 0.5 mg TP/L. The upper range may be extended by sample dilution.

2. PERSONAL QUALIFICATIONS

2.1 Laboratory personnel shall have a working knowledge of the analysis procedures and will have at a minimum either attended the department-sponsored inspection and enforcement training or received training from an MSU employee knowledgeable of the proper sample analysis procedures.

3. HEALTH AND SAFETY

3.1 The analysis involves handling of freshwater samples that may contain live microorganisms and therefore pose some threat of infection. Laboratory personnel who are routinely exposed to such water samples are encouraged to protect themselves from water borne illnesses by wearing clean disposable gloves and washing their hands frequently.

3.2 The calibration standards, samples, and most reagents used in this method pose no unusual hazard to an analyst employing standard safety measures including protective clothing and safety goggles. Care must be taken when handling concentrated sulfuric acid and sodium hydroxide.

3.3 This procedure requires use of an autoclave or pressure cooker capable of heating samples to 120EC. All safety directions for using these devices should be followed carefully.

4. SUMMARY OF METHOD

4.1 All forms of phosphorus, including organic phosphorus, are converted to orthophosphate by an acid-persulfate digestion. The persulfate digestion procedure and phosphate determination follow EPA 365.2, with the size of the sample reduced.

A 10-ml volume of a well-mixed water sample is combined with sulfuric acid and ammonium or potassium persulfate and heated to approximately 120E in an

autoclave or pressure cooker. This quantitatively converts phosphorus compounds to orthophosphate. The digested sample is then analyzed for orthophosphate based on its reaction with a combined reagent containing ammonium molybdate, antimony potassium tartrate, and ascorbic acid to form intensely-colored molybdenum blue.

4.2 The desired performance criteria for this measurement are:

- X Detection limit: 0.005 mgTP/L
- X Precision: ∀ 20%
- X Accuracy: ∀ 20%
- X Minimum Quantification Interval: 0.001 mg TP/L

4.3 According to EPA 365.2. the applicable range for the method is 0.01 mg TP/L to 0.5 mg TP/L and may be extended by dilution. EPA 365.2 describes performance for undigested orthophosphate samples but not for digested samples.

5. INTERFERENCES

5.1 No interferences is normally observed for copper, iron, or silicate. However, high concentrations of iron can cause precipitation of, and subsequent loss, of phosphorus.

5.2 Arsenate may interfere when present at concentrations higher than phosphorus.

5.3 Sample turbidity and natural color may interfere. Turbidity may be removed by centrifugation or filtration after digestion.

5.4 Phosphate adsorbed on glass surfaces may affect measurements at low phosphate levels. Use of acid-washed glassware dedicated to this analysis prevents this interference.

5.5 A number of sources suggest that there is a problem with deposition of reaction products on cell windows. Some methods incorporate a surfactant to minimize this effect.

6. DEFINITIONS. The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

6.1 Analytical batch – The set of samples processed at the same time to a maximum of 10 samples.

6.2 Calibration blank – A sample of deionized water treated in the same manner as the calibration standards, but without the analyte.

6.3 Calibration standard – A solution prepared from the primary dilution standard solution or stock standard solutions. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

6.4 Field blank (FMB) – An aliquot of deionized water treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all pre-analysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

6.5 Field duplicate – Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

6.6 Laboratory reagent blank – An aliquot of deionized water treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

6.7 Laboratory control check (LCC) – A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard).

6.8 Laboratory duplicate – Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

6.9 Quality control check sample (QCC) – A sample containing analytes of interest at known concentrations (true values). The quality control check sample is obtained for a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

6.10 Method detection limit (MDL) – The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero. This is normally taken as three times the standard deviation of a series of measurements of blanks.

7. EQUIPMENT AND SUPPLIES

7.1 Balance – analytical, capable of accurately weighing to the nearest 0.0001 g.

7.2 Glassware – Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

7.3 Glass culture tubes with linerless polypropylene caps, 20 mm OD H 150 mm long. Clean before first use by heating to 120EC with digestion reagent. Rinse with 6M HCl and deionized water between uses.

7.4 Spectrophotometer: A spectrophotometer capable of measurements at 650 or 880 nm with a pathlength of 1.0 cm or longer is required. Instruments currently available that meet these requirements are Spectronic Unicam 20 Genesys, Hitachi UV-2001 or Shimadzu UV-1600 or equivalent.

7.5 Spectrophotometer cells: Cells, including flow cells, with path lengths of 1.0 cm or longer, should be used. This procedure will normally employ a flow cell with 5.0 cm path length.

7.6 Heating unit: Use either an autoclave or pressure cooker capable of heating samples to 121°C (15 – 20 PSI).

8. REAGENTS AND STANDARDS

8.1 Deionized water: Use deionized water that has been purified with a Barnstead/Thermolyne purification system that includes ion exchange and organic purification cartridges. Use this water for all procedures.

8.2 Sulfuric acid, 5.4M (11N): *Cautiously* add 310 ml concentrated sulfuric acid to an equal volume of water. CAUTION: This mixture will become very hot. Dilute to 1 L.

8.3 Antimonyl potassium tartrate solution: Dissolve 0.3 g $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$ (antimony potassium tartrate hemihydrate) in about 50 ml water and dilute to 100 ml. Store at 4°C in a dark bottle.

8.4 Ammonium molybdate reagent: Dissolve 4 g $(NH_4)_6Mo_7O_{24} \cong 4H_2O$ in 100 ml deionized water. Store at 4°C in a plastic bottle. Note: This solution (4% (w/v) ammonium molybdate) is commercially available.

8.5 Ascorbic acid, 0.1M: Dissolve 1.76 g ascorbic acid in deionized water and dilute to 100 ml. This solution is stable for approximately 1 week if stored at 4°C.

8.6 Combined reagent: Mix the above reagents (8.2.1, 8.3– 8.5) in the following portions for 100 ml of the mixed reagent. 23 ml 11N H_2SO_4, 27 ml water, 5 ml antimony potassium tartrate (8.3), 15 ml ammonium molybdate (8.4), 30 ml ascorbic acid (8.5), and enough water to make 100 ml.

8.6.1 Each solution should be at room temperature before mixing.

8.6.2 Mix in the specified order and mix well after each addition.

8.6.3 If turbidity forms in the combined reagent, shake and let stand for a few minutes until turbidity disappears before proceeding.

8.6.4 The stability of the solution is limited. It should be prepared fresh for each day's run, and used for a maximum of 8 hours.

8.7 Ammonium persulfate. Use ACS reagent grade $(NH_4)_2S_2O_8$. Dissolve in water at concentration of 0.32 g per ml. Prepare volume appropriate to the number of samples that will be run (at 0.25 ml per sample) – see table at right. Prepare fresh daily. (0.25 ml = 0.08 g $(NH_4)_2S_2O_8$).

Max # samples	g $(NH_4)_2S_2O_8$	Vol (ml)
40	3.2	10.0
100	8.0	25.0
200	16.0	50.0

8.8 Sodium hydroxide solution, 6M: Dilute 31 ml 50% NaOH solution (commercially available) to 100 ml. Store in plastic bottles.

8.9 Sodium hydroxide solution, 1M: Dilute 10 ml 6M NaOH (8.8) with 50 ml water.

8.10 Phosphate stock solution (1.000 mg P/L): This standard is commercially available. Alternately, dissolve 2.197 g anhydrous KH_2PO_4 and dilute to 500 ml in a volumetric flask. 1.00 ml = 0.100 mg $PO_4^{3\&}$ - P. Two batches of stock solution are needed, using different sources of phosphate (e.g., different lot numbers from the same supplier or different suppliers). Use one batch to prepare calibration standards and the other to produce quality control standards.

8.11 Phosphate intermediate solution (10.0 mg P/L): Dilute 5.00 ml of the phosphate stock solution (8.10) to 500.0 ml. 1.00 ml = 0.010 mg P.

8.12 <u>Preparation of phosphate calibration and quality control standards:</u> Prepare standards according to the table below. Use within 24 hours.

Solution	ml intermed. std.	Final ml	Concentration	Use
RBL	(deionized water)	---	0.000 mg $PO_4^{3\&}$-P/L	Calibration blank
TP-1	0.10	100.0	0.010 mg $PO_4^{3\&}$-P/L	Calibration standard
TP-2	0.20	100.0	0.020 mg $PO_4^{3\&}$-P/L	Calibration standard
TP-3	0.50	100.0	0.050 mg $PO_4^{3\&}$-P/L	Calibration standard
TP-4	1.00	100.0	0.100 mg $PO_4^{3\&}$-P/L	Calibration standard
TP-5	2.00	100.0	0.200 mg $PO_4^{3\&}$-P/L	Calibration standard
TP-6	5.00	100.0	0.500 mg $PO_4^{3\&}$-P/L	Calibration standard
LCC	5.00	250.0	0.200 mg $PO_4^{3\&}$-P/L	Lab control check
*QCC-	2.00*	100.0	0.200 mg $PO_4^{3\&}$-P/L	Quality control check

RBL = Reagent Blank; C = Calibration standard; LCC = Laboratory Control Check; QCC = Quality Control

* QCC solutions are prepared using alternate phosphate standard solution, i.e., not the same standard used to prepare the calibration standards

9. **PROCEDURE**

9.1 <u>Preparation of matrix spike samples:</u> Prepare two matrix spike samples using 10-ml aliquots of a water sample (or a smaller aliquot diluted to 10 ml) from the same sample. Spike each with 0.200 ml phosphate standard solution. (This should increase observed concentration by 0.200 mg/L.) Carry each through the sample preparation and analysis procedure (9.3 and following).

9.2 <u>Preparation of samples and standards – digestion:</u> All samples and standards (including quality control solutions) should be processed in the same manner.

9.2.1 Adjust the pH of a well-mixed sample to 6.0-8.0 using 6M NaOH and 1M H_2SO_4 or HCl.

9.2.2Transfer 10 ml of a well-mixed sample (or an aliquot of sample diluted to 10 ml) to a screw-cap culture tube.

9.2.3 Add 0.25 ml of the $(NH_4)_2S_2O_8$ solution (8.7) and 0.2 ml 5.4 M H_2SO_4 to each tube and mix.

9.2.4 Cap tubes loosely. – It is best to initially tighten the caps, invert the tubes a few times to ensure good mixing, and then unscrew the caps until the seal just becomes loose.

9.2.5 Place tubes in rack in either autoclave or pressure cooker.

9.2.6 For autoclave, follow manufacturer's directions and heat at 121EC for 30 minutes.

9.2.7 For pressure cooker: Add sufficient water to pressure cooker to bring water to a depth of at least 5 cm. Heat the pressure cooker on a hotplate set to high until the water in the cooker is boiling, as evidenced by a steady stream of steam emerging from the pressure cooker's vent. Maintain constant boiling (adjusting heat as needed) for 30 minutes. Allow pressure cooker to cool in air for about 30 minutes. After this initial cooling, it is normally possible to open the pressure cooker safely.

9.2.8 Remove the tubes from the autoclave or pressure cooker and cool to 20 - 30EC.

9.3 Neutralizing digested samples:

9.3.1 Add 0.40 ml 6M NaOH and 1 drop phenolphthalein solution to each sample and mix. *Adjust the volume of 6M NaOH if appropriate.*

9.3.2 Add 6M NaOH until the solution just turns pink, and then add 5.4 M H_2SO_4 until the pink color just clears.

9.4 Spectrophotometer setup:

9.4.1 The spectrophotometer should be allowed to warm up at least 30 minutes prior to the start of measurements.

9.4.2 Set the wavelength to 880 nm.

9.4.3 The spectrophotometer should be set up with a holder appropriate to the size cell used (normally 5 cm cell).

9.5 Color development and measurements:

9.5.1 Add 1.5 ml mixed molybdate reagent solution and mix to the first ten tubes, noting time.

9.5.2 Samples that appear turbid should be centrifuged or filtered.

9.5.3 Just before starting measurements, add mixed molybdate reagent solution to the next ten tubes, again noting time.

9.5.4 Add mixed molybdate reagent to other tubes to maintain an approximately 10 minute interval between time of mixing and measurement.

9.6 Spectroscopic measurements:

9.6.1 Zero the spectrometer using deionized water.

9.6.2Start measurements approximately ten minutes after addition of the mixed reagent.

9.6.3 Measurements may be continued up to thirty minutes past addition.

10. QUALITY CONTROL

10.1 Quality control program: The minimum requirements of the quality control program for this analysis consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks and other laboratory solutions as a continuing check on performance. The laboratory must maintain performance records that define the quality of the data that are generated.

10.1.1 Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in Sections 9.1 and 10.4.

10.1.2 Analyses of laboratory blanks are required to demonstrate freedom from contamination.

10.1.3 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control.

10.1.4 The laboratory should maintain records to define the quality of data that is generated.

10.2 Initial demonstration of performance. The following must be satisfied before the analytical procedure may be used for samples and before a new analyst may analyze samples.

10.2.1 Method Detection Limit (MDL) – To establish the ability to detect the analyte, the analyst shall determine the MDL by carrying through 7 or more separately prepared reagent blank solutions through the analytical procedure in Section 9. The average value, X, and the standard deviation of the values, s, shall be calculated. The MDL is equal to 3s (3 H standard deviation). The MDL and average value, X, should both be less than or equal to 0.005 mg P/L.

10.2.2 Initial Precision and Recovery – To establish the ability to generate acceptably precise and accurate results, the operator shall perform 10 replicates of a mid-range standard (0.200 mg TP/L), according to the procedure in Section 9. Using the results of the replicates compute the average value, S, and the standard deviation, s, for the analyte. The value of X should be within ∀ 10% of the true value. The standard deviation should be less than or equal to 10% of the average value.

10.3 The RBL, LCC, and QCC should be measured along with the standards at the start of the analytical cycle. The criteria are as follows:

Solution	Acceptable range	Comments
RBL	# 0.005 mg TP/L	ideally less than or equal to the required detection limit
LCC	0.180 - 0.220 mg TP/L	within ∀ 10% of the true value
QCC	0.180 - 0.220 mg TP/L	within ∀ 10% of the true value

10.4 With each sample batch of ten samples, the following should also be run (acceptance criteria noted):

Solution	
RBL	Ideally < 0.001 mg TP/L
LCC	0.180 - 0.220 mg TP/L
Lab Duplicate	greater of ∀20% or ∀ 0.005 mg TP/L
Field Duplicate	greater of ∀20% or ∀ 0.005 mg TP/L
2 matrix spike solutions	both 80% - 120% recovery

11. CALCULATIONS.

11.1 Calibration: Obtain a standard curve by plotting absorbance of standards (including the reagent blank) versus concentration. The data will be fit to a linear equation using a spreadsheet program such as Excel.

11.2 Calculation of concentrations: The concentration of each solution will be calculated based on the polynomial equation for the regression data. The concentrations will represent the concentration of analyte in the 10-ml aliquot in (9.2.1).

11.3 Calculation of water sample concentrations, corrected for dilution: For samples for which dilution was required, the concentration in the original water sample is calculated as:

$$C_{sample} = C_{analysis} \times \frac{10.0 \text{ ml}}{V_{aliquot}}$$

where C_{sample} is the concentration in the original water sample, $C_{analysis}$ is the concentration of the solution as determined in (11.2), and $V_{aliquot}$ is the volume of the aliquot diluted to 10 ml in (9.2.1).

11.4 Reporting results: Results should be reported to 0.001 mg TP/L precision.

11.5 The evaluation of MDL and precision require calculation of standard deviation. Standard deviations should be calculated as indicated on the right, where n = number of samples, x = concentration in each sample. Note: This is the sample standard deviation calculated by the STDEV function in Microsoft Excel.

$$s = \left(\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1} \right)^{1/2}$$

11.6 Calculation of recoveries: Recovery of matrix spike solutions shall be calculated as indicated on the right, where S = concentration observed for spiked sample, U = concentration observed for unspiked sample, and 0.200 is the concentration increase expected upon spiking. Both S and U are concentrations based on (11.2), i.e., not adjusted for dilution of an aliquot. The factor 1.02 corrects for the small volume change upon spiking.

$$\% recovery = \frac{1.02 \times S - U}{0.200}$$

12. POLLUTION PREVENTION:

12.1 All wastes from these procedures shall be collected and disposed of according to existing waste policies within the MSU Chemistry Department.

12.2 Volumes of reagents made should mirror the number of samples being analyzed. These adjustments should be made to reduce waste.

REFERENCES

EPA Method 365.2, Phosphorus, All Forms (Colorimetric, Ascorbic Acid, Single Reagent).

Standard Methods for the Examination of Water and Waste Water, Method 4500-P, Phosphorus, APHA, 19th Edition, 1995, especially B. Sample Preparation, and E. Ascorbic Acid Method.

"21.0: Determination of Total Phosphorus," EPA Handbook of Methods for Acid Deposition Studies: Laboratory Analysis for Surface Water Chemistry," EPA publication 600/4-87/026, August 1987.

APPENDIX A: Variations from EPA Method 365.2

Sample size: The volume of water sample is reduced from 50 ml to 10 ml and the amounts of sulfuric acid and $(NH_4)_2S_2O_8$ have been adjusted proportionately, as indicated in the table below.

Changes:	EPA 365.2	This Method
Sample size:	50 ml	10 ml
5.4M (11N) sulfuric acid added (ml):	1.0	0.20
Ammonium persulfate added (g):	0.4	0.080

Note that a similar EPA digestion procedure (EPA 1987) employs a 10 ml sample.

pH adjustment: EPA 365.2 indicates that the pH of each digested sample and standard should be adjusted to 7.0 ± 0.2 by addition of 1N NaOH. The method employed here uses a less critical pH adjustment (9.3) that is, however, consistent with Standard Methods 4500-P B and E. This variation is justified as follows:

- It should be noted that precise adjustment of the pH of an unbuffered solution in this range is difficult – addition of 1 μL (1/50 drop) 1N NaOH to 50 ml deionized water should increase the pH by more than one unit.

- In addition, it is noteworthy that in the same step (8.1.4) in which the pH 7.0 ± 0.2 neutralization is specified, the method also states that if a sample is not clear after the neutralization step, 2-3 drops 11N H_2SO_4 should be added – enough acid to drop the pH below 2.0. This suggests that precise pH adjustment is not really critical.

- In addition, the combined reagent contains 2.5 N sulfuric acid. Addition of 3 ml of this solution to 50 ml of a pH 7.0 sample (as specified in Method 365.2) results in a solution that is 0.141 N acid, so that the trace excesses of acid or base in samples ranging from pH 6.0 to 8.0 are insignificant.

- Method 365.2 indicates that the pH should be adjusted using 1 N NaOH. In the digestion step, 1.0 ml 11 N acid is added to a 50 ml sample (equivalent to 0.40 ml for a 20 ml sample). Neutralization of this amount of acid with 1 N NaOH requires 11 ml for a 50 ml sample (4.4 ml for a 20 ml sample). This represents a very significant volume change. In this method, the initial step of the neutralization is carried out using 6N NaOH, decreasing the required volume of base considerably.

Addition of ammonium persulfate: In the original method, ammonium persulfate is added as a solid using an appropriate size scoop. As the sample volume is reduced from 50 ml to 10 ml, the amount of ammonium persulfate must be reduced from 0.4g to 0.08 g. However, it would be difficult to add 0.08 g using a scoop. Instead,

ammonium persulfate is delivered as an aqueous solution (0.25 ml of 0.32 g/ml solution). This provides the required amount very reproducibly.

Preparation of combined reagent: EPA 365.2 requires preparation of both 11 N and 5 N sulfuric acid, for digestion and combined reagent preparation, respectively. In this method, 11 N sulfuric acid is used to prepare the mixed reagent, eliminating the need for the 5N sulfuric acid and reducing waste generation.

Detection limits: The desired detection limit for this method is < 0.005 mg TP/L. Method 365.2, an EPA method intended for measuring phosphorus in surface waters, does not specify a detection limit, though it does specify that the method is applicable to samples in the range of 0.01 to 0.5 mg P/L. In the Precision and Accuracy section, reproducibility for a 0.029 mg P/L orthophosphate sample was ±0.010 mg P/L, suggestion a detection limit substantially higher than 0.005 mg P/L. Note that the performance data described for EPA 365.2 is based on undigested orthophosphate samples.

Standard Operating Procedures
For Total Nitrogen

Version 1

Missouri State University

Prepared by: ____ Date: ________________
Ph.D. Chemistry

Approved by: ____ Date: ________________
Quality Assurance Coordinator

Table of Contents

1. Scope and Applicability

This Standard Operating Procedure provides the MSU laboratory personnel with guidance on the procedure for determining total nitrogen (TN) in surface water samples. TN is a measure of the all forms of nitrogen present in a sample. This method may give poor recoveries for organic compounds which contain nitrogen-nitrogen double bonds or terminal nitrogen groups (e.g., H-N=C). As described here, the detection limit is # 0.1 mg TN/L and the upper range 5 mg TN/L. The upper range may be extended by sample dilution.

2. Summary of Method

2.1 The procedure outlined below follows that described by Crumpton, Isenhart, and Mitchel.

A water sample is combined with an alkaline persulfate oxidizing solution and heated to approximately 120E in an autoclave or pressure cooker. This quantitatively converts most nitrogen compounds to nitrate. The digested sample is acidified with hydrochloric acid, and then its absorbance is measured at three wavelengths (230, 225, and 220 nm). The absorbance data are used to compute the second derivative at 225 nm. Comparison of the second derivative with that of similarly-treated standards allows estimation of total nitrogen.

2.2 The desired performance criteria for this measurement are:

X Detection limit: 0.1 mg TN/L

X Precision: ± 20%

X Accuracy: ± 20%

X Minimum Quantification Interval: 0.1 mg TN/L

The applicable range for the method is # 0.1 mg TN/L to 5 mg TN/L and may be extended by dilution.

3. Definitions The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

3.1 Analytical batch – Set of samples processed at the same time - max of 12 samples.

3.2 Calibration blank – A sample of deionized water treated in the same manner as the calibration standards, without the analyte.

3.3 Calibration standard – A solution prepared from the primary dilution standard solution or stock standard solutions. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.

3.4 Field blank (FMB) – An aliquot of deionized water treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all pre-analysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.5 Field duplicate – Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.6 Laboratory reagent blank (RBL) – An aliquot of deionized water treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to

determine if the if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7 Laboratory control check sample (LCC) – A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard).

3.8 Laboratory duplicate – Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

3.9 Quality control check sample (QCC) – A sample containing analytes of interest at known concentrations (true values). The quality control check sample is obtained for a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

3.10 Method detection limit (MDL) -- The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

4. Health and Safety

4.1 The analysis involves handling of freshwater samples that may contain live microorganisms and therefore pose some threat of infection. Laboratory personnel who are routinely exposed to such water samples are encouraged to protect themselves from water borne illnesses by wearing clean disposable gloves and washing their hands frequently.

4.2 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

4.3 Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis.

4.4 The following chemicals have the potential to be highly toxic or hazardous; for detailed explanations consult the MSDS.

X Sodium hydroxide

X Hydrochloric acid

4.5 This procedure requires use of an autoclave or pressure cooker capable of heating samples to 120EC. All safety directions for using these devices should be followed carefully.

5. Interferences

5.1 Sample turbidity may interfere. Turbidity can be removed by filtration of the digested solution through a 0.45µm pore diameter membrane filter prior to analysis, or by centrifugation.

5.3 Sample color that absorbs strongly around 225 nm (after digestion) interferes.

6. Personnel Qualifications

Laboratory personnel shall have a working knowledge of the analysis procedures and will have at a minimum either attended the department-sponsored inspection and enforcement training or received training from an MSU employee knowledgeable of the proper sample analysis procedures.

7. Equipment and Supplies

7.1 Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

7.2 Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

7.3 Glass culture tubes with linerless polypropylene caps, 20 mm OD × 150 mm long. Clean tubes before use by heating to 120EC with digestion reagent, or by soaking in 5% HCl. New tubes may be used without prior cleaning.

7.6 Spectrophotometer: Hitachi UV-2001 or Shimadzu UV-1600, or equivalent.

7.7 Spectrophotometer cells: 1 cm or longer path length (flow cells may be used)

7.8 Heating unit – Use one of the following:

X Autoclave

X Pressure cooker

8. Reagents and Standards

8.1 Deionized water: Use deionized water that has been purified with a Barnstead/Thermolyne purification system (or equivalent) that includes ion exchange and organic purification cartridges. Use this water for all procedures.

8.2 6 M HCl (6N HCl): Add concentrated HCl to an equal volume of water with mixing.

8.3 6 M NaOH: Prepare by one of the following methods:

1. Dissolve 240 g ACS reagent grade NaOH per liter of water.
2. Dilute 320 ml 19 M NaOH (commercially available) per liter.

8.4 Nitrate solutions: Prepare two sets of the following, using different sources of potassium nitrate (e.g., different lot numbers from the same supplier or different suppliers). Use one to prepare calibration standards and the other to produce quality control standards.

1. Stock nitrate solution (1.00 mg N/ml): Dry KNO_3 in an oven (105EC) for 24 hours. Dissolve 7.218 g in water with 2 ml $CHCl_3$ (preservative) and dilute to 1 L. This solution is stable for at least 6 months. 1.00 ml = 1.00 mg $NO_3^{\&}$-N. Commercially prepared nitrate solutions may be purchased instead.
2. Intermediate nitrate solution (0.10 mg N/ml): Dilute 25.0 ml nitrate stock solution to 250 ml. This solution is stable for six months. 1.00 ml = 0.100 mg $NO_3^{\&}$-N.

8.5 Urea stock solution (1.00 mg N_{org}/ml) : $CO(NH_2)_2$. Dissolve 536 mg urea and dilute to 250.0 ml. Store in refrigerator. 1.00 ml = 0.10 mg N_{org}.

8.6 Urea intermediate standard solution (0.100 mg N_{org}/ml): Dilute 10.0 ml urea stock solution to 100 ml with water. Store in refrigerator. Prepare monthly. 1.00 ml = 0.100 mg N_{org}.

8.7 Preparation of nitrate calibration and digestion efficiency standards: Prepare standards according to the table below. Prepare fresh daily.

Standard solution	Prepare using	ml intermed (0.100 mg N/L) standard solution	Final ml	Concentration	Use
RBL	-----	0.00	250.0	0.00 mg $NO_3^{\&}$-N/L	Calibration blank
TN-1	Intermediate nitrate standard solution (0.10 mg N/L)	0.10	100.0	0.10 mg $NO_3^{\&}$-N/L	Calibration standard
TN-2		0.20	100.0	0.20 mg $NO_3^{\&}$-N/L	Calibration standard
TN-3		0.50	100.0	0.50 mg $NO_3^{\&}$-N/L	Calibration standard
TN-4		1.00	100.0	1.00 mg $NO_3^{\&}$-N/L	Calibration standard
TN-5		2.00	100.0	2.0 mg $NO_3^{\&}$-N/L	Calibration standard
TN-6		5.00	100.0	5.0 mg $NO_3^{\&}$-N/L	Calibration standard
LCC		1.00	100.0	1.0 mg $NO_3^{\&}$-N/L	Lab control check
QCC	Alternate intermediate nitrate standard*	1.00	100.0	1.0 mg $NO_3^{\&}$-N/L	Quality control check
DEC	Urea intermediate standard	2.0	100.0	2.0 mg N_{org}/L	Digestion efficiency check

RBL = Reagent Blank; C = Calibration standard; LCC = Laboratory Control Check; QCC = Quality Control Check; CE = Column Efficiency Check; DEC = Digestion Efficiency Check * Prepared using alternate nitrate standard solution, i.e., not the same standard used to prepare the calibration standards.

8.8 Digestion reagent: Dissolve 60.0 g potassium persulfate ($K_2S_2O_8$, N < 0.001%) per liter of 1.5 M NaOH. Prepare 1.5 M NaOH by diluting 80 ml 50% NaOH solution (commercially available; N < 5 ppm) per liter of deionized water. If the total nitrogen in a reagent blank is greater than 0.01 mg/L, recrystallize the potassium persulfate as follows:

Dissolve 75 g $K_2S_2O_4$ (reagent grade, < 0.001% N) in 500 ml 60EC water. Filter the solution rapidly through loosely packed Pyrex wool and cool in ice water to about 4EC while stirring continuously. Collect the crystals by vacuum filtration on a sintered-glass filter and wash with small amounts of ice water. Dry as

rapidly as possible in a vacuum over anhydrous calcium chloride. Store in a vacuum desiccator over anhydrous calcium chloride.

9. Procedure

9.1 <u>Preparation of matrix spike samples:</u>

1. Prepare two matrix spike samples using 10-ml aliquots of water sample (or a smaller aliquot diluted to 10 ml) from the same sample.
2. Spike with 0.10 ml intermediate urea standard (0.10 mg N_{org}/L) solutions. This should increase observed concentration by 1.0 mg/L.) Carry each through the sample preparation and analysis procedure (9.2 and following).

9.2 <u>Preparation of samples – digestion:</u> All samples and standards (including quality control solutions) should be processed in the same manner.

1. Transfer a portion of each well-mixed sample to a beaker or flask, and then add NaOH until the solution is just neutral (measure using litmus, pH paper, or a pH meter).
2. Combine 10 ml sample (or an aliquot of sample and enough water to equal 10 ml) and 1.5 ml digestion reagent in a culture tube and seal securely with polypropylene cap. The analyst may determine an appropriate volume based on previous measurements at a site or other information, and then adjust the volume of sample used to minimize the need for later dilutions or reruns.
3. Place tubes in rack in either autoclave or pressure cooker.
4. For autoclave, follow manufacturer's directions and heat at 120EC for 30 minutes.
5. For pressure cooker: Add sufficient deionized water to pressure cooker to bring water to a depth of at least 5 cm. Heat the pressure cooker on a hotplate set to high until the water in the cooker is boiling, as evidenced by a steady stream of steam emerging from the pressure cooker's vent. Maintain constant boiling (adjusting heat as needed) for 60 minutes. Allow pressure cooker to cool in air for at least 30 minutes. After this initial cooling, a stream of cold water from a faucet may be used to speed up the cooling process. Do not open the cooker until it has cooled to near room temperature.
6. CAUTION: The tubes may be under pressure. Wearing of eye protection is essential. Open each tube carefully to vent any pressure buildup. (Note: After the digestion procedure, many samples will contain some precipitate and/or will appear cloudy. This normally clears up when acid is added in the next step.)
7.

9.3 <u>Sample treatment:</u>

1. Add 0.4 ml 6M HCl to each sample and stir. (The light colored precipitate that forms during the digestion process will usually dissolve completely upon acidification.)
2. Filter turbid samples through a 0.45 µm membrane filter, or centrifuge.

9.4 <u>Spectroscopic measurements:</u>

1. Allow spectrophotometer to warm up at least 15 minutes before starting data collection.

2. Use a 1-cm quartz (silica) cuvette for all measurements. Other cell path lengths may be used. A flow cell may be used to expedite measurements.

3. Run a baseline adjustment scan over the range of 230 – 220 nm (or wider), with deionized water in the cuvette that will be used for measurements.

4. Set the spectrophotometer to take readings at 230, 225, and 220 nm.

5. Record absorption measurements of the following:

a. Reagent blank
b. Standards TN-1 and TN-2 (0.1 and 0.2 mg TN/L)
c. Reagent blank
d. Standards TN-3 and TN-4 (0.5 and 1.0 mg TN/L)
e. Reagent blank
f. Standards TN-5 and TN-6 (2.5 and 5.0 mg TN/L)
g. Reagent blank

6. Next, run the laboratory control standard check (LCC), quality control check (QCC), and digestion efficiency check (DEC).

7. Run samples. With every batch of 12 samples maximum, also run:

a. Laboratory control check (LCC)
b. Reagent blank (RBL)
c. Two matrix spike samples from the same sample
d. One laboratory duplicate.
e. One field duplicate.

8. Any samples for which the absorbance at 220 nm is greater than 1.0 should be diluted and rerun.

9. The procedure described above may be implemented with a programmed method that provides data output in spreadsheet format. A flow cell system may be used for spectrophotometric measurements.

10. Calculations

10.1 Calculation of second derivatives: Carry out the computation, $4\times(A_{230} + A_{220} - 2\times A_{235})$ (this is actually 100×second derivative) for each data set. Note that the Hitachi UV-2001's computational method for three wavelength photometric measurements is based on a parameter that is directly proportional to the second derivative, so that its results are equivalent to those described above.

10.1 Calibration: For each range of standards, obtain a standard curve by plotting the second derivatives of standards (including the reagent blank) versus concentration. Fit the data to a 2^{nd}-order equation using a spreadsheet program such as Excel. It is most convenient to fit the data with the second derivative as "x" and the concentration as "y" to facilitate calculation of concentrations of samples from absorbance data. Note that the Hitachi UV-2001's computational program provides concentration output based on this type of calculation.

10.2 Calculation of concentrations: The concentration of each solution will be calculated based on the 2^{nd}-order equation for the regression data. The concentrations will represent the concentration of analyte in the 10-ml aliquot in (9.2.1).

10.3 Calculation of water sample concentrations, corrected for dilution: For samples for which dilution was required, the concentration in the original water sample is calculated as:

$$C_{sample} = C_{analysis} \times \frac{10.0 \text{ ml}}{V_{aliquot}}$$

where C_{sample} is the concentration in the original water sample, $C_{analysis}$ is the concentration of the solution as determined in (10.2), and $V_{aliquot}$ is the volume of the aliquot diluted to 10.0 ml in (9.2.1). If additional dilution was carried out (e.g., for samples with $A_{220} > 2.0$), include an additional correction factor.

10.4 Reporting results: Results should be reported to 0.1 mg TN/L precision.

10.5 Standard Deviation: The evaluation of MDL and precision require calculation of standard deviation. Standard deviations should be calculated as:

$$s = \left\{ \frac{\Gamma x^2 - \frac{(\Gamma x)^2}{n}}{n \& 1} \right\}^{½}$$

where n = number of samples, x = concentration in each sample. Note: This is the sample standard deviation calculated by the STDEV function in Microsoft Excel.

10.6 Calculation of recoveries: Recovery of matrix spike solutions shall be calculated as:

$$\% \text{ recovery} = \frac{(S - U)}{T} \times 100\%$$

where S = observed for spiked sample, U = observed for unspiked sample, T = spike value (normally 0.25 mg/L or 0.50 mg/L). Both S and U are concentrations based on (10.2), i.e., not adjusted for dilution.

11. QA/QC

11.1 Quality control program: The minimum requirements of the quality control program for this analysis consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks and other laboratory solutions as a continuing check on performance. The laboratory must maintain performance records that define the quality of the data that are generated.

1. Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in Sections 9.1, 10.6, 11.3, and 11.4.
2. Analyses of laboratory blanks are required to demonstrate freedom from contamination.
3. The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control.
4. The laboratory should maintain records to define the quality of data that is generated.

11.2 Initial demonstration of performance. The following must be satisfied before the analytical procedure may be used for samples and before a new analyst may analyze samples.

1. Method Detection Limit (MDL) – To establish the ability to detect the analyte, the analyst shall determine the MDL by carrying through 7 or more separately prepared reagent blank solutions through the analytical procedure in Section 9. The average value, X, and the standard deviation of the values, s, shall be calculated. The MDL is equal to 3s (3 × standard deviation). The MDL and average value, X, must both be less than 0.10 mg N/L.
2. Initial Precision and Recovery – To establish the ability to generate acceptably precise and accurate results, the operator shall perform 10 replicates of a mid-range standard (0.50 mg $NO_3^{\&}$-N/L for low range, 1.0 for high range), according to the procedure in Section 9. Using the results of the replicates compute the average value, X, and the standard deviation, s, for the analyte. The value of X should be within ± 20% of the true value. The standard deviation should be less than or equal to 20% of the average value.

11.3 The RBL, LCC, QCC, CEC, and DE should be measured along with the standards at the start of the analytical cycle. The criteria are as follows:

Solution	Acceptable range	Comments
RBL	# 0.10 mg TN/L	less than or equal to the required detection limit
LCC	0.80 - 1.20 mg TN/L	within ± 20% of the true value
QCC	0.80 - 1.20 mg TN/L	within ± 20% of the true value
DEC	2.0 – 3.0 mg TN/L	corresponds to 80 – 120% efficiency for oxidation of urea to nitrate

11.4 With each sample batch of twelve samples, the following should also be run (acceptance criteria noted):

Solution	
RBL	< 0.10 mg TN/L
LCC	0.8 – 1.20 TN/L
Lab Duplicate	greater of ±20% or ± 0.20 mg TN/L
Field Duplicate	greater of ±20% or ± 0.20 mg TN/L
2 matrix spike solutions	both 80% - 120% recovery

11.5 Calibration: Calibration employs a quadratic equation to represent the relationship between the second derivative of absorbance observed for each standard and its concentration. Based on this equation, the absorbance of each standard should predict the concentration of the standard to within ± 20% accuracy.

12. Pollution Prevention: All wastes from these procedures shall be collected and disposed of according to existing waste policies within the MSU Chemistry

Department. Volumes of reagents made should mirror the number of samples being analyzed. These adjustments should be made to reduce waste.

13. References

"Nitrate and organic N analyses with second-derivative spectroscopy," Crumpton, Isenhart, and Mitchell, *Limnol. Oceanogr.*, 37(4), 1992, 907 – 913.

"18.0: Determination of Total Nitrogen," EPA Handbook of Methods for Acid Deposition Studies: Laboratory Analysis for Surface Water Chemistry," EPA publication 600/4-87/026, August 1987.

Standard Methods for the Examination of Water and Waste Water, Method 4500-N_{org} D, Persulfate Method (Proposed), APHA, 19^{th} Edition, 1995.

"Simultaneous Determination of Total Nitrogen and Total Phosphorus in Water Using Peroxodisulfate Oxidation," Ebina, Tsutsui, and Shirai, *Water Res.* 17(12), pp. 1721 - 1726, 1983.

Appendix I: Method Information.

Method: The Crumpton method was recommended by the Jones group at the University of Missouri. The greatest potential for interference – high absorbance by organic matter – has not been observed in any of our samples.

Digestion: A variety of alkaline persulfate methods have been proposed (Crumpton (1992), EPA (1987), Standard Methods 4500-N_{org} D (1995), Ebina (1983)), differing in the concentrations of persulfate and hydroxide, and in the ratio of digestion reagent to sample. We are following the procedure described by Crumpton, which is also employed by the Jones group at the University of Missouri.The EPA protocol (1987) did not include a standard to evaluate the efficiency of the persulfate digestion step. Crumpton's work employed urea for evaluating digestion efficiency.

Nitrate determination – spectroscopic methods: In Crumpton's work, the calibration range was extended to 15 mg TN/L, corresponding to absorbance values greater than 5.0 at 220 nm. With conventional spectrophotometers, absorbance measurements are unreliable at such high absorbance values.

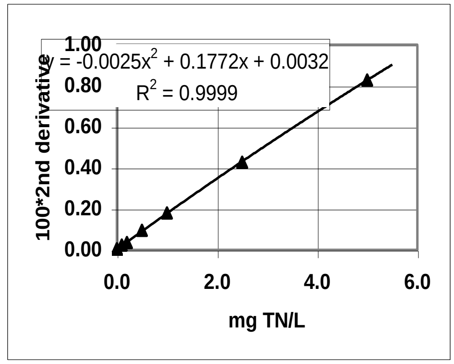
Comments about the method:

1. Our experience with this method has shown that the desired sensitivity and detection limit may be achieved using a 1-cm cell.
2. Our calibration procedure calls for measurement of four reagent blanks rather than a single reagent blank. This change makes the calibration at low concentrations more reliable.
3. The spectrophotometer is zeroed with a reagent blank solution rather than deionized water. This compensates for the influence of the digestion reagent on the background.

4. A plot of second derivative versus concentration over the concentration range 0 – 5 mg TN is slightly curved. Therefore, the data is fit to a 2^{nd} order (quadratic equation) rather than to a linear equation.

II. Method Performance Data

1. Calibration data: Right is a representative calibration curve for this method. Note that this plot includes four replicates of the blank, which appear superimposed on this plot. Over the range of calibration from 0 – 5 mg TN/L, slight curvature is observable. The use of a second order (quadratic) data fit compensates for the nonlinearity.



Note: In the calibration procedure as implemented, the x- and y-axes are reversed so that in the regression equation, "x" is the value of the second derivative and y is the concentration. This facilitates the computations. The quality of the fit is equivalent to that shown here.

2. Laboratory control checks: Measurement of 9 laboratory control checks (1.0 mg TN/L) over four dates yielded values in the range from 0.94 to 1.06 mg TN/L, with an average value of 0.98 mg TN/L and a standard deviation of 0.05 mg TN/L (5%).

3. Quality control checks: Measurement of 7 quality control checks (1.0 mg TN/L) over four dates yielded values in the range from 0.90 to 1.01 mg TN/L, with an average value of 0.96 mg TN/L and a standard deviation of 0.03 mg TN/L.

4. Reagent blanks and detection limit: Measurement of 9 digested reagent blanks over four dates yielded values in the range from –0.16 to 0.14 mg TN/L, with 7 of the nine in the range –0.05 to +0.05 mg TN/L. Eliminating the two extreme values as outliers, the average value is –0.01 mg TN/L and a standard deviation of 0.036 mg TN/L, for a detection limit of 0.11 mg TN/L.

5. Digestion efficiency: Our measurements have shown that digestion of urea samples gives results within the acceptable range.

6. Matrix spike recovery: Measurement of eight spiked solutions (two duplicates of four different samples) yielded recoveries in the range of 82 – 110%, with an average value of 97%. Recoveries for seven of the eight measurements fell between 90 – 110%.

7. Field blanks: Two field blanks yielded results of 0.04 and 0.05 mg TN/L.

8. Laboratory duplicates: Evaluation of five sets of laboratory duplicates found percent differences (difference/average as percentage) ranging from 0.9 to 10.2%, with an average value of 4.0%. The largest difference corresponded to a sample taken under high flow conditions that contained high levels of sediment.

9. Field duplicates: Two sets of field duplicates had percent differences of 9 and 18%. The sample with the larger difference was taken under conditions of high flow.