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An Empirical Water Quality and Best Management Practice Prioritization Model for Select Arkansas Watersheds

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Biological Engineering

by

James McCarty University of Arkansas Bachelor of Science in Biological Engineering, 2006

> July 2015 University of Arkansas

This thesis is approved for recommendation to the Graduate Council.

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ABSTRACT

The purpose of this study was to prioritize subwatersheds using water quality data and watershed characteristics. Water quality data was provided through studies by the Arkansas Natural Resources Commission, Beaver Water District, Arkansas Water Resources Center, and publicly available USGS gage data. A total of 114 sites across five HUC-8 watersheds were analyzed, including 12 USGS gages. Watershed characteristic data was retrieved from USGS and Arkansas GeoStore geodatabase repositories. A significant linear relationship between baseflow and stormflow nutrient concentrations was established allowing for the use of baseflow concentrations in the prioritization methodology. Pearson correlation, linear regression, classification and regression tree, and change point analysis were used to study relationships between watershed characteristics and four constituents; nitrate-nitrogen, total nitrogen, soluble reactive phosphorus, and total phosphorus. Human disturbance of the landscape, particularly forested area and agricultural production in the riparian buffer were the most significantly correlated with nutrient concentrations. The density of poultry houses within the watershed as well as a combined human disturbance index were also significantly correlated to nutrient concentrations. These relationships were used to develop prioritization methodologies for HUC-12 subwatersheds, ranking them in order of predicted constituent concentration. The first method utilized percent forest within the riparian buffer to separate watersheds by the predicted change point in nutrient concentrations; ultimately, those exhibiting less than 50% forested buffer were identified as a priority. The second method also used significant change points to classify nutrient trends as either high or low, but included multiple metrics: agricultural land use in the riparian buffer, forested riparian buffer, human use index, and poultry house density. Subwatersheds were ranked higher in priority as they increased in the number of predictors indicating high nutrient concentrations. Finally, as a way to corroborate the results, analysis of variance was performed on subwatersheds identified as a priority versus those that were not using available water quality data. Priority subwatersheds contained significantly higher nutrient concentrations. Empirical watershed models and prioritization schemes such as this one may provide a viable alternative to extensive deterministic watershed modeling in watersheds lacking adequate water quality data.

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I. INTRODUCTION

Watershed models are used to fill in the gaps in our understanding of watershed hydrology, the effects of human influence on the landscape, and identify nutrient sources. Physical watershed models require data from multiple sources, including meteorology, hydrology (H), water quality (WQ), permitted effluent discharges, and even satellite imagery of soils, land use and topography. Model calibration and validation are critical steps in model application, producing a representation of the watershed being assessed and predicting H/WQ based on the criteria of the study (Moriasi et al 2007).

Ultimately, these models are used to further our understanding of how H/WQ will likely respond to watershed changes or possibly to "influence legal, regulatory, and programmatic decision making" (Harmel et al. 2006). Watershed models might be used to evaluate the effects of best management practices (BMPs) on H/WQ (e.g., Gitau & Chaubey 2010) or to identify subwatersheds that are potential nutrient sources relative to the rest of the catchment (e.g., Pai et al 2011). These subwatersheds could be prioritized (i.e., subwatershed prioritization) to help local, state and federal programs focus time, energy and resources to efficiently address WQ problems and likely result in measurable improvements. For example, Saraswat et al (2010a, 2010b, 2013a, 2013b, & 2013c) prioritized subwatersheds in several HUC-8 watersheds in Arkansas based on nutrient yields from the landscape, separating the subwatersheds in categories representing low to high priorities for future funding.

The problem facing many watershed modelers is limitations on the availability of data, both temporally and spatially. While meteorology, permitted effluent discharges, soils, land use, and topography are readily available for the entire watershed, H/WQ are often limited in availability across the watershed or not available at all. To account for watersheds with limited or no H/WQ data, parameterization from a model of another similar watershed may be used as a surrogate (Wagener & Wheater 2006). This method, called regionalization, has been used successfully to calibrate/validate watersheds; however, confidence is highly dependent on the similarity of the paired catchment (Sellami et al. 2013). In data-limited situations, some states have even found it suitable to develop and use watershed models that have neither been calibrated nor validated for H/WQ (e.g., see Saraswat et al 2013a & 2013c). WQ data collection for model calibration and validation is a significant budgetary and temporal investment that is

not always feasible under the current fiscal constraints of governing bodies. However, it is important that non-calibrated models do not become the default approach for data-limited watersheds as they may or may not accurately predict nutrient sources and prioritize subwatersheds correctly (McCarty et al 2015). When considering that resources of local, state, and federal governments will be employed based on the recommendations of a model, it becomes even more necessary to ensure that there is high confidence in the model and its predicted priority subwatersheds. The confidence in subwatershed prioritization has been increased when the model output was compared to landscape characteristics (Pai et al 2011) or measured WQ data (McCarty et al 2015).

If a watershed model is limited in the spatial or temporal scope of H/WQ for calibration and validation, a suggested alternative may be to explore the use of the available WQ and watershed characteristic data to help prioritize subwatersheds using simple statistical relationships. The goal of this study was to develop a decision tree based on statistical analysis to help local, state and federal programs prioritize subwatersheds for BMP implementation and financial resources with priority U.S. Geological Survey 8-digit hydrologic unit code (HUC-8) watershed in Arkansas. The specific objectives were to:

- establish a positive linear relationship between nutrient concentrations observed during baseflow and stormflow;
- with an observed significant positive relationship, statistical analysis will then be used to show relationships between baseflow nutrient concentrations and watershed characteristics;
- finally, those watershed characteristic-nutrient relationships will be used to develop a decision tree to prioritize subwatersheds.

II. LITERATURE REVIEW

1. NUTRIENTS AND WATER QUALITY

Eutrophication of US water bodies as a result of excess nutrients from human influence has been identified as an important problem impacting surface waters today. The consequences of eutrophication of our water bodies include increased algal growth, loss of habitat, large diurnal dissolved oxygen swings, loss of designated use, loss of aquatic biodiversity and fish kills, as well as decreased life span for lakes and reservoirs (Carpenter et al 1998). Harmful algal blooms (HABs) have been associated with eutrophic conditions, and the toxins produced by cyanobacteria can have harmful effects on humans and livestock (Carpenter et al 1998). Nutrient loadings to drinking water supplies also impact the formation of disinfection byproducts (DBPs), which result from natural organic matter in the drinking water interacting with disinfectants used by drinking water treatment plants (Mash et al 2014).

While point sources of nutrients have been on the decline since the 1960's (Sharpley et al 1999), nonpoint sources from combined agricultural and urban runoff today are often the largest contributors to excess nutrients in our streams. Studies have shown a positive relationship between soil nutrients in agricultural fields and nutrient concentrations in runoff during rainfall events (Burwell et al 1975, Sharpley 1985, Pote et al 1996, Sims et al 1998, Sharpley et al 1999). Multiple studies have documented the positive relationship between land use influenced by human activities (e.g., row crops, pasture and urban development) in the catchment and nutrient concentrations in streams and rivers (McFarland & Hauck 1999, Omernick 1976, Peterson et al 1998, Giovannetti et al 2013, Jones et al 2001, Strayer et al 2003).

As water interacts with the environment during a runoff event or transport though the subsurface, the land surface and subsurface and its characteristics play a pivotal role in what nutrients will be transported to the stream. Agricultural lands may contribute to greater phosphorus and nitrogen concentrations due to fertilizer enrichment while also contributing to sedimentation from cultivation practices (McFarland & Hauck 1999, Carpenter et al 1998). Urban lands may contribute to nutrient enrichment through increased impervious surfaces which is correlated to increased suspended solids in urban watersheds, as well as changes in hydrology which cause erosion within the fluvial channel. Urban areas also include nonpoint sources such as lawn fertilizers, construction areas, septic systems, and pet wastes (Carpenter et al

1998). Reduction in forests and wetlands to make way for pasture and development decreases the watersheds ability to assimilate nutrients, changes the variety of habitat, and disrupts geomorphic processes, ultimately impacting stream functioning and degrading habitat (Allan 2004).

2. WQ MONITORING

Nutrient levels that lead to eutrophication are measured using WQ monitoring programs. These programs need to have clear objectives as most have limited financial and personnel resources. Two of the most relevant goals in WQ monitoring are addressing in-stream ecologically relevant nutrient concentrations and identifying load transport to standing waters. Each requires a specific sampling strategy. Nutrient concentrations during baseflow conditions are the most important for aquatic biota, and therefore, require a sampling at multiple places throughout the watershed (Stamm et al 2013). Load transport requires discharge and WQ monitoring across a range of flows because of changes in nutrient concentrations during runoff events (Miller & Drever 1977). Determining the nonpoint source contributors to baseflow concentrations requires a broad sampling strategy that captures the variation in land use throughout the catchment. Giovannetti et al. (2013), Massey et al. (2013), and Haggard et al. (2010) each had over 20 baseflow sampling sites. Sampling for load transport also benefits from multiple sampling sites, however, it is cost prohibitive in most watersheds to have any more than a handful.

Load estimation for a stream or river can be done several ways. Water quality monitoring using in situ automatic sampling equipment, called auto samplers, has high capital cost, but is consistent. Properly maintained and calibrated equipment will ensure that the entire discharge range is captured. Water quality monitoring by hand, or manual sampling, has lower initial costs, but requires a crew on standby to capture storm events. This may prevent a crew from being able to access multiple sites at once, and depending on the distance needed to travel, may result in not adequately describing the range in discharge. Either the high capital cost of auto samplers or the limitations of manual sampling make it difficult to quantify nutrient loads at more than a handful of sites within a watershed (Harmel et al 2006b).

Auto samplers are programmed to take time-interval or flow-interval samples. Time-interval samples are triggered once the flow reaches a minimum threshold and are taken at regular intervals. Flow-interval samples are taken based on a specific flow volume interval (e.g., 1000 m³). Time-interval sampling is

simple and economical, while flow-interval sampling provides better load accuracy as the greater proportion of samples is during higher flows. Time-interval and flow-interval sampling require continuous discharge measurements. Time-interval requires discharge for the flow component of the load calculation and flow-interval requires discharge to inform when samples should be taken.

Manual and auto sampling programs can utilize discrete or composite samples. Composite samples should always be flow weighted, in other words, the varying samples placed in the bottle either manually or automatically are proportional to the discharge at the time they were collected. There are many ways to estimate loads. Simple load calculations for composite samples can be calculated by multiplying the total flow from the storm event by the composite nutrient concentration. Pollutant loads from discrete samples can be calculated using the following equation (1):

$$Load = \sum_{i=1}^{n} C_i Q_i Dt \tag{1}$$

The load is equal to the sum of the products for a series of discrete measurements. For each sample during a storm event, discharge (Q_i) is multiplied by concentration (C_i) and then multiplied by the interval in time between observations (Dt) (Gulliver et al 2010). This yields a rough approximation of loads that becomes more accurate when sample numbers are increased. As the time between samples increases, the quality of the load becomes poorer. If high intensity flow and concentration data are available, loads can be derived by integration of the previous equation. High intensity sampling with an auto sampler can yield excellent results, however, there are a limited number of bottles and capacity within bottles, which restricts the runoff duration that can be captured (Harmel 2006b).

Discrete samples taken over a period of time often only capture a few samples per storm event. Taken over the course of a season or even a year may result in a data set that can be used to predict loads using a statistical method. There are multiple methods and programs available to compute loads e.g., USGS's LOADEST (Runkel et al 2004), and LoadRunner (Booth et al 2007). Input into each of these programs requires the time and date of the samples, the nutrient concentration at that time, and the corresponding discharge. A regression or rating curve model is then used to approximate a load-discharge relationship which is used to estimate loads. Models range from simple linear regression

(equation 2) to 2nd order polynomial functions that include Julian day of sampling (equation 3) in order to account for changes in seasonality. A sample of the range in complexity of load models is given by:

$$y(L) = a_0 + a_1 lnQ \tag{2}$$

$$y(L) = a_0 + a_1 lnQ + a_2 lnQ^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime) + a_5 dtime + a_6 dtime^2$$
(3)

where *L* is equal to the load, a_0 through a_5 are model coefficients, *Q* is the stream discharge, and *dtime* is decimal time. Selection of the correct model can be optimized using Akaike Information Criteria (AIC, Runkel et al 2004).

Sampling programs that capture the spatial-temporal variations in the watershed are required in order to adequately describe nutrient sources. Nonpoint source nutrients are associated with sources such as urban, pasture, and crop production (McFarland & Hauck 1999, Omernick 1976, Peterson et al 1998, Giovannetti et al 2013, Jones et al 2001, Strayer et al 2003). Based on the location of these practices within a watershed, nonpoint source pollution tends to be a spatially diverse problem (Biswas et al 1999; Javed et al 2009). Site selection is designed to quantify water chemistry across a variety of land uses in order to account for the spatial variations. There should be as many sites as resources will allow, which is subjective. Giovannetti et al (2013), Haggard et al (2010) and Massey et al (2013) all had a minimum of 20 sites within a HUC-8 watershed. Water chemistry also varies temporally with seasonal trends in nutrient concentrations (Haggard et al 2003), and water sampling should be routine and cover at least a year to capture these temporal trends (Harmel et al 2006b).

3. MODELLING

Physical models, such as the Soil and Water Assessment Tool (SWAT), can be used to fill in the gaps in our understanding of watershed hydrology, the effects of human influence on the landscape, and identify nutrient sources across the entire watershed, adequately characterizing each HUC-12 outlet. Physically-based watershed models play an increasing role in how we use federal, state, and local resources for the implementation of BMPs to address eutrophication (Pai et al 2011). Most modern physically-based watershed models are based loosely on the Stanford Watershed Model (Crawford & Linsley 1966) which tried to include all elements of the hydrologic cycle. Singh & Woolhiser (2002) describe over 40 models

that have been used to address water resources and environmental issues, including flooding, stream bank erosion, sedimentation, management of water resources, and military applications.

Models have shown the ability to predict N and P with statistically significant results (Abbaspour et al 2007). In physically-based models, there is often insufficient data to fully characterize spatial variability. Additionally, real hydrologic processes are represented by imperfect model processes. This has resulted in a need to calibrate and validate watershed models. It was shown in McCarty et al (2015) that without this calibration and validation, models may or may not accurately predict nutrient transport and sources across the watershed. Calibration is a trial and error process where a handful of parameters are adjusted to achieve similarity in simulated and observed streamflow and water quality at a particular monitoring site. Ideally, this site will be situated at the watershed outlet (Cao et al 2006). The watershed model calibrated and validated at one point in the catchment, usually representing a large drainage area of mixed nutrient sources, is then used to predict loads at smaller catchments. This practice is typical of most watershed models, even though there is a high degree of spatial-temporal variability across the watershed.

4. SUBWATERSHED PRIORITIZATION

Physical models have been used to evaluate BMPs, TMDLs, and water quality targets (Santhi et al 2006; Harmel & Smith 2007), predict nutrient loads from the landscape (Young et al 1989; Preston & Brakebill 1999; Pai et al 2010), and to prioritize subwatersheds (Pai et al 2011). Prioritization is the process of selecting or ranking subwatersheds out of a larger watershed area based on a set of predefined criteria (Maas et al 1985; Tripathi et al 2003). The criteria used may be nutrient concentration, loads, or some other criteria based on conceptual models and/or known land use-water quality relationships.

Initial efforts to prioritize fields or watersheds focused more on establishing which landscapes were critical based on criteria such as manure sources and fertilization rate and timing. Maas et al (1985), developed guidelines for selecting critical areas within agricultural watersheds. Their basis for determining a critical area was a nine step process that included

characterizing the WQ impairment,

- estimating pollutant reductions,
- · determining if reductions can be met by reducing nonpoint sources,
- identifying the largest agricultural pollutant sources,
- ranking the magnitude of those sources,
- and evaluating the distance of those sources to the impaired water body.

Methods were tested on 32 agricultural watersheds ranging in size from 800 to 12,000 hectares, but the classification into priorities was not compared against measured WQ data.

Biswas et al (1999) prioritized subwatersheds on the basis of watershed morphometry. Watershed shape parameters had negative correlation with rainfall-runoff ratio and form factor was also inversely related to sediment yield. Stream length, order, bifurcation ratio, drainage density, texture ratio, and relief ratio all have established or conceptual relationships with the potential for soil erosion. Using these morphometric characteristics, watersheds were ranked in order of erosion risk. Watershed rankings were then validated using the sediment yield index showing agreement in the results. However, the results were not validated using loads from measured WQ data.

Javed et al (2009) expanded on this work (Biswas et al 1999) classifying subwatersheds into low, medium, and high erosion risk categories for morphometric and land use characteristics (e.g., forest, scrub, water, cultivated land, etc.). Morphometric categories were ranked similar to Biswas et al (1999). For land use prioritization, watersheds were ranked according to percent changes in particular land use categories over a specific time interval. For instance, increase in cultivated land would be given a high priority whereas increase in open forest would be give a low priority; the basis of these rankings was the conceptual model that forested watersheds have lower stream nutrient concentrations and loads relative watershed with increasing human activities (e.g., cultivated crops, pasture, or urban development). Rankings were summed into a compound value representing morphometric and land use rankings for each subwatershed and a low, medium, and high range for compound values was developed to rank each subwatershed. These methods were repeated on a different watershed with similar results (Javed et al 2011), however again the results of this prioritization study were not confirmed with measured WQ data. In a recent study for the Illinois River Watershed Partnership (Haggard et al 2010), Illinois River subwatersheds were prioritized based on the relationship of stream nutrient concentrations to land use. Water quality data was available from every subwatershed outlet in the Arkansas portion of the watershed and used to establish regression relationships with stream nutrient concentrations and combined percent urban and pasture, as well as percent forest land uses; a confidence interval was fitted to each regression. Nutrient concentrations in streams were positively correlated to the combined urban and pasture and negatively correlated to the forest land use. Watershed outlets that were above the confidence band (i.e., ones with high nutrients relative to other subwatersheds with similar land use properties) were selected as high priority. Sites falling within the confidence band were classified as medium priority, and sites below the confidence band (i.e., sites with low nutrients relative to other subwatersheds with similar land use) were classified as low priority.

Subwatersheds have also been prioritized based on the output of a calibrated and validated SWAT model. In Tripathi et al (2003), SWAT was used to determine nutrient losses and sediment yields in subwatersheds. Ranks were assigned to subwatersheds according to sediment yield. Subwatersheds were considered critical for nutrient losses if they exceeded the EPA nutrient criterion threshold of 10 mg L⁻¹ for NO₃-N and 0.5 mg L⁻¹ for SRP (Tripathi et al 2003).

Using a similar approach to Tripathi et al (2003), Pai et al (2011) used a calibrated and validated SWAT model to predict loads at the subwatershed scale, subtracting loads from upstream subwatersheds to isolate individual subwatershed contributions. Percentile rank was used to classify the subwatersheds flow-weighted concentrations, based on load divided by total flow. Watersheds in the highest percentiles (80-100%) classified as high priority for nutrients and those with the lowest percentiles (0-20) classified as low with an additional gradient of priorities in between. Pai et al (2011) used several methods to validate their subwatershed priorities. Subwatershed flow-weighted nutrient concentrations were positively correlated with percentage of pasture area and negatively correlated with forested area, following the conceptual model established with WQ data for this region (e.g., Haggard et al 2010; Haggard et al 2003; Giovanetti et al 2013). The priorities developed from the Illinois River watershed study (Haggard et al 2010) were compared to those developed for the same watershed by Pai et al (2011), showing

substantial overlap in the subwatersheds listed as medium and high for priorities; i.e. nutrient concentration or loads were high relative to other subwatersheds.

5. HYPOTHESIS

The following hypothesis will be tested in this research:

Baseflow and Stormflow Nutrient Concentration Comparison

- H₀1: The slope of nutrient concentrations observed during baseflow compared with nutrient concentrations observed during stormflow will not be different than zero (α=0.05).
- H_a1: The slope of nutrient concentrations observed during baseflow compared with nutrient concentrations observed during stormflow will be significantly different than zero (α=0.05).

Watershed Characteristics and Nutrient Concentration Comparison

- H₀2: The slope of nutrient concentrations compared with watershed characteristics will not be different than zero (α =0.05)
- H_a2: The slope of nutrient concentrations compared with watershed characteristics will be significantly different than zero (α =0.05).

Deviation along Watershed Characteristics with Nutrient Concentration

- H₀3: There will not be a change in deviation along watershed characteristics (x) with nutrient concentrations (y), (α=0.05).
- H_a3: There will be a significant change in deviation along watershed characteristics (x) with nutrient concentrations (y), (α=0.05).

III. METHODS

1. STUDY AREA DESCRIPTIONS

The five watersheds assessed in this study come from three different Level IV ecoregions (Omernick, 1987) that span Arkansas along with sections of Oklahoma and Missouri. Each watershed has different land scape characteristics that are attributable to their ecoregion or human influence (Table 1). The watersheds were selected for their inclusion in the Arkansas Non-Point Source priority watershed list (ANRC, 2011), as well as the availability of WQ data relevant to the objectives of this study. The watersheds ranged in size from 197,000 ha (Strawberry River watershed) to 661,000 ha (Upper Saline River watershed). The Illinois River watershed contained the highest population density (663 persons km⁻²), while the other watersheds had population densities less than 200, and the Strawberry River watershed contained the lowest population density (55 persons km⁻²). Mean elevations ranged from 119 (Upper Saline River watershed) to 439 m above sea level (Beaver Reservoir watershed). Urban development was low (5-10%) across all watersheds, whereas forest and pasture were more variable. The Illinois River watershed only contained 5%. The Upper Saline River watershed contained the highest proportion of agricultural land use (primarily pasture) at 45%, while the Upper Saline River watershed only contained 5%. The Upper Saline River watershed contained the highest percentage (76%) of forested lands. Water coverage was higher in the Beaver Reservoir watershed due to the presence of two large reservoirs in the White River system.

								L	and Use		
Watershed	HUC #	Area (ha)	Population Density ¹ (persons/km ²)	Ecoregion	Mean Elevation (m) (std. dev.)	Annual Precipitation (cm)	Urban	Pasture/ Crops	Forest	Water	Other ²
Poteau	11110105	493000	189	Arkansas Valley (37)	236 (97)	121	5	30	61	1	3
Upper Saline	08040202	444000	143	Ouachita Mountains (36)	119 (68)	133	7	5	76	<1	12
Strawberry	11010012	197000	55	Ozark Highlands (39)	176 (52)	124	5	32	59	<1	4
Illinois	11110103	428000	663	Ozark Highlands (39)	334 (66)	119	10	45	43	<1	2
Beaver	11010001	661000	121	Ozark Highlands (39)	439 (94)	119	5	30	61	4	0

Table 1. Descriptive information for the watersheds under study.

¹ - CAST, 2006

² - Other = barren, scrub, and wetlands

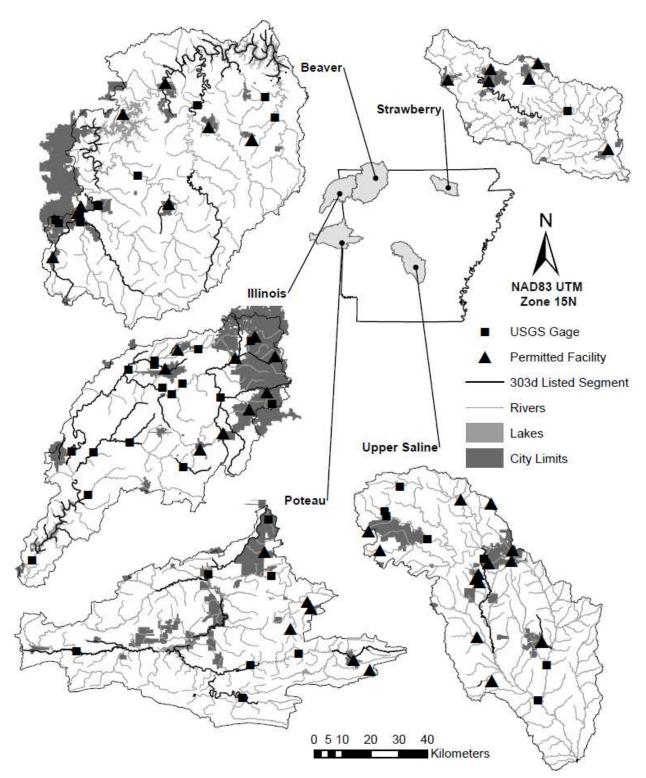


Figure 1. Study watershed map detailing the HUC-8 boundary, select rivers, 303d listed water bodies, discharge permitted facilities, active USGS Gages, and urban centers.

Poteau River Watershed

The Poteau River watershed (HUC 11110105) spans the central Arkansas-Oklahoma state line. The two main tributaries on the Arkansas side, the Poteau and James Fork Rivers flow westerly. Once inside Oklahoma, the Poteau River turns north where it eventually intersects the Arkansas River near the city of Fort Smith, AR. Other major tributaries include the Black Fork and Fourche Maline rivers as well as Brazil Creek. There are seven active USGS gages in the watershed (Figure 1).

The Poteau River watershed occupies the Arkansas Valley ecoregion of Arkansas and Oklahoma. Historic land uses typical of the Arkansas Valley include a mix of forest, savanna, and prairie. Presently, rugged areas are typically forested and conversely, level areas have been cleared for livestock. Stream gradients in the Arkansas Valley are typically lower than the surrounding Ozark Highlands and Ouachita Mountains (EPA 2012).

The Poteau River watershed has some significant urban centers that include the cities of Fort Smith, Poteau, and Pocola. On the Arkansas side of the watershed, it is mostly rural apart from Fort Smith, a city of roughly 80,000. Due to the location of Fort Smith, its impact on the watershed as a whole is negligible. Population, urban, and industry growth for the watershed as a whole is steady.

Rivers listed under the section 303d program include sections of the Black Fork, Fourche Maline, Brazil Creek, and multiple reaches of the Poteau River (ANRC, 2012; Figure 1). There are six permitted discharge facilities in the Arkansas portion of the watershed, whereas locations for permitted facilities in Oklahoma were not available upon request. Water-quality problems include elevated metals and phosphorus enrichment from point and nonpoint sources (ANRC, 2012).

Upper Saline River watershed

The Upper Saline watershed (HUC 08040203) flows southeast out of the Ouachita National Forest into the Central Plains, finally draining into the Ouachita River. Major tributaries include the North, Alum, Middle, and South Forks of the Upper Saline, as well as Hurricane Creek. There are seven active USGS gaging stations within the watershed (Figure 1).

The Upper Saline River's headwaters reside in the Ouachita Mountains ecoregion and are heavily forested with a mix of oak, hickory, and pine. The anthropogenic activities within this watershed include urban development, logging, recreation, and pasture management, although the Upper Saline River watershed has less poultry farming than that seen in the other watersheds studied. The lower portion of the Upper Saline River watershed resides in the South Central Plain ecoregion where extended floodplains contain forested bottomland and more elevated positions contain a mix of oak, hickory and pine (EPA, 2012).

The watershed contains three major urban centers, the cities of Benton and Sheridan, and Hot Springs Village. The city of Benton, as a satellite to Little Rock, has experienced exponential growth over the last twenty years. Hot Springs village, a recreational retirement village, has also seen increased growth. However, population density within the village does not approach what is seen in a typical city with average lots sizes greater than 0.13 hectares.

Stream reaches classified as impaired under section 303d include a length portion of the Upper Saline River as well as Big Creek (ANRC, 2012). There are 15 active permitted discharge facilities within the watershed, however, a large contingency of the watershed remains rural and therefor uses septic systems. Water-quality parameters listed for non-attainment of designated use include dissolved oxygen, minerals, BOD, and mercury contamination.

Strawberry River watershed

The Strawberry River watershed (HUC 11010012) runs northwest to southeast where it drains into the Black River. Major tributaries include North Big Creek and South Big Creek. There is one active USGS gage within the watershed (Figure 1), which currently only records river stage.

The Strawberry River watershed resides in the Ozark Highlands Central Plateau ecoregion. The terrain is less rugged than the other Ozark Highlands ecoregions that reside on the Springfield Plateau. Karst features also occur but are less prolific. Level areas are dominated by pastureland and rugged areas by forest. The bottom portion of this watershed transitions into the Mississippi Alluvial Plain ecoregion where there is flatter terrain and an abundance of crop land (EPA 2012).

The watershed is sparsely populated (20,000 people) with only one significant urban area, the Horseshoe Bend Retirement community, which would be equivalent to a suburban landscape (ANRC, 2012). Population growth in this area is slow, with the major industry being livestock production. Most residents, due to the watersheds rural nature, are on septic systems.

Sections categorized as impaired by section 303d include a 60.3 km section of the Strawberry River due to turbidity (ANRC, 2012). Additional pollutants of concern include suspended sediments and fecal coliform bacteria with suspected sources being unpaved roads, streambank erosion, and grazing in riparian areas. There are seven permitted discharge facilities, the most significant being Horseshoe Bend.

Beaver Reservoir Watershed

The Beaver Reservoir watershed (HUC 11010001), flows northerly with the headwaters located in rural and forested areas of Washington and Madison counties. Beaver Reservoir, a 106 km stretch of the White River is located in the watershed. Major tributaries include the White River, the Kings River, Richland Creek, and War Eagle Creek. There are 10 active USGS monitoring stations located in the watershed (Figure 1).

The Beaver Reservoir watershed resides in the Ozark Highlands ecoregion of Arkansas (EPA 2012) that is characterized by highly soluble and fractured limestone with karst features. Streams with gravel substrate and heavy spring influence are common. Northwest Arkansas, which includes the Beaver Reservoir watershed, is a fast growing region driven by strong corporate influence. The reservoir at the center of this watershed is the drinking water supply for Northwest Arkansas' 500,000+ people. It is also one of the most popular recreation destinations in the area. Large urban centers include Fayetteville, Springdale, Rogers, and Bentonville. Most of the urban areas lie to the west of the watershed boundary and the majority of discharge from point sources end up in adjacent catchments. The city of Fayetteville discharges half of their effluent to this watershed and there are additional smaller communities with discharge permits within the watershed.

Water-quality concerns from point and non-point sources include turbidity, siltation, nutrients, and pathogens. Multiple studies have been performed in Northwest Arkansas to assess the impact of point and non-point sources on nutrient concentrations in streams and rivers (Giovannetti et al 2013; Haggard et al 2003; Haggard et al 2007; Migliaccio et al 2007; Hufhines et al 2011). Rivers within the watershed classified as impaired on the 303d list include portions of the White River, West Fork of the White River, and Kings River (ANRC, 2012).

Illinois River Watershed

The Illinois River watershed (HUC # 11110101), flows southwest, with its upper reaches in Northwest Arkansas and its tailwaters in Oklahoma. The river flows into Lake Tenkiller in Oklahoma and finally the Arkansas River, near Gore, OK. Main tributaries include Osage, Spring, and Flint Creeks (ANRC, 2012). There are 17 active USGS monitoring stations (Figure 1). The watershed resides in the Ozark highlands ecoregion (EPA 2012) as described in the Beaver Reservoir watershed. The headwaters of the Illinois River watershed reside in Northwest Arkansas, sharing many similarities to the Beaver Reservoir watershed.

Impaired waterways listed for non-attainment of designated use include sections of Osage Creek, Clear Creek, Baron Fork, and the Illinois River (ANRC, 2012). Some of the major permitted facilities on the Arkansas side of the watershed include WWTPs for the city of Fayetteville, Rogers, Springdale, and Siloam Springs. Permitted facilities data was not available for the state of Oklahoma. Like the Beaver Reservoir watershed, the Illinois River watershed has been designated a nutrient surplus area from applied poultry litter, received extensive study (Brion et al 2010, Ekka et al 2006, Haggard 2010, Jarvie et al 2012), and shares similar pollution concerns.

2. WATER QUALITY DATA

Data for the Poteau River, Upper Saline River and Strawberry River watersheds were from a study by the Arkansas Water Resources Center (AWRC) designed to evaluate the performance of SWAT models developed for each watershed (Table 2, Massey et al 2013). Data for the Beaver Reservoir watershed were collected from a study by the Beaver Water District and University of Arkansas with a goal to understand the relationship between land use and stream WQ (Table 2, Giovannetti et al 2013). Data for

the Illinois River watershed were from a study conducted by the AWRC to recommend watershed management strategies to the Illinois River Watershed Partnership (Table 2, Haggard et al 2010). In addition to the collected samples from the three studies cited above, five USGS stream gages were selected to provide additional data relative to the objectives of this study. Two were in the Illinois River watershed (Gages 07196900 and 07195000) and three in the Beaver Reservoir watershed (Gages 07050500, 07049000, and 07048600). Water quality data retrieved for these gages from the USGS database were for the years 2007-2014.

		Sampling		Number	
Watershed	Data Source	Frequency	Sampling Period	of Sites	Nutrients Sampled
Beaver	Giovannetti et al. 2013	Monthly	06/2005-07/2006	20	NO ₃ -N, TN, SRP, TP
Illinois	Haggard et al. 2010	Monthly	02/2009-11/2009	29	NO3-N, TN, SRP, TP
Poteau	Massey et al. 2013	Monthly	10/2011-9/2012	20	NO ₃ -N, TN, SRP, TP
Saline	Massey et al. 2013	Monthly	10/2011-9/2012	20	NO3-N, TN, SRP, TP
Strawberry	Massey et al. 2013	Monthly	10/2011-9/2012	20	NO ₃ -N, TN, SRP, TP

Table 2. Water quality data sources, sampling periods, and constituents.

The water quality constituents selected for study were Nitrate-Nitrogen (NO₃-N), Total Nitrogen (TN), Soluble Reactive Phosphorus (SRP), and Total Phosphorus (TP). In Giovannetti et al. (2013), Massey et al. (2013), and Haggard et al. (2010) water samples were collected from the vertical centroid of flow, where the water was actively flowing and likely well mixed, using a Wildlife Supply Company horizontal alpha water sampler, telescoping sample pole, or by hand. Quality assurance/quality control (QA/QC) protocol, laboratory analysis methods, and method detection limits are all consistent with those described in McCarty et al. (2015).

Site selection for Giovannetti et al. (2013), Massey et al. (2013), and Haggard et al. (2010) was based on varying land use and also ease of access. All of the sampling temporal periods approached a year or more in length, capturing potential seasonal variations in concentrations (Table 2). Samples from these studies were collected monthly during baseflow conditions and during select stormflow events. Massey et al (2015) collected stormflow at USGS stream gages within each watershed (7 out of 60 sites) while Giovannetti et al (2013) and Haggard et al (2010) both collected stormflow at all sites (n=54). In order to sample during baseflow conditions, two criteria were used: no runoff producing rain in the previous 48

hours, and no significant change in the hydrograph from the previous day (±10%). When a particular site did not have available discharge, the closest USGS gage was used to determine if baseflow conditions were present. Baseflow water quality was sampled monthly for the watershed studies at a total of 114 sites.

Stormflow WQ was sampled in a similar manner to baseflow. Sampling for stormflow conditions was conducted when a rainfall event produced a significant rise in the hydrograph (>10%). When a particular site did not have available discharge, the closest USGS gage as well as visual observation of the flow level was used to determine if stormflow conditions were present. Samples were collected during the rising, peak, and falling limbs of the hydrograph.

Water samples from the five additional USGS stream gages were collected by USGS personnel at routine intervals using the equal-width-increment, or equal-discharge-increment approach described in USGS (2006). QA/QC and sample processing were in accordance with Wilde et al (2004). Water samples were analyzed at the National Water Quality Laboratory with laboratory analysis methods and method detection limits for NO₃-N, TN, SRP, and TP described in Patton & Kryskalla (2003). The USGS does not collect samples by baseflow and stormflow. Therefore, the USGS samples had to be separated into baseflow and stormflow samples to match the data from Giovannetti et al. (2013), Massey et al. (2013), and Haggard et al. (2010). Using USGS gage discharge at the time of sampling, baseflow separation software (Lim et al. 2005) was used to divide the discharge into baseflow and stormflow discharge components. Flow from a particular day was categorized as baseflow when greater than 90 percent of the total flow was determined to be baseflow by the separation software. Water quality data collected on a baseflow day was considered baseflow water quality and the inverse was true for stormflow.

3. LAND USE METRIC DEVELOPMENT AND SUBWATERSHED EXTRACTION

The drainage area of each sample site was delineated using a Digital Elevation Model (DEM) in ArcGIS (ESRI 2011). Layers needed to perform this analysis included the DEM, HUC-8 and HUC-12 boundaries, national hydraulic dataset flow lines, and site locations. GIS data sources included the Arkansas GeoStore Data Repository, USGS National Map, TIGER US Census Data, and the National Atmospheric Deposition Program. The sites are nested within drainage area boundaries, so the geospatial information

is reflective of the upstream delineated catchment. In this study, the catchments are not necessarily independent due to nesting.

The 2006 National Land Cover Database (NLCD06, Fry et al. 2011) was used to develop 21 out of 33 total metrics. Details within the NLCD06 layer show total area of forest, wetland, pasture, barren, and forest land uses, which have all been shown to significantly impact stream nutrient concentrations (McFarland & Hauck 1999; Omernick 1976; Giovannetti et al 2013; Strayer et al 2003). Metrics for forest and pasture categories were also selected to determine if there were specific effects on nutrients when varying densities were located in the riparian zones. Jones et al. 2001 found riparian forest to be the most important variable in predicting NO₃-N concentrations in streams. While Jones et al. (2001) explored a 30 m distance for forest and agriculture, this study included 60, 90, and 120 m buffers. Finally, urban, pasture, and row crops were combined into a Human Use index to account for the human disturbance to the landscape using a single indicator (Table 3).

Other layers were used to provide detail that does not exist within the NLCD06 database. The potential for erosion and increased suspended solids was explored by examining the density of roads, the predominance of hydrologic soil groups C and D, and watershed characteristics like stream density, gravelius index, and average slope per site catchment. As shown in Jones et al. (1997), there is a relationship between stream particulate phosphorus and suspended sediment. Census population data per county was extrapolated to yield site catchment population density. Poultry production data was used to determine the poultry house density per site catchment. Finally, nitrate deposition data from the atmospheric nitrate deposition program was used to determine mean and total nitrate deposition per site catchment (Table 3).

Land Use Metric	Unit	Metric Definition
% Forest (%FOR)	%	(Sum of the areas of NLCD06 categories 41, 42, & 43 within the
		delineated watershed)/(total delineated watershed area)
% Urban (%URB)	%	(Sum of the areas of NLCD06 categories 22, 23, & 24 within the
		delineated watershed)/(total delineated watershed area)
% Barren (%BAR)	%	(Area of NLCD06 category 31 within the delineated
		watershed)/(total delineated watershed area)
% Wetland (%WETL)	%	(Area of NLCD06 category 90 & 95 within the delineated
		watershed)/(total delineated watershed area)
% Pasture (%AG)	%	(Sum of the areas of NLCD06 categories 81 & 82 within the
		delineated watershed)/(total delineated watershed area)
Forested Riparian Buffer	%	(Sum of the areas of NLCD06 categories 41, 42, & 43 within a 30,
Proportion (FORXS30, 60,		60, 90, & 120 m river buffer of the delineated watershed)/(total
90, 120)		delineated watershed area)
% Forested Riparian Buffer	%	(Sum of the areas of NLCD06 categories 41, 42, & 43 within a 30,
(%FORXS30, 60, 90, 120)		60, 90, & 120 m river buffer of the delineated watershed)/(total 30,
		60, 90, 120 m riparian buffer area)
Pasture Riparian Buffer	%	(Sum of the areas of NLCD06 categories 81 & 82 within a 30, 60,
Proportion (AGXS30, 60,		90, & 120 m river buffer of the delineated watershed)/(total
90, 120)		delineated watershed area)
% Pasture Riparian Buffer	%	(Sum of the areas of NLCD06 categories 81 & 82 within a 30, 60,
(%AGXS30, 60, 90, 120)		90, & 120 m river buffer of the delineated watershed)/(total 30, 60,
		90, 120 m riparian buffer area)
Human Use Index (HUI)	%	(Sum of the areas of NLCD06 categories 22, 23, 24, 81, & 82
		within the delineated watershed)/(total delineated watershed area)
Road Density (RDDEN	m/ha	(Total length of road within the delineated watershed)/(total
		delineated watershed area)
Roads by Streams (RXS)	m/ha	(Length of road within a 30 m buffer of streams)/(total delineated
		watershed area)
Population Density	n/a	Mean population density per delineated watershed area, as
(POPDEN)		calculated by dasymetric mapping tool and weighted by urban
		land use
Poultry House Density	n/a	(Total number of poultry houses in the delineated watershed)/(total
(PHD)	<i></i>	delineated watershed area*10000)
% Hydrologic Soil Group D	%	% of Total delineated watershed area with HSG D soils
(%HSGD)		
% Hydrologic Soil Group C	%	% of Total delineated watershed area with HSG C+D soils
& D (%HSGCD)		
Mean Nitrate Deposition	kg/ha	Mean annual atmospheric NO3 deposition (kg/ha)
(NADP)	1.	
Total Nitrate Deposition	kg	(NADP/10000)*Total Delineated Watershed Area (m ²)
(NADPTOT)	m/aa	(Total length of atracma within the delineated watershed)//total
Stream Density (STRDEN)	m/ac	(Total length of streams within the delineated watershed)/(total
Gravelius Index	n/a	delineated watershed area)
	n/a	(0.28*delineated watershed perimeter)/(square root of total
(GRAVIND) Average Slope (AVGSLP)	degraaa	delineated watershed area) Average slope of the delineated watershed
Average Slope (AVGSLP)		

Table 3. Land use metrics for predicting water quality and their development.

NLCD06 values can be obtained through Fry et al. (2011).

4. STATISTICAL ANALYSIS

Water quality data provided by Giovannetti et al. (2013), Massey et al. (2013), and Haggard et al. (2010) was in the form of geometric mean nutrient concentrations for each site within the watersheds. For each site, a baseflow and stormflow geometric mean was provided. Geometric mean was also chosen to summarize WQ data for the additional USGS gages. The primary reason for this was to match the data provided by Giovannetti et al. (2013), Massey et al. (2013), and Haggard et al. (2010). Geometric mean is typically applied to log-normally distributed datasets. However, our confidence in distribution fitting was low due to the number of samples taken at each site (n<30). All statistical analysis were completed using a significance level of 0.05. Statistical tests were performed on two separate WQ databases, one that included sites downstream of permitted discharge facilities (114 sites) and one that excluded those sites (74 sites).

Linear regression and multiple linear regression (MLRA) were performed using JMP Pro 11 (JMP Pro 2014) with stepwise forward selection. A regression model was constructed using baseflow and stormflow concentrations at sites where there was data separated into the two flow regimes (n=61). Regression and MLRA models were created pairing WQ and land use metrics. Pearson correlation between land use and WQ was also explored. After completion of the multiple linear regression models (MLRA), multicollinearity was evaluated between predictors with allowable variance inflation factors (VIF) of less than 5 or tolerance value (1/VIF) of greater than 0.2.

Change points in the WQ data and their associated significance and confidence intervals were assessed using nonparametric change point analysis (nCPA, Qian et al. 2003; King and Richardson 2003) in R 3.1.1 (R Core Team 2014). This was done to model the how the variance in WQ data changed in accordance with watershed characteristics (Table 3). A 90% confidence interval was calculated using bootstrap simulations set to resample the original dataset with randomized data replacement and recalculate the change point over 1000 times. Statistical significance was approximated using a permutation test. The difference in the means of the permuted datasets was then compared to the difference in the means of the change point separated data, with the ratio between yielding a p-value.

Classification and regression tree analysis (CART) was utilized to determine if there were additional splits in the WQ data associated with land use metrics. CART analysis was performed using MVPART library (Therneau et al. 2014) in R 3.1.1 (R Core Team 2014). Regression trees were constructed for each water quality constituent (NO₃-N, TN, TP, SRP) using all of the developed land use metrics (Table 3). CART tree size was determined using V-fold cross-validation (De'ath and Fabricius 2000). Model crossvalidations were conducted by dividing the data into 10 similarly sized, randomized subsets. As each new tree split was determined, cross-validation selected 9 of the 10 data subsets to re-create the tree model and then predict the remaining subset. This process yielded the relative error associated with each tree split. Pruning of the model was then conducted using the cross-validation minimum error rule (De'ath and Fabricius 2000). Each tree split had to yield at least ten observations, each terminal branch was required to have least eight observations, with an effective minimum split of 16 observations.

IV. RESULTS AND DISCUSSION

1. BASEFLOW CONCENTRATIONS

Geometric mean concentrations of NO₃-N, TN, SRP, and TP during baseflow were variable across the five watersheds. However, when comparing minimum and maximum geometric mean concentrations for each watershed and constituent, these values were within one order of magnitude. This shows overlap in the ranges of concentrations among the five watersheds, but the data from the individual watersheds was often grouped low or high relative to the other datasets. This suggests that qualitatively, the nutrient concentrations at sites within one watershed were not wholly different from any of the other watersheds. Overall, the medians of the geometric mean nutrient concentrations across watershed sites were highest in the Illinois River watershed and lowest in the Strawberry river watershed (Table 4).

	NO ₃ -N (mg L ⁻¹)	TN (mg L ⁻¹)	SRP (mg L ⁻¹)	TP (mg L ⁻¹)
Beaver				
Range	0.050 - 2.280	0.170 - 2.330	0.003 - 0.150	0.009 - 0.212
Median	0.377	0.520	0.008	0.019
llinois				
Range	0.210 - 4.580	0.680 - 4.520	0.010 - 0.160	0.020 - 0.170
Median	2.320	2.340	0.040	0.070
Poteau				
Range	0.020 - 0.472	0.289 - 1.496	0.001 - 0.156	0.014 - 0.265
Median	0.058	0.528	0.003	0.045
Saline				
Range	0.003 - 5.291	0.105 - 6.324	0.003 - 0.069	0.012 - 0.144
Median	0.031	0.365	0.004	0.028
Strawberry				
Range	0.022 - 0.482	0.132 - 1.053	0.003 - 0.032	0.009 - 0.256
Median	0.085	0.289	0.004	0.015

Table 4. The range in baseflow geometric mean nutrient concentrations observed across sites within each watershed. Data for sites below permitted discharge facilities is also included.

Geometric mean NO₃-N concentrations during baseflow varied three order of magnitude across watersheds ranging from 0.003 to 5.29 mg L⁻¹ (Table 4). The median of the geometric mean NO₃-N concentrations across watersheds varied two orders of magnitude with the lowest median value observed at the Upper Saline River watershed (0.031 mg L⁻¹) and the highest at the Illinois River watershed (2.32 mg L⁻¹). Sites within the Beaver Reservoir, Illinois River, and Upper Saline River watersheds showed a

greater range in geometric means (less than 0.21 to greater than 2.28 mg L⁻¹) than sites within the Poteau River and Upper Saline River (0.02 to 0.5 mg L⁻¹) watersheds. However, there was still overlap in ranges for NO₃-N among all the watersheds.

Nitrate concentrations represented on average approximately 51% of the total nitrogen, ranging from 1% to over 95% across the watersheds. The baseflow geometric means of TN across all watershed sites ranged from 0.11 to 6.3 mg L⁻¹. Both the lowest and highest baseflow geometric mean for a site was observed in the Upper Saline River watershed (Table 4). The range in geometric mean concentrations of TN varied an order of magnitude across all watersheds, but all of the ranges overlapped to some degree. The median baseflow geometric mean TN concentration across watersheds ranged from 0.289 (Strawberry River watershed) to 2.34 (Illinois River watershed) mg L⁻¹, although the median was less than 0.60 mg L⁻¹ for the other watersheds.

Geometric mean SRP concentrations during baseflow at each site varied two orders of magnitude across the watersheds, and ranged from 0.003 to 0.160 mg L⁻¹ (Table 4). Median values of baseflow geometric mean SRP concentrations across watersheds also varied an order of magnitude; the lowest median value (0.003 mg L⁻¹) was from the Poteau River watershed, while the highest median value (0.04 mg L⁻¹) was from the Poteau River watershed, while the highest median value (0.04 mg L⁻¹) was from the Illinois River watershed. The range in SRP geometric means was similar across the Beaver Reservoir, Illinois River, and Poteau River watersheds (less than 0.01 to greater than 0.15 mg L⁻¹), whereas the range in the other two watersheds was tighter on the lower end. Overall, the range in SRP concentrations overlapped well across these watersheds.

The proportion of TP as SRP was variable across the streams sampled in each of these watersheds, ranging from 5 to over 95% with an average of 39%. Similar to SRP, baseflow geometric mean TP concentrations across sites varied two orders in magnitude ranging from 0.009 to 0.265 mg L⁻¹ (Table 4). The median of the baseflow geometric mean TP concentrations was highest for sites in the Illinois River watershed (0.07 mg L⁻¹), and lowest in the Strawberry River watershed (0.015 mg L⁻¹). Again, the range in geometric mean of the TP concentrations overlapped across these watersheds.

2. BASEFLOW AND STORMFLOW WATER QUALITY REGRESSION

Geometric mean concentrations of nutrients during baseflow and stormflow at each site were compared in a regression model. When sites from the five watersheds were combined, a significant (P<0.0001) and positive linear relationship was found for NO₃-N, TN, SRP, and TP (r²>0.46, Figure 2). The geometric mean concentrations of NO₃-N, TN and SRP at baseflow explained more than 70% of the variability in stormflow concentrations when data was combined across all watersheds. Geometric mean concentrations of TP at baseflow explained 46% of the variability in stormflow concentrations.

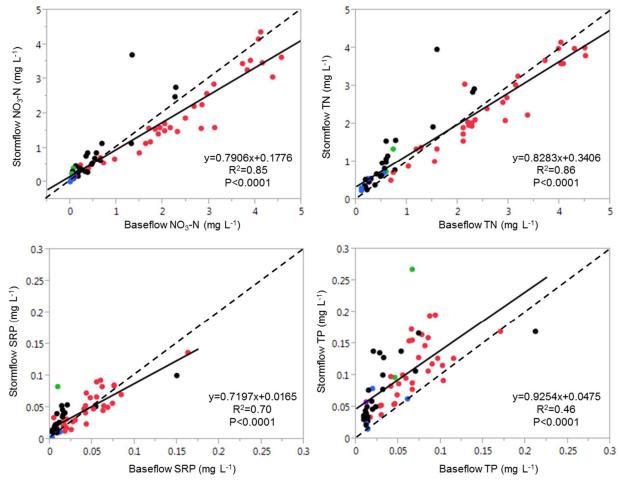


Figure 2. Regression of baseflow versus stormflow constituent concentration data across the Beaver Reservoir, Illinois River, Poteau River, Strawberry River, and Upper Saline River watersheds. The dashed black line represents the 1:1 relationship whereas the solid black line represents the baseflow to stormflow regression trend line. Watersheds are separated by color: Beaver Reservoir watershed=Black, Illinois River watershed =Red, Poteau River watershed =Green, Upper Saline River watershed =Blue, and Strawberry River watershed =Purple.

Geometric mean concentrations of nutrients during baseflow and stormflow were also compared for sites within the Beaver Reservoir and Illinois River watersheds separately. These also showed significant positive correlation for NO₃-N, TN, SRP, and TP (r^2 >0.43). There was not enough data to support a similar regression model for sites within the Poteau River, Upper Saline River, and Strawberry River watersheds separately, therefore, their data was combined. The result of combining sites within the Poteau River, Upper Saline River, upper Saline River, upper Saline River, and Strawberry River watersheds was similar to the outcome when all sites were included. A significant and positive linear regression was found for NO₃-N, TN and SRP (r^2 >0.49), while TP was marginally significant (r^2 =0.32, P=0.054).

Overall, the range in geometric mean concentrations across the nutrients were similar under baseflow or stormflow conditions across and within the watersheds (0.72 – 0.92). The slopes of these linear regressions were all just less than one with intercepts above zero. For sites that had overall low concentrations (less than 1.0 mg L⁻¹ NO₃-N, TN; less than 0.05 mg L⁻¹ SRP), geometric mean concentrations for NO₃-N, TN, and SRP tended to be greater during stormflows relative to baseflow. However, for sites that had overall high concentrations, NO₃-N, TN and SRP tended to have greater concentrations during baseflow compared to stormflow. This suggests that nutrient concentrations in streams were likely diluted by rainwater (~0.8 mg L⁻¹ NO₃-N, NADP 2011). Similar dilution trends were also observed by Poor & McDonnell (2007). Dilution was most evident in the Illinois River watershed (red data points), whereas the other watersheds had stormflow concentrations that were consistently greater than baseflow concentrations.

Geometric mean TP concentrations during stormflow were generally greater than those observed during baseflow. This observation is likely the result of particulate Phosphorus transport during runoff events (Sims et al 1998; Sharpley et al 1994). Brion et al (2010) suggested that a similar increase in phosphorus during storm events within a smaller headwater catchment of the Illinois River watershed was also likely due to particulate phosphorus from sediment in runoff or phosphorus being released from instream sediments. This was not seen in the SRP concentrations relationship as it is a measure of dissolved phosphorus, while TP is the combination of dissolved and particulate phosphorus.

The statistically significant regressions found for each constituent suggest that when concentrations are high for baseflow, the concentrations will also be high for stormflow as well. In addition, when concentrations are low for baseflow, the concentrations will most likely be low for stormflow. Analysis of variance (ANOVA) was conducted and revealed that the variation between geometric mean nutrient concentrations observed during baseflow and stormflow was not statistically different (P>0.2) than the variation within baseflow and stormflow for NO₃-N, TN, and SRP. This suggests that when examining the data across all watersheds, baseflow and stormflow NO₃-N, TN, and SRP concentrations for a given site are not significantly different. These nutrient concentration relationships for baseflow and stormflow conditions are important to the next portion of this study because the concentrations during baseflow across all the sites monitored in these five watersheds were used to establish statistical relationships with watershed characteristics.

3. LAND USE RELATIONSHIPS

Baseflow nutrient concentrations were significantly correlated to multiple land use metrics across the five watersheds (Table 5). The analysis conducted for the full database which included permitted discharge facilities (n=114 sites) had sites that were outliers due to high effluent concentrations. These sites reduced overall correlation with land use. As one of the objectives of this study is to determine the influence of land use on WQ, the Pearson correlation analysis presented will be for the reduced database (n=74) that excluded sites downstream from permitted discharge facilities.

The proportion of pasture within a 30 m riparian buffer out of the entire subwatershed pasture area had the highest correlation with geometric mean concentrations of nutrients. Nitrate-N and TN had correlation coefficients greater than 0.80 while SRP had a correlation coefficient of 0.68 and TP a correlation coefficient of 0.48. The 60, 90, and 120 m riparian buffers for this metric also had high correlation with nutrients. Poultry House Density (PHD) and Human Use Index (HUI) were the next highest correlations, showing that as the density of poultry houses and human development increased in the watershed so did geometric mean concentrations of nutrients in the stream. Poultry house density was most highly correlated with NO₃-N, TN, and SRP with correlation coefficients greater than 0.72, while TP had a

correlation coefficient of 0.52. Human Use Index was shared the highest correlation with NO₃-N and TN (r>0.72), while SRP had a correlation coefficient of 0.64 and TP a correlation coefficient of 0.52.

When examining the metrics each constituent was most correlated with, NO₃-N and TN shared the highest correlation (r>0.80) with the proportion of pasture within a 30 m riparian buffer out of the entire subwatershed pasture area (AGSX30). Nitrate-N and TN also shared high correlation (r>0.70) with percentage pasture in the subwatershed (%AG), Human Use Index (HUI), and poultry house density (PHD). As area devoted to these activities increased, geometric mean concentrations increased.

Soluble reactive P was most highly correlated with PHD and had a correlation coefficient of 0.76. Soluble reactive P also showed high positive correlation (r>0.62) with AGXS30, percent pasture (%AG), percent pasture in the 30 m riparian buffer (%AGXS30), and HUI. Total P was most highly correlated (r=-0.59) with percentage of forest within a 30 m riparian buffer (%FORXS30). Total P also showed high correlation (r=0.56) with percent pasture within a 60 m riparian buffer (%AGXS60) as well as percent forest in the subwatershed (%FOR) with a correlation coefficient of -0.54.

Multiple studies have documented the positive relationship between land use influenced by human activities (e.g., row crops, pasture and urban development) in the catchment and nutrient concentrations in streams and rivers. Similar to the relationships found here, these studies showed a positive correlation with agriculture and nutrients and a negative correlation between forest and nutrients (McFarland & Hauck 1999; Omernick 1976; Giovannetti et al 2013; Strayer et al 2003). Where this study differs is in the inclusion of more detailed watershed characteristics, such as riparian land uses and poultry production. While the previous studies all identified urban, agriculture, and pasture as being correlated with increased nutrient concentrations, the results here highlight two important factors. First, there is a spatial connectedness between land use and water quality where riparian land uses appear to be more important than overall subwatershed land use. Secondly, specific agricultural practices, such as poultry production also had high correlation with nutrients, suggesting that the driving factor for increased nutrient concentrations in these watersheds is not the presence of pasture, but the application of poultry litter on those pasture areas.

Table 5. Simplified Pearson correlation matrix for land use metrics (independent variable) and water quality constituents (dependent variable). Land use metrics displayed were significantly correlated to constituents (P<0.05) and had an absolute value of the correlation coefficient greater than 0.25. Riparian buffer metrics were condensed to show only the distance that shared the highest correlation with all constituents. Abbreviations for land use metrics are given in Table 3.

	Ν	ΤN	SRP	ΤР	%FOR	%AG	RDDEN	RXS	%RXS	FORXS120	%FORXS120	AGXS30	%AGXS30	HUI	NADEP	PHD	STRDEN	SLOPE
N	1.00	0.98	0.78	0.45	-0.67	0.72	0.37	0.48	0.37	-0.53	-0.65	0.80	0.68	0.71	-0.54	0.73	0.63	-0.37
TN		1.00	0.79	0.57	-0.70	0.74	0.37	0.46	0.34	-0.56	-0.70	0.82	0.72	0.74	-0.50	0.72	0.65	-0.45
SRP			1.00	0.75	-0.59	0.65	0.28	0.32	0.27	-0.49	-0.58	0.68	0.62	0.64	-0.53	0.76	0.49	-0.35
TP				1.00	-0.54	0.49	0.27	0.20	0.16	-0.51	-0.58	0.48	0.53	0.52	-0.27	0.52	0.30	-0.47

Total-N and NO₃-N were highly correlated across these watersheds (r=0.98). Both showed the same relation with land use metrics, where correlation coefficients were nearly identical in magnitude and direction. This relationship held true within each watershed as well. This suggests that for the purposes of this study, NO₃-N and TN are interchangeable, and to make the results simpler, NO₃-N was removed from the remainder of the analysis.

4. **REGRESSION ANALYSIS**

While Pearson correlation was used to evaluate the strength and direction of association between nutrient concentrations and all the developed land use metrics, a linear model was used to predict nutrient concentrations from land use. Sites below permitted discharge facilities were not included in the regression analysis in order to isolate the influence of land use on water quality. In the correlation analysis it was determined that the proportion of pasture land use in the 30 m riparian buffer relative to the entire subwatershed pasture area (AGXS30) had the highest correlation across all four constituents. Therefore, it was selected for the initial single metric regression model (Figure 3). The proportion of pasture within a 30 m riparian buffer out of the entire subwatershed pasture area (AGXS30) was significant for each constituent (P<0.0001), but r² was variable, ranging from 0.67 for TN to 0.23 for TP (Table 6).

The results also highlight how sites from each watershed vary within the linear model (Figure 3). The Illinois River watershed in red, had high nutrient concentrations and riparian pasture relative to other watersheds. In contrast, the sites within the Strawberry River watershed had nutrient concentrations that did not exhibit a signal with AGXS30 (slope~0). Nutrient concentrations were roughly the same regardless of AGXS30. This could observation can be interpreted by examining the relationships between pasture and poultry production. In the Illinois River, Poteau River, and Beaver Reservoir watersheds where poultry production is comparatively high, correlation analysis suggests that the application of poultry litter is responsible for the relationship between pasture and WQ. The Strawberry River watershed, on the other hand, has comparatively very little poultry production. In light of this fact, the results are consistent with the suggested poultry-WQ relationship.

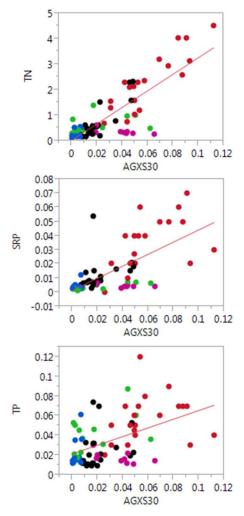


Figure 3. Results showing linear regression plots relating land use metrics to water quality constituents. Watersheds are separated by color: Beaver Reservoir watershed=Black, Illinois River watershed=Red, Poteau River watershed=Green, Upper Saline River watershed=Blue, and Strawberry River watershed=Purple.

Table 6. Results of linear regression analysis relating water quality constituents to AGXS30 land use	
metric. AGXS30 was significant at P<0.05.	

Constituent (mg L ⁻¹)	Number of Sites	Metric	Total Variation Explained (r ²)	Р
TN	74	AGXS30	0.67	< 0.0001
Equation: TN = 0.034+3	2.391*(AGXS	30)		
SRP	74	AGXS30	0.46	< 0.0001
Equation: SRP = 0.001+	-0.431*(AGXS	30)		
TP	74	AGXS30	0.23	< 0.0001
Equation: TP = 0.022+0	.441*(AGXS3	0)		

If, however, poultry litter application is driving the pasture-WQ relationship, the question should be asked, why was pasture and not poultry house density the most highly correlated across all nutrients? The answer to this may be one of several things. There may be some other activity taking place in the riparian pasture areas that is additive in explaining variance in the WQ data. Or, the quality of the data used to build the poultry house density layer is lower than that used for pasture area. The poultry house location layer provided by the state of Arkansas does not distinguish between active or inactive poultry houses. All poultry houses were included in the metric, regardless of their operational status with the assumption that even inactive houses may still be contributing to nutrient concentrations in streams from legacy litter applications. Finally, it may be an issue of resolution in the data. Of the sites included in the analysis, 15 of 74 had zero poultry houses, while 73 of 74 had some proportional riparian pasture (AGXS30). The truncated range in the poultry metric may have contributed to the correlation being lower than that of AGXS30, even if poultry litter application was the most significant contributor to nutrient concentrations.

Stepwise forward multiple linear regression selected the proportion of pasture land use in the 30 and 60 m riparian buffer relative to the entire subwatershed pasture area (AGXS30 and AGXS60), percentage of forest in the 30 m riparian buffer, and poultry house density (PHD) as the most significant metrics to predict WQ. A significant model was developed for each constituent (Figure 4). The percentage of variability in WQ explained by these metrics ranged from 40% for TP to 71% for TN (Table 7). This is an improvement over the single metric linear regression models. Variance inflation factors were all below the suggested threshold for multicollinearity (VIF<5) and tolerance values were all greater than 0.4 (Neter et al. 1996). However, Pearson correlation analysis revealed collinearity between PHD and AGXS30 of 0.74. This suggests that it may not be appropriate to utilize both AGXS30 and PHD in a multiple linear regression model as it runs the danger of being over-fitted because of the redundancy of the two predictors. Correlation between PHD and %FORXS30 was not as strong comparatively (r=-0.57).

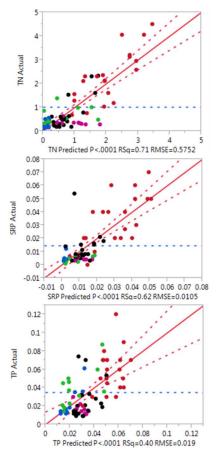


Figure 4. Results showing predicted to observed plots for water quality constituents. Models were generated using stepwise multiple linear regression analysis relating land use metrics to water quality. Solid red lines represent a one-to-one relationship. Watersheds are separated by color: Beaver Reservoir watershed=Black, Illinois River watershed=Red, Poteau River watershed=Green, Upper Saline River watershed=Blue, and Strawberry River watershed=Purple.

Table 7. Results of stepwise regression analysis relating water quality constituents to land use metrics.

Constituent	Number of		•	Total Variation	
(mg L⁻¹)	Sites	Metric	VIF	Explained (%)	Р
TN	74	AGXS30	2.18		< 0.0001
		PHD	2.18	0.71	0.008
Equation: TN = 0	0.019 + 24.883	8*(AGXS30) +	0.009*(P	HD)	
SRP	74	PHD	1.88		< 0.0001
		AGXS60	1.88	0.62	0.014
Equation: SRP =	= 0.0012 + 0.0	004*(PHD) + (0.0763*(A	GXS60)	
TP	74	%FORXS30	1.48		0.0002
		PHD	1.48	0.4	0.021
Equation: TP = 0	0.056 + 0.0002	2*(PHD) - 0.04	4*(%FOR	RX S 30)	

5. CART AND NCPA

In the linear analysis, we excluded sites with point sources because they reduced the impact of land use within the analysis. CART, however, has the advantage of being able to use categorical data such as the presence or absence of permitted discharge facilities upstream of the sampling site. Categorical data as well as continuous data can be selected for tree splits. CART analysis was performed on the full dataset, including point-source influences, with the hope that the categorical point source variable would be used as one of the primary tree splits to separate the sites with high concentrations due to point sources. As will be seen however, this was not the case, requiring a separate analysis with the point sources removed. The entire land use metric dataset was used during the CART analysis. Results indicated that a significant hierarchical structure exists between nutrients and land use metrics regardless of the inclusion or exclusion of point sources.

While CART provided primary tree splits within the nutrient data based on land use metrics, it did not provide the significance or uncertainty associated with the splits. In addition, CART will select the most appropriate split, but there may have been others that were significant and meaningful for the purposes of this study. Change point analysis was then used to find additional change points besides the primary tree split as well as the significance and uncertainty associated with those change points.

Full Data Set Analysis

When sites downstream of permitted discharge facilities were included in the model, the pruned constituent regression trees included two variables: forested percentage of the 30 m riparian buffer (%FORXS30) and proportion of forest in the riparian area (90 m) relative to the entire forested area (FORXS90). Additional buffer distances (60, 90, 120 m) were analyzed for each riparian metric and included in the model. CART analysis showed that the 30 and 90 m buffer distances were the most significant across all three nutrients (Figure 5). Even though the presence of point sources was included in the model as a categorical variable, CART failed to select it as a primary tree split.

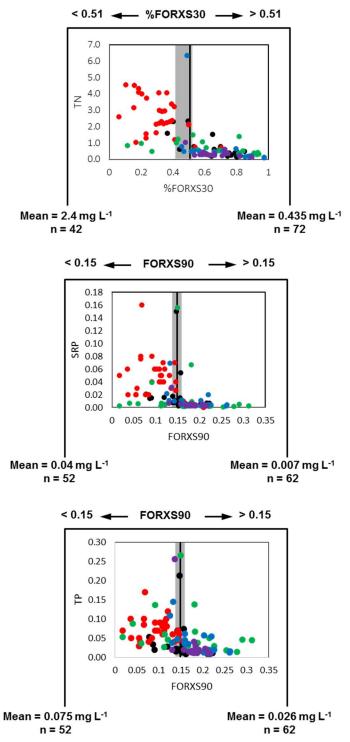


Figure 5. Results for CART (classification and regression tree) analysis of water quality constituents for all watershed sampling sites. Scatterplots illustrate the response of constituents at each tree split. The vertical solid line represents threshold of the predictor that best explains the variation in the constituent data. The vertical grey box surrounding the threshold line indicates the 90% confidence interval of the threshold. Split value is display above each tree split. The constituent mean and number of samples is displayed at each terminal point of a split. Watersheds are separated by color: Beaver Reservoir watershed=Black, Illinois River watershed=Red, Poteau River watershed=Green, Upper Saline River watershed=Blue, and Strawberry River watershed=Purple.

Soluble reactive P and TP tree splits occurred when 15% of the watershed forested land use was within the 90 m riparian buffer. For SRP, sites below 15% averaged 0.04 mg L⁻¹, while sites above averaged 0.007 mg L⁻¹. For TP, sites below 15% averaged 0.075 mg L⁻¹, while sites above averaged 0.026 mg L⁻¹. The CART model for TN contained a single tree split when 51% of the riparian buffer was forested (%FORXS30). When forested riparian buffer was greater than 51%, TN averaged 0.435 mg L⁻¹. Sites with less than 51% forested buffer averaged 2.4 mg L⁻¹.

Looking closer at the data and how each watersheds sites are spread within the models, it can be seen that forested riparian area for the Illinois River watershed is lower than the other sites but concentrations are generally higher (Figure 5). The Upper Saline River and Strawberry River watersheds, when compared to the Illinois River watershed, have lower nutrient concentrations, while the Poteau River and Beaver Reservoir watersheds are in between the two. Sites with the highest concentrations (TN greater than 5.0 mg L⁻¹; SRP and TP greater than 0.15 mg L⁻¹) in Figure 5 are exclusively due to point source influence.

The top ten change points for each constituent and their associated significance are displayed in Table 8. Change point analysis for the CART splits revealed that each contained a statistically significant relationship; r²-values for each constituent were greater than 0.28. The coefficient of determination for each change point was summed across nutrients and then used to rank change points high to low. In this way, the top ranking change point explained the most variability across all three nutrients. The change point that explained the most variability across all three constituents was percentage of forested riparian buffer (%FORXS60).

Table 8. Nonparametric change point analysis (nCPA) statistics for the entire predictor data set. All sites and their subsequent constituent concentrations are included. The top ten significant change points are displayed for each constituent. CART selected change points are bolded.

	Change					
		Point	r ²	Р	5%	95%
TN						
%	FORXS30	0.509	0.56	0.001	0.409	0.529
%	6FORXS60	0.504	0.55	0.001	0.382	0.509
	AGXS30	0.066	0.54	0.001	0.045	0.066
	AGXS60	0.129	0.54	0.001	0.089	0.132
	AGXS90	0.178	0.53	0.001	0.141	0.196
	AGXS120	0.205	0.52	0.001	0.189	0.252
	HUI	0.467	0.52	0.001	0.456	0.58
	%AGXS30	0.434	0.51	0.001	0.408	0.435
%	6FORXS90	0.363	0.51	0.001	0.363	0.519
%	FORXS120	0.447	0.5	0.001	0.347	0.529
SRP						
	FORXS90	0.15	0.29	0.001	0.138	0.157
I	FORXS120	0.195	0.29	0.001	0.179	0.204
%	6FORXS60	0.504	0.29	0.001	0.388	0.516
	AGXS30	0.051	0.28	0.001	0.035	0.066
	AGXS60	0.12	0.28	0.001	0.066	0.133
	AGXS90	0.156	0.28	0.002	0.099	0.194
%	6FORXS30	0.528	0.28	0.001	0.419	0.59
	FORXS60	0.107	0.28	0.001	0.088	0.108
	AGXS120	0.22	0.27	0.001	0.126	0.252
%	6FORXS90	0.485	0.26	0.003	0.36	0.575
ТР						
	FORXS90	0.15	0.28	0.002	0.138	0.157
I	FORXS120	0.195	0.28	0.001	0.186	0.206
%	6FORXS30	0.528	0.27	0.001	0.487	0.609
%	6FORXS60	0.504	0.27	0.001	0.474	0.675
	FORXS60	0.106	0.25	0.002	0.092	0.11
%	6FORXS90	0.485	0.23	0.001	0.475	0.659
	FORXS30	0.057	0.22	0.002	0.049	0.066
%	FORXS120	0.486	0.22	0.002	0.469	0.659
	%AGXS60	0.404	0.2	0.003	0.332	0.457
	%AGXS90	0.409	0.19	0.005	0.341	0.461

One particular issue with using riparian land use as a predictor of WQ and therefore a possible management tool is with spatial resolution of rivers included in the analysis. The GIS river file used in this analysis included all perennial, ephemeral, and intermittent streams. This resolution of streams may be

too fine when translating the results to decision makers. For instance, the results show a strong correlation between forested riparian area and WQ. A decision maker might then conclude that increasing forested buffer in perennial channels would have a significant impact on WQ. What these results support however is that one would have to increase forested buffer in perennial, ephemeral, and intermittent streams in order to see results. Buck et al. (2003) found that the stream order played a significant role in the predictive power of land use. In larger streams, upstream land use was shown to be more important, while in smaller streams, more localized land use was more important for determining water quality. Future studies should seek to establish relationships by flow category (or stream order) to determine if the length of stream miles to be treated based on land use-water quality relationships could be shortened.

Point Sources Excluded Analysis

When sites below permitted discharge facilities were not included in the CART analysis, the pruned constituent regression trees contained two variables: poultry house density (PHD), and %FORXS30. Both TN and SRP contained a single split at 38.4 poultry houses per 4000 hectares (PHD). When PHD was greater than 38.4, TN averaged 2.45 mg L⁻¹ and SRP averaged 0.036 mg L⁻¹. When PHD was less than 38.4, average TN was 0.548 mg L⁻¹ and SRP was 0.008 mg L⁻¹. TP contained a single split at 54% forested riparian buffer (%FORXS30). Sites with greater than 54% forested buffer averaged 0.023 mg L⁻¹ TP while sites with lower averaged 0.055 mg L⁻¹ TP (Figure 6).

The top ten change points for each constituent are displayed in Table 9. Change points for the CART selected splits were significant and explained a greater portion of the variability than the dataset that included sites below permitted discharge facilities (r^2 >0.43). PHD was most significant for TN and SRP (r^2 >0.53), while %FORXS30 was most significant for TP (r^2 =0.43).

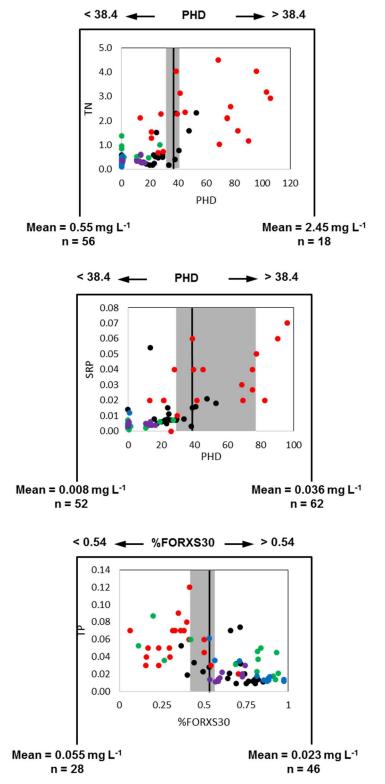


Figure 6. Results for CART (categorical and regression tree) analysis of water quality constituents excluding sites with point-source influence. Format as in Figure 5.

Table 9. Nonparametric change point analysis (nCPA) statistics for the entire predictor data set.
Constituent concentrations from sites with point source influence are excluded. The top ten significant
change points are displayed for each constituent. CART selected change points are bolded.

	Change Point	r ²	Р	5%	95%
TN			<u> </u>	• / •	
PHD	38.36	0.62	0.001	33.97	41.13
HUI	0.467	0.61	0.001	0.451	0.607
AGXS30	0.067	0.6	0.001	0.0416	0.071
AGXS60	0.135	0.6	0.001	0.083	0.145
AGXS90	0.208	0.6	0.001	0.132	0.219
%FORXS30	0.517	0.59	0.001	0.409	0.52
%FORXS60	0.486	0.59	0.001	0.387	0.491
%FORXS90	0.46	0.59	0.001	0.363	0.477
%FORXS120	0.447	0.59	0.001	0.347	0.73
%FOR	0.478	0.58	0.001	0.339	0.484
SRP					
PHD	38.36	0.53	0.001	27.59	78.805
AGXS90	0.155	0.5	0.001	0.147	0.211
AGXS60	0.1	0.49	0.001	0.088	0.142
AGXS120	0.205	0.48	0.001	0.193	0.294
HUI	0.467	0.47	0.001	0.449	0.579
%FOR	0.476	0.46	0.001	0.339	0.487
%AGXS90	0.482	0.46	0.001	0.411	0.548
%AGXS120	0.49	0.46	0.001	0.419	0.546
%AGXS60	0.465	0.457	0.001	0.396	0.535
%AG	0.462	0.45	0.001	0.253	0.62
ТР					
%FORXS30	0.535	0.43	0.001	0.401	0.551
%FORXS60	0.483	0.42	0.001	0.388	0.548
%FORXS90	0.46	0.42	0.001	0.363	0.486
%FORXS120	0.447	0.42	0.001	0.388	0.477
%AGXS60	0.465	0.42	0.001	0.405	0.491
%AGXS90	0.482	0.42	0.001	0.411	0.503
%AGXS120	0.49	0.42	0.001	0.419	0.514
FORXS120	0.186	0.41	0.001	0.168	0.208
FORXS90	0.148	0.39	0.001	0.13	0.16
HUI	0.467	0.38	0.001	0.448	0.535

When sites below permitted discharge facilities were removed, predictive ability with change points was increased. Significant change points were found for almost all the predictors and 22 out of 30 were associated with riparian buffers (Table 9). A common change point that explained the most variability

across all three constituents was found using the same method detailed in the full dataset analysis. The predictor that that explained the most variation among all constituents was %FORXS30, which differs from the predictor selected for the full dataset analysis by a 30 m distance. Forested riparian buffer (%FORXS30) was the top most predictive change point for TP, but it was the 12th most predictive change point for SRP (r^2 =0.44) and the 6th for TN (r^2 =0.59).

The point source excluded analysis confirm the findings of Cox et al. (2013) which established a relationship between poultry house density and WQ for baseflow and stormflow conditions. Cox et al. (2013) found that for the Illinois River watershed, poultry litter accounted for a majority of the phosphorus loading to the watershed. Other studies have also demonstrated the water quality impacts from poultry litter runoff (Haggard et al 2005b; Ciparis et al 2012; Sauer et al 1999 & 2000).

6. PRIORITIZATION OF SUBWATERSHEDS

Human influence on land use change in the riparian zone proved to have the greatest influence on water quality as demonstrated by the statistical methods used here. Agreement among the statistical methods makes it easier to move forward with prioritization of HUC-12 subwatersheds using a change point, as it marks a statistically clear change between lower and higher nutrient concentrations for a give land use metric.

A single-metric prioritization methodology was developed in order to provide a simple approach for watershed management. Ideally, it would be the single most important land use metric when predicting nutrient concentrations. In this way, decision makers would only have to examine a watershed for a single factor. As shown using change points, when sites below permitted discharge facilities were removed from the analysis, percent forest in the 30 m riparian buffer (%FORXS30) explained the most variability across all nutrients.

A multi-metric prioritization methodology was also developed to explain more of the variability in nutrient concentrations by using additional land use metrics. For the multi-metric analysis, there were four metrics that explained the most variability when analyzed for change points: %FORXS30, HUI, Poultry House Density (PHD), and proportion of the entire watershed's agricultural land use that resides in the 60 m

riparian buffer (AGXS60). However, we wanted to strive for simple predictors, therefore we selected a common buffer distance for our riparian land use metrics of 30 meters, which would complement the single-metric watershed priority selections as well as provide an easy comparison between the two significant riparian indicators, pasture and forest. This necessitated the use of percent pasture within the 30 m buffer (%AGXS30) in place of the more confusing metric AGXS60. The percentage of pasture within a 30 m buffer (%AGXS30), similar to the percentage of forest within a 30 m buffer (%FORXS30), are metrics that give the percentage of a particular land use within a 30 m riparian buffer out of the entire buffer area. This differs from AGXS60 in that AGXS60 gives the percentage of pasture land use within the riparian buffer out of the entire watersheds land use. The land use metric substitutions that replaced those selected by change point analysis yielded a total reduction in predictive power of roughly 2%. For most predictors, the change points were the same across all constituents, however, for PHD, the change point ranged from 38.4 - 43.4. For simplicities sake, an average PHD across the three nutrients of 40 was used to represent the change point. Priority HUC-12s are displayed for each watershed in Figures 7 through 11.

Beaver Reservoir Watershed

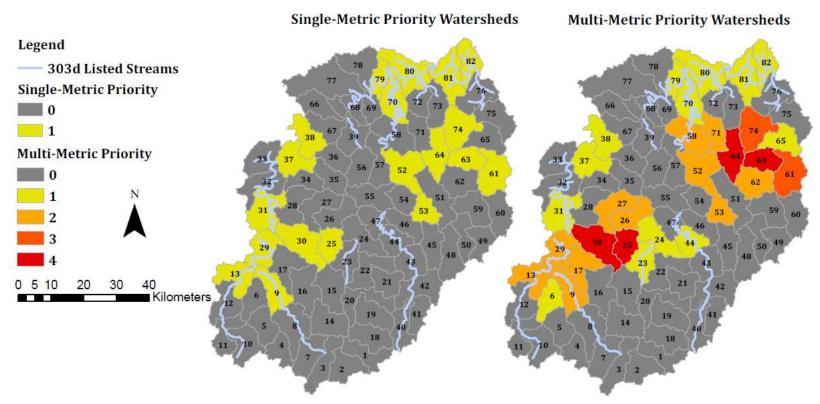


Figure 7. Single and Multi-Metric watershed priority map for the Beaver Reservoir watershed.

Illinois River Watershed

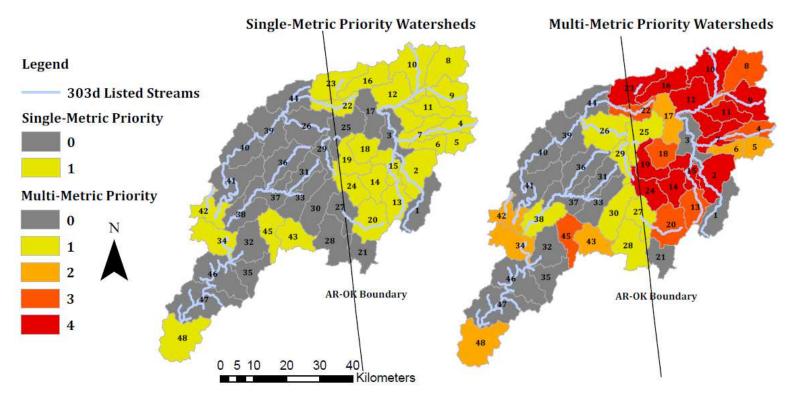


Figure 8. Single and Multi-Metric watershed priority map for the Illinois River watershed.

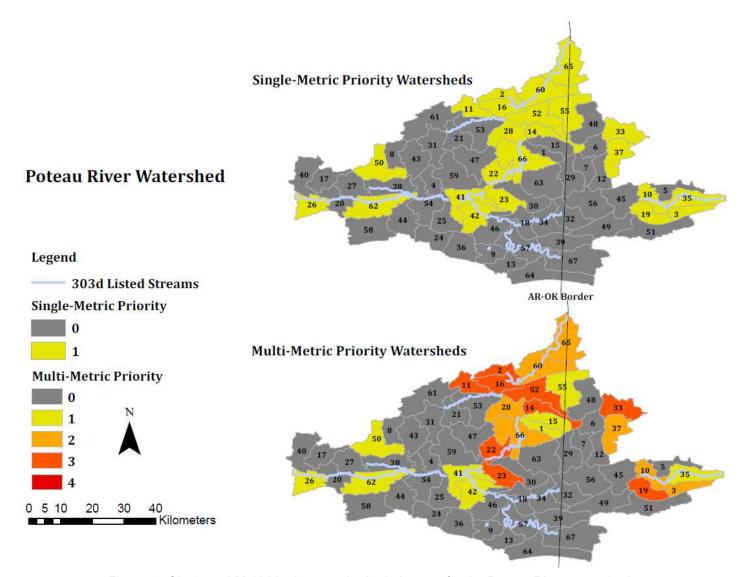
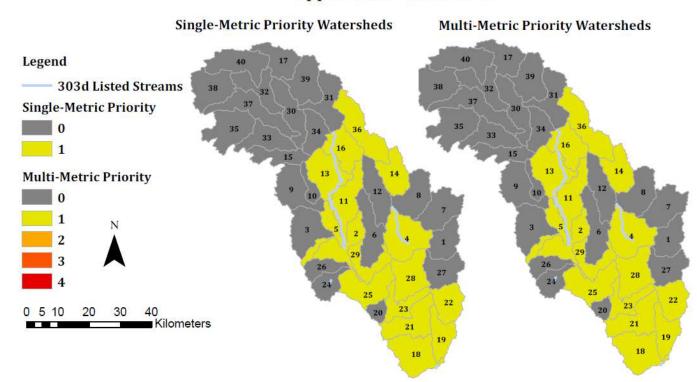


Figure 9. Single and Multi-Metric watershed priority map for the Poteau River watershed.



Upper Saline Watershed

Figure 10. Single and Multi-Metric watershed priority map for the Upper Saline River watershed.

Strawberry River Watershed

Legend

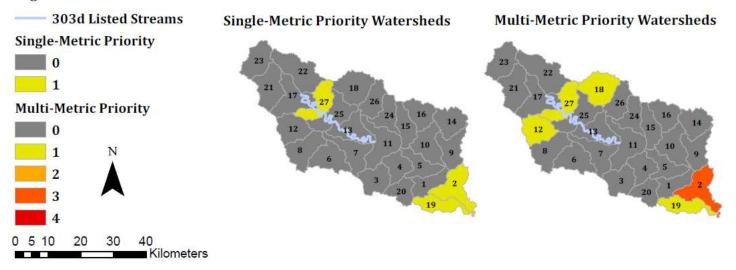


Figure 11. Single and Multi-Metric watershed priority map for the Strawberry River watershed.

When comparing the subwatersheds that were selected as a priority for the single-metric versus the multimetric methodology, there is considerable overlap. The greatest percentage of priority subwatersheds were found for the Illinois River watershed with over half of the subwatersheds selected by either methodology. In contrast, at most only five subwatersheds were selected for the Strawberry River watershed representing around 20% of its total subwatersheds. The multi-metric methodology provided additional priority subwatershed resolution for every watershed except the Upper Saline River watershed, which did not have a single basin that met the priority criteria for HUI, PHD, or %AGXS30.

Most watershed models will use observations from a single watershed to quantify land use and nutrient relationships (Saraswat et al 2010a, 2010b, 2013a, 2013b, 2013c; Haggard et al 2010). In this study though, the criteria to prioritize each subwatershed was normalized across five watersheds. This method has its advantages and disadvantages. When priorities are normalized across all five watersheds, it is useful to see that water quality problems faced in the Strawberry River or Upper Saline River watersheds pale in comparison to those faced in the Illinois River and Beaver Reservoir watersheds. Because of this, the Strawberry River and Upper Saline River watersheds have very few subwatersheds that even registered as priorities. If looking to prioritize watersheds at the state level, this can be beneficial, as it provides resolution as to which subwatersheds are the most important. However, when looking at the priorities from the watershed level, there is not as much resolution in watersheds like the Upper Saline River watersheds. This could lead to difficulties determining where to focus efforts to restore water quality.

When examining the priority maps developed in other studies, our priorities are consistent with their findings. The most agreement is found in priorities for the Poteau River (Saraswat et al. 2013b), Illinois River (Haggard et al. 2010; Saraswat et al. 2010a), and Beaver Reservoir (Saraswat et al. 2010b) watersheds. However, due to the low resolution of priorities offered by our study in the Upper Saline River (Saraswat et al. 2013c) and Strawberry River (Saraswat et al. 2013a) watersheds, priority agreement is not as apparent. In a comparison study of the STEPL, SPARROW, and SWAT models for the Beaver Reservoir watershed, the SPARROW and SWAT models compared favorably even though SPARROW is a multiple regression model and SWAT is a deterministic model (Morgan, 2007). However,

unlike these previous models, this analysis can be easily applied to other watersheds with similar land uses and agricultural practices. Future studies should expand on this work and group specific regions by watershed characteristics that are most associated nutrient concentrations. In this way, managing a watershed for nonpoint source nutrients with limited H/WQ data could be as simple as applying the appropriate land use model and validating the results with a targeted sampling program.

We performed a final check to ensure that the priority selections complimented the actual water quality conditions sampled. Sites were isolated from the multiple sampling studies whose delineated watersheds were a match for the HUC-12 boundaries. In this way, the water quality seen at the site would be directly correlated to the land use within the HUC-12 and not be influenced by HUC-12s upstream. Sites with point source influence were removed from this analysis. A one way ANOVA was performed on the data set for each nutrient. Results showed that sites selected as a priority had significantly higher nutrient concentrations that those that were not selected (Figure 12). Draft EPA TN nutrient criteria concentrations for Level III Ecoregions IX and XI are 0.69 and 0.31 mg L⁻¹, respectively while TP criteria for IX and XI are 0.037 and 0.01 mg L-1, respectively (Evans-White et al. 2014). Sites selected as a priority for TN had a mean concentration of 2.06 mg L⁻¹, far higher than the established nutrient criteria, while those not selected had a mean of 0.53 mg L⁻¹. Sites selected as a priority for TP had a mean concentration of 0.069 mg L⁻¹ while those not selected were 0.026 mg L⁻¹. These results are not conclusive as our watersheds span multiple ecoregions, however, it confirms that in general, sites selected as a priority exceeded the nutrient criteria set by the EPA while sites that were not selected were more closely in line with those nutrient limits. As more watershed concentration data becomes available, it will be possible to separate out these relationships by watershed and Level III Ecoregion to determine if priority subwatersheds are exceeding their specific ecoregion nutrient criteria.

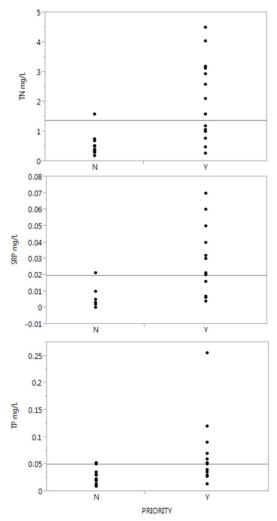


Figure 12. Priority site selection ANOVA showing the difference in concentrations for sites selected as a priority by the land use metrics.

The ANOVA results also indicate that some of the subwatersheds selected as a priority contained baseflow geometric mean nutrient concentrations that were below the draft EPA nutrient criteria for TP and TN. Again, this highlights the importance of confirming the results of this priority analysis with a targeted sampling program before any management strategies are put into place. One of the strengths of this analysis is that it narrows the scope of the watershed that will need to be assessed. Instead of a broad sampling program that captures the spatial variability in land use, a targeted sampling program can be used that is aimed at confirming the predicted concentration levels.

V. CONCLUSIONS

This study examined the relationship between developed land use metrics and baseflow WQ in order to develop a prioritization methodology for select Arkansas watersheds (HUC-8). Linear regression was used to test the hypothesis that the slope of nutrient concentrations observed during baseflow compared with nutrient concentrations observed during stormflow will be zero. Regression slopes were not equal to zero and linear relationships were significant allowing us to reject the null hypothesis that slope of nutrient concentrations compared with watershed characteristics will be zero. Correlation analysis showed significant positive and negative land use-water quality relationships. For specific land use metrics, slopes were not equal to zero and linear relationships were significant. Results from correlation and regression analysis determined that the null hypothesis H₀2 could be rejected. Finally, CART and nCPA were used to test the hypothesis that there will not be any change or deviation along watershed characteristics (x) with nutrient concentrations (y). Change point was able to identify multiple significant changes in deviation along land use metrics with nutrient concentrations allowing us to reject H₀3.

As baseflow WQ was used in this study, it was necessary to validate its use. Land use impacted WQ is typically thought of as coinciding with runoff events, however, additional factors have shown that streams impacted for nutrients due to land use have higher baseflow concentrations as well. We were able to confirm a significant and positive linear relationship for the five watersheds used in this study showing that streams with higher stormflow nutrient concentrations also have higher baseflow concentrations and vice versa.

Riparian buffer zones, a spatial category assessed in previous studies were further studied here by exploring land uses a variety of distances from the stream centerline. Land use within the riparian buffers were shown to have increased significance compared to the overall watershed land use. The majority of the highest correlated land use indicators for each nutrient were associated with the riparian buffer. This relationship held true regardless of the inclusion or exclusion of point source effluent impacted sites. As increased distances were included as part of the stream buffer that took up a larger portion of the

watershed area, the closer they resembled the watershed land use as a whole. Peak significance varied between 30 and 60 m for differing land use metrics.

The most significant metrics identified by correlation, regression, and nCPA were used to establish a model that was subsequently applied to all subwatersheds (HUC-12s) to make recommendations on their priority for use of local, state, and federal resources. Through ANOVA, subwatersheds selected as a priority were shown to have higher concentrations of nutrients than those not selected. Established nutrient criteria were also used to confirm the results. In addition, there was significant overlap of subwatersheds selected as priorities with those selected from other studies.

While most studies of this kind will examine a single watershed, we sought to incorporate the effects over a large portion of the state of Arkansas with the intention of seeing if there were common relationships regardless of ecoregion or other various spatial contexts. While we were able to establish significant relationships across the entire dataset, when analyzing each watershed in isolation, they did not always hold true. For some of the watersheds the reasons were simple. For instance, the dominance of the poultry industry in the NW corner of the state created a significant WQ relationship that was able to overwhelm the dataset in such a way that it remained significant even after the inclusion of non-poultry producing areas such as the Strawberry River and Upper Saline River watersheds.

The most significant outcome of this study is its application to watersheds with similar land uses and nutrient concentrations. There are multiple HUC-8 watersheds within the Ozark Highland ecoregion that have high poultry production and pasture within the riparian buffer. Consequently, they are also very limited in H/WQ data. A simple approach to managing these watershed would be to apply this model and then verify the selected priority subwatersheds with a limited monitoring program. This approach reduces the overall number of sites as well as the uncertainty in selecting sites to monitor.

This study has shown its value for the State of Arkansas in furthering its understanding of land use-WQ relationships. While this study focused on the confines of the state boundary, further analysis should be focused on a three or four state region. In this way, watersheds could be grouped into more "like" categories to examine relationships that are specific to that area. Watersheds in the NW corner of

Arkansas NE corner of Oklahoma, and SW corner of Missouri would likely be lumped together due to the Ozark Highlands ecoregion, but also because of the strong presence of poultry production. Watersheds in Eastern Arkansas would likely be lumped together with those from Western Mississippi in the Mississippi Alluvial Plain Ecoregion. Land use relationships here would likely center around the impacts of crop production, furthering the need to understand agricultural impacts in the riparian zones. Prioritization models based around areas of similar land use would be beneficial in reducing the amount of water quality monitoring that is necessary to adequately characterize a watershed. Ultimately they would enable the efficient use of local, state, and federal resources for water quality mitigation.

VI. REFERENCES

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