

---

Masters Theses

Student Theses and Dissertations


---

Fall 2019

## Temporal changes of nutrients within the Lower Grand River Watershed and selected sites

Weston Scott Duley

Follow this and additional works at: [https://scholarsmine.mst.edu/masters\\_theses](https://scholarsmine.mst.edu/masters_theses)

 Part of the [Bioresource and Agricultural Engineering Commons](#), [Geological Engineering Commons](#), and the [Hydrology Commons](#)

Department:

---

### Recommended Citation

Duley, Weston Scott, "Temporal changes of nutrients within the Lower Grand River Watershed and selected sites" (2019). *Masters Theses*. 7915.

[https://scholarsmine.mst.edu/masters\\_theses/7915](https://scholarsmine.mst.edu/masters_theses/7915)

This thesis is brought to you by Scholars' Mine, a service of the Missouri S&T Library and Learning Resources. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact [scholarsmine@mst.edu](mailto:scholarsmine@mst.edu).

TEMPORAL CHANGES OF NUTRIENTS WITHIN THE LOWER GRAND RIVER  
WATERSHED AND SELECTED SITES

by

WESTON SCOTT DULEY

A THESIS

Presented to the Faculty of the Graduate School of the  
MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree  
MASTER OF SCIENCE IN GEOLOGICAL ENGINEERING

2019

Approved by:

Katherine Grote, Advisor  
David Rogers  
Ryan Smith

© 2019

Weston Scott Duley

All Rights Reserved

## ABSTRACT

This report presents the results of a study carried out in collaboration with the U.S. Geological Survey (USGS) and the Missouri Department of Natural Resources (MDNR) to estimate total nitrogen (TN) and total phosphorus (TP) at five USGS monitoring sites within Lower Grand River Watershed (LGRW) and two monitoring sites on the Missouri River. The objective of this study was to quantify temporal changes in TN and TP concentrations and compare those to best management practices (BMPs).

In this study, the approach to the analysis of long-term surface water-quality data by using Weighted Regressions on Time, Discharge and Seasons models (WRTDS). The model method is formulated to enable flexibility in long-term trend representations, discharge-related components, and concentrations of TN and TP seasonal components. The WRTDS model is designed make estimates of the actual concentrations and fluxes as well as estimates that eliminate the influence of year-to-year variations in discharge. The method is designed to use weighted regressions on time, discharge and season to estimate concentrations. This method is designed to be a tool which identifies changes that are taking place within a watershed related to surface-water nonpoint sources of contamination.

In this case, the results given by the WRTDS models were used to determine if best management practices implemented over the study period, have had any significant effect on TN and TP concentrations. At each monitoring location, water quality data was compared to temporal changes within the watershed to determine the effectiveness of BMPs implemented over the study period.

## ACKNOWLEDGMENTS

I would like to thank Dr. Grote for offering advising throughout my education. The US Geological Survey personnel who have offered training and guidance throughout this project. Without the mission of the US Geological Survey, this project would not have been possible. I would also like to thank Dr. Smith and Dr. Rogers for offering guidance throughout the project.

## TABLE OF CONTENTS

	Page
ABSTRACT.....	iii
ACKNOWLEDGMENTS .....	iv
LIST OF ILLUSTRATIONS.....	vii
LIST OF TABLES.....	ix
NOMENCLATURE .....	x
<b>SECTION</b>	
1. INTRODUCTION.....	1
1.1. PROBLEM AND OBJECTIVE .....	1
1.2. STUDY AREA .....	3
1.2.1. Geology and Soil Classifications. ....	8
1.2.2. Hydrology.....	9
1.3. WATER QUALITY AND PREVIOUS CONCERNS.....	9
1.4. BEST MANAGEMENT PRACTICES .....	10
1.4.1. Mississippi River Basin Initiative 2012. ....	11
1.4.2. Planning Assistance to States 2014.....	11
1.4.3. My Healthy Watershed Plan 2016.....	12
2. METHODS.....	13
2.1. SITE SELECTION .....	13
2.2. SAMPLE DATA COLLECTION .....	13
2.3. WRTDS MODEL .....	14

2.4. STATISTICAL ANALYSES .....	18
2.5. SEASONAL ANALYSIS .....	19
3. RESULTS.....	21
3.1. THE EFFECTS OF BMP .....	21
3.2. SEASONAL VARIATION .....	28
3.3. LONG TERM TRENDS.....	31
4. CONCLUSIONS .....	34
5. RECOMMENDATIONS .....	36
BIBLIOGRAPHY.....	38
VITA.....	40

## LIST OF ILLUSTRATIONS

	Page
Figure 1.1. Location of the Lower Grand River Watershed. ....	4
Figure 1.2. Digital Elevation model Lower Grand Watershed. ....	5
Figure 1.3. Grand River Watershed area land use (USGS, 2016). ....	6
Figure 1.4. Lower Grand River Watershed area soil type. ....	8
Figure 3.1. 6900050 Medicine Creek total nitrogen. ....	23
Figure 3.2. 6900640 Muddy Creek total nitrogen.....	23
Figure 3.3. 6901500 Locust Creek total nitrogen. ....	24
Figure 3.4. 6902995 Hickory Branch total nitrogen. ....	24
Figure 3.5. 6900640 Muddy Creek total phosphorous. ....	25
Figure 3.6. 6900050 Medicine Creek total phosphorous.....	25
Figure 3.7. 6902995 Hickory Branch total phosphorous.....	26
Figure 3.8. 6901500 Locust Creek total phosphorous. ....	26
Figure 3.9. Comparative box and whisker plots which show how nutrient concentrations change with each BMP over the study period.....	27
Figure 3.10. Monthly flow-normalized total nitrogen concentrations for all short-term sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek. ....	29
Figure 3.11. Monthly flow-normalized total phosphorous concentrations for all short- term sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek. ....	29
Figure 3.12. Seasonal box and whisker plots for concentrations in for all short-term sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek. ....	30



Figure 3.13. Monthly FN nitrate flux for all for all sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek.....	31
Figure 3.14. Monthly FN phosphate flux for all for all sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek.....	31
Figure 3.15. Flow normalized TN Annual concentrations for all sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek, 6818000, 6902000 Grand River, Missouri River St. Joseph and 6934500 Hermann.....	32
Figure 3.16. Flow normalized TP Annual concentrations for sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek, 6818000, 6902000 Grand River, Missouri River St. Joseph and 6934500 Hermann. ....	33
Figure 5.1. Farmland with effective tree and earth barriers.....	37

**LIST OF TABLES**

	Page
Table 1.1. Land-use percent by type.....	6
Table 1.2. Land-use and drainage area. ....	7
Table 1.3. Best management practices timeline.....	10
Table 2.1. Seasonal Timeline.....	20
Table 3.1. Flow normalized total nitrogen.....	21
Table 3.2. Flow normalized total phosphorous.....	22

**NOMENCLATURE**

Symbol	Description
$\beta$	Weighted Regression Coefficient
$Q$	Discharge in cubic feet per second
$c$	Concentration of constituent (mg/l)
$\ln$	Natural log
$\varepsilon$	Residual error
$n$	Sample size
$s$	Standard deviation
$d$	Effect size

## 1. INTRODUCTION

### 1.1. PROBLEM AND OBJECTIVE

In 2014 the EPA placed the Lower Grand River on the impaired waters list for high levels of nitrates, low levels of dissolved oxygen, and high counts of bacteria (EPA, variously dated). Areas across the Midwest with land use areas identified as agricultural areas, are vulnerable to excessive nutrient runoff. Erosion of sediment from stream banks and fields is common in the LGRW. Stream flows are high during periods of high rainfall due to the clay soil in the area which reduces water infiltration to the subsurface. Replacement of deep-rooted native tree with short rooted non-indigenous plants, compaction and tilling of soil by land use activities increase surface water runoff (MDNR, 2014).

The environmental effects of excess nutrients in surface water and groundwater can be detrimental to the environment. Surface water runoff in areas often bears excess nutrients from soil, commercial fertilizers and animal manure. High concentrations of nitrogen concentrations can result in deficiency that can degrade water use for drinking supply, agriculture, recreation and aquatic habitat (Creekmore, 1999; Femmer, 2011). High levels of nitrate in streams can increase algal biomass, which can proliferate impairments by reducing light availability, and impede levels of dissolved oxygen by uptake of excess organic material (Creekmore, 1999; Femmer, 2011). Increases in nitrogen in streams have been attributed to anthropogenic activities including use of fertilizers in agricultural areas, waste water generation, and increased atmospheric deposition from the combustion of fossil fuels (Caraco and Cole, 1999). Since 1992, the

EPA has listed nutrients among the top five reported causes of impairment in evaluated streams and rivers. Agriculture has consistently been attributed the leading source of impairment (EPA, variously dated). Because of the harmful effects of excess nutrients on water bodies and being one of the primary causes of the hypoxic zone or "dead zone" in the Gulf of Mexico, the Mississippi Watershed was identified as a top priority for USDA nutrient reductions. (Rabalais, 2002). The hypoxic zone is created when oxygen diffusion outweighs the decomposition of organic matter, resulting in a level of oxygen below the critical threshold.

The U.S. Department of Agriculture (USDA) has begun implementing several best management practices (BMPs) throughout the study period which identify as the Mississippi River Basin Healthy Watershed Initiative (MRBI, 2012), Planned Assistance to the States (PAS) and the My Healthy Watershed Plan (MHWP, 2016). The goal of this project was to establish water quality data collection and analytical methods within the study area to evaluate the effectiveness of BMPs, and how they impact temporal changes of excess nutrients.

It can be difficult to characterize the relationship between discharge, water quality, and land-use management practices. Due to seasonal changes, application of fertilizers and the number of livestock within a watershed, agricultural activities within a watershed can be highly variable (Krempa, 2016). Better implementations of BMPs may improve soil health and control of gully erosion, but any meaningful evidence of changes to water quality can take years or decades to detect (Scientific and Technical Advisory Committee, 2013). Nutrients can be stored for decades in groundwater and concentrations

of stream nutrients can reflect historical landscape practices regardless of recent conservation practices (Van Meter and Basu, 2015).

The focus of the study with USGS and MODNR is to describe stream nutrient changes by using TN and TP concentrations that were adjusted to remove the effects of streamflow variability at selected sites within the study area. To remove streamflow variability, the WRTDS model uses weighted regression of concentrations of discharge, time, and season. The primary objectives of the study are to quantify long-term temporal changes in TN and TP concentrations, compare those concentrations among sites and respective BMPs. Changes in TN and TP changes with the Lower Grand River may be attributed to conservation practices the efforts implemented by MRBI, PAS, MWHP, and other conservation efforts over the study period. Another objective of the study was to identify critical sampling periods during the year where nutrient concentrations are consistently high, or where nutrient concentrations show the most consistent baseline to remove bias from selective sampling.

By completing these objectives, it is possible to relations to conservation practices and land use activities over the duration of the study. Temporal changes in TN and TP concentrations were adjusted to remove concentration variability caused by streamflow variability, and long-term annual TN and TP concentrations were compared among sites.

## **1.2. STUDY AREA**

Figure 1.1 LGRW is in Northwest Central Missouri and South-Central Iowa. The watershed is approximately forty-five miles northeast of Kansas City and forty-five-mile northwest of Columbia, MO.

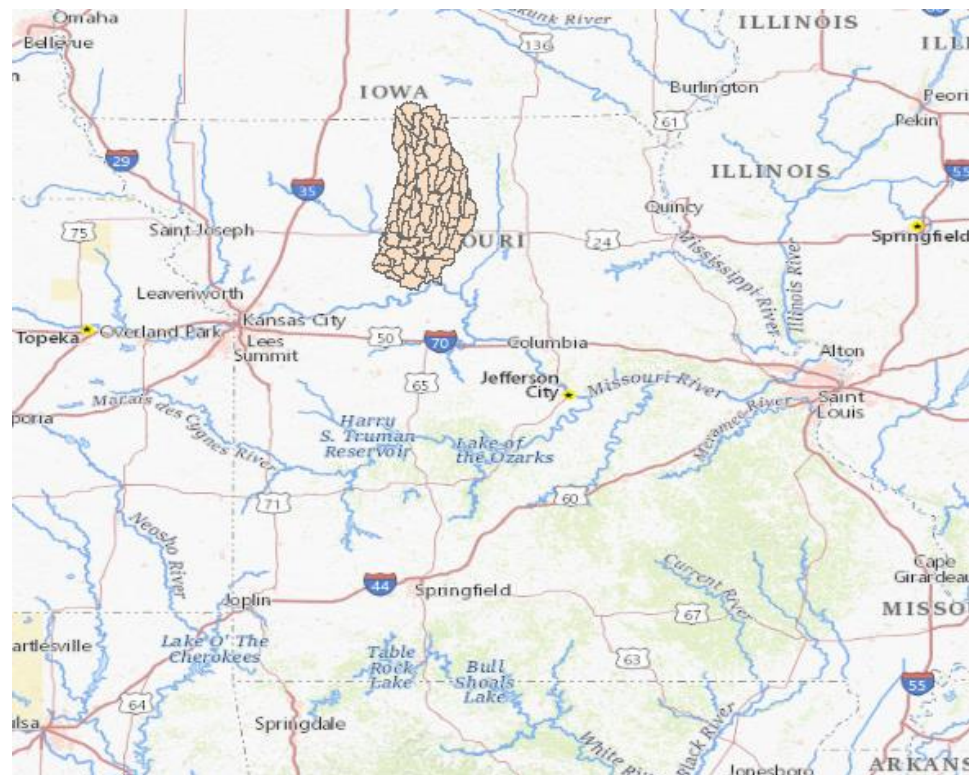


Figure 1.1. Location of the Lower Grand River Watershed.

According to the US Army Corps of Engineering (1963) the drainage area of the Grand River basin is approximately 7,900 mi<sup>2</sup>. This hydrologic system flow from the North to South, and drains into the Missouri River, and ultimately discharges into Mississippi River Delta in the Gulf of Mexico. The basin is approximately 150 mi in length and 90 mi in width. Nearly one-fifth of the drainage pattern is south, and four-fifths is north of the main stem, which is asymmetrical in this system and acts as a distribution channel for many parallel tributary basins of different elongated form. (USACOE, 1963). The average gradient for streams within the watershed ranges from 3 ft/mi to 44 ft/mi (Figure 1.2.).

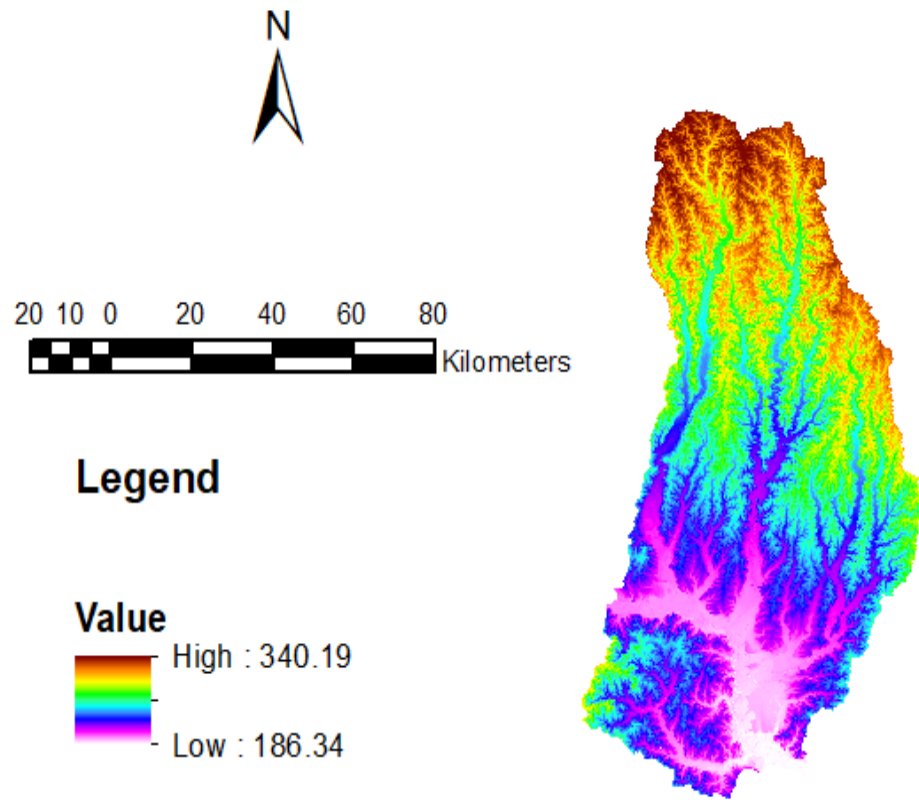


Figure 1.2. Digital Elevation model Lower Grand Watershed.

The northern reach of the watershed is primarily pasture and rolling hills, and the southern reach has a shallower gradient and is dominated by crop agriculture (MODNR, 2016). The primary land use land cover (LULC) in the LGRW is agricultural, which for the purpose of this study was a combine layer of pasture, hay and cultivated crops Table 1.1. The remaining LULC types are categorized as open water, developed, grassland, forest and wetlands, which can be viewed in Figure 1.3. The site locations are also given in Figure 1.3, the black circles with red lettering indicate the short-term independent sites chose for this study.



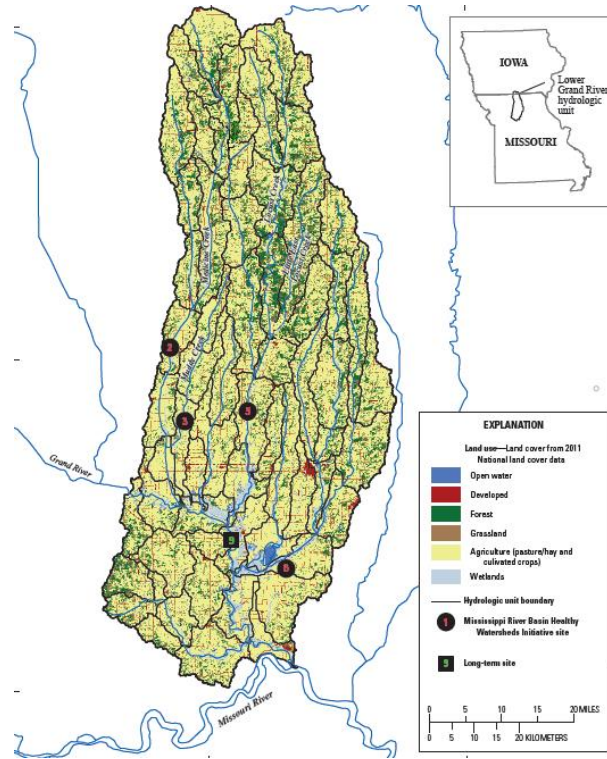


Figure 1.3. Grand River Watershed area land use (USGS, 2016).

Table 1.1. Land-use percent by type.

LULC Category	Percent by type
Agriculture	79
Forest	11
Developed	6
Other	4

For each independent site location, drainage area for each site range from 36 km<sup>2</sup> to 17,931 km<sup>2</sup>. In Table 1.2, LULC percent agriculture ranges from 72% to 88% agriculture. There is very little influence from developed land which consists of urban

environments, roads and other paved areas. Developed area is 6% in the LGRW. Short-term and long-term sites have been established throughout the study period. Short-term sites have data ranging from 2010 to present and long-term sites have data ranging from 1969 to present.

Table 1.2. Land-use and drainage area.

MRBI ID	US Geological Survey Station ID	US Geological Survey Station Name	Type	Drainage Area (km <sup>2</sup> )	Percent Agriculture LULC
2	6900050	Medicine Creek	Short Term	952	79
3	6900640	Muddy Creek	Short Term	187	84
5	6901500	Locust Creek	Short Term	1435	72
6	6902995	Hickory Branch	Short Term	36	86
9	6902000	Grand River	Long Term	17,931	78

Water resources are used for drinking water, recreation, irrigation, fishing, and marine ecosystems in the watershed. Municipal supply for drinking water comes from Milan City Lake, Locust Creek, West Yellow Creek, Elmwood Lake, Marceline City Lake, and several shallow alluvial wells. A yield 3.5 million gallons per day comes from surface water sources. The streams within the watershed that were identified by the state and EPA's 2014 303(d) list of impaired waters include East Fork Locust Creek, the Grand River, Hickory Branch, Little Medicine Creek, East Fork Medicine Creek, and Medicine Creek. Impairments for these streams include high counts of bacteria, high

levels of suspended sediment, high nutrients, and low dissolved oxygen (MODNR, 2016).

**1.2.1. Geology and Soil Classifications.** The basin is composed primarily of an alternating sequence of limestone, shale and sandstone. The whole region has been glaciated and wind-blown loess deposits were formed. Most of the areas located near rivers and flood plains are composed of fine grain silt loam soils. In Figure 1.4, clay soils are prevalent in many of the areas where agricultural activity takes place.

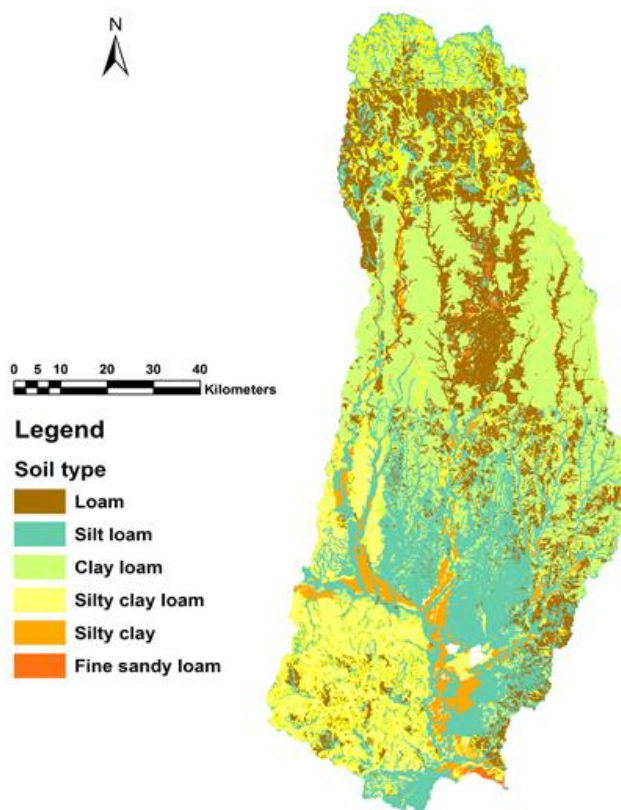


Figure 1.4. Lower Grand River Watershed area soil type.

The alluvial consists mainly of the Wabash sequence, the most widespread and readily erodible of which are the silt loams (MODNR, 2016).

**1.2.2. Hydrology.** The annual precipitation for the watershed ranges from 32-36 in (USDA, 2017). The greatest amount of precipitation normally occurs in May at 4.49” and June 5.77” (USDA, 2017). The basin is covered by glacial till, a clayey material that greatly resists the movement of precipitation to the subsurface due to its low permeability (Detroy & Skelton, 1983). The clay soil have been compacted over time from agricultural processes. Streams within the watershed exhibit rapid flow increases during periods of rainfall, but quickly return to low flow conditions. The rapid change in high flow to low flow conditions is likely due to losing reaches of the streams. Most of the runoff occurs during June when soils are fully saturation after high amounts of precipitation and cannot absorb any more moisture (NRSC, 2017).

According to Detroy and Skelton (1983) there are 1,000 third-order and larger streams within the Grand River Watershed. The number of streams makes the Grand River Watershed hydrologically complex. Most streams within the watershed with drainage areas less than 50 square miles will stop flowing for seven consecutive days or more at some time every two years. Streams in the Grand River Watershed are not sustained by groundwater inflow because of low hydraulic conductivity of clays of shales in the area. The Grand and Thompson rivers show groundwater inflow in downstream reaches (Detroy and Skelton, 1983).

### **1.3. WATER QUALITY AND PREVIOUS CONCERNS**

Recreation is one of the primary uses of the Lower Grand River, but conditions are poor due to limited access to rivers, streambank instability, sheetwash runoff, and fecal coliform violations. (MODNR, 2016). Waters are periodically impaired due to low

levels of dissolve oxygen (DO) within downstream reaches of local sewage treatment plants. High levels of nutrients have been found during previous studies. Water quality problems in streams north of the Missouri River are typically highly turbid from suspended sediment, elevated water temperatures, high acidity, pesticides, excess nutrients, low DO, and loss of pool habitat (USDA, 2002). Under natural conditions, most rivers are turbid from scour along streambeds, rapid debris removal, and river bank erosion. Increases in total nitrogen and recreational bacterium counts have been attributed to a prevalence of increasing nitrogen wastes runoff mostly in the form of animal manure (MODNR, 2016).

#### 1.4. BEST MANAGEMENT PRACTICES

Best management practices (BMPs) are defined by the Environmental Protection Agency (EPA) to describe water quality issues and how those issues will be addressed (EPA, 2011). Within the LGRW, several actions throughout the study period have been implemented to mitigate soil erosion and animal waste. These time periods can be seen in Table 1.3. The goal of BMPs is to improve water quality within watersheds of impairment which are identified by the EPA.

Table 1.3. Best management practices timeline.

BMP	Year										
	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	
Mississippi River BI											
Planning Assistance											
Healthy Watershed											

**1.4.1. Mississippi River Basin Initiative 2012.** The NRCS and local government planners provide assistance to farmers, government agencies and local authorities to improve water quality within select watersheds that are part of Mississippi River Basin. Funding began for the USGS study in 2010. By 2012 had practices established in the region such as cover crops, prescribed grazing, and irrigation control (NRCS, variously dated). Cover crops reintroduce indigenous plant species which help reduce the effects of nutrient runoff. These plants species act a barrier which breakup rainfall before reaching the soil surface. This process slows down the surface water flow caused by heavy precipitation, which give the soil a greater chance to absorb water before becoming excess nutrient runoff. Prescribed grazing designates areas which are outside of direct runoff areas to streams. This process helps prevent the amount of animal manure which runs off into nearby streams. Animal manure runoff commonly attributes to high nutrient concentrations in streams. Better irrigation systems will help divert animal waste biproducts and reduce nutrient concentrations in streams (NRCS, 2012).

**1.4.2. Planning Assistance to States 2014.** The Planning Assistance to States (PAS) practice was completed for Locust Creek and select sites within the LGRW in 2014. This program was carried out by the US Army Corps of Civil Engineers (USACE) under the Water Resources Development Act. This BMP looked at solutions to reduce soil erosion, sedimentation and improving water by constructing stream bank stability installation, levees and cantilevers (USACE, 2019). Streambank instability is one of the greatest concerns within the LGRW. By making streambanks more stable, there will be less mass wasting which will reduce the amount of nutrients entering streams through streambank sediments. Levee and cantilever installations assist by stabilizing

streambanks and reducing the risks of flooding. Streams with a high flood stage often flow over agricultural fields and carry all excess nutrient waste to the main body (NRCS, 2012).

**1.4.3. My Healthy Watershed Plan 2016.** The purpose of the Lower Grand Healthy Watershed Plan is to present the ideas, desires, and vision of participating stakeholders. Priorities and technical guidance are identified by stakeholders. The primary established objective is to reduce streambank and soil erosion from agricultural fields within the watershed by treating soils to improve water infiltration and through non-structural and structural conservation practices. Additional plans include reducing the amount of sediment, nutrient and bacteria transports to impaired streams (MODNR, 2016). An additional goal was to reduce flooding by improving levees and reducing log jams. According to the University of Missouri, a practice known as side and top-dressing application of fertilizers help reduce the amount of excess nutrient runoff. This process of applying fertilizers takes place after crops are already growing in place. The further along a crop is in its growing, the greater capacity it has to uptake excess nutrients. By applying fertilizers later in the growing season, crops are able to uptake more nutrients, reducing the amount of nutrients that become excess runoff (Fullhage, 2000).

## 2. METHODS

### 2.1. SITE SELECTION

Maps representing LULC, soil type, digital elevations, and depth to groundwater were produced in ArcGIS and were used to evaluate geological properties the watershed. Four sites were chosen by determining they were independent of all other locations, which means the data collected for these sites does not affect other sites. This not only reduces redundancy but also shows great significant of water quality when evaluating the overall health of the watershed. The Grand River site was also selected since all independent sites previously mentioned drain through its location before leaving the watershed and discharging into the Missouri River. Missouri River at St. Joseph and Hermann were selected because St. Joseph represents water quality before the Lower Grand Unit discharges into the Missouri River, Hermann represents all water quality after the Lower Grand Unit discharges into the Missouri River. By evaluating these two Missouri River sites, the impact of the Lower Grand River has on the Missouri River can be evaluated.

### 2.2. SAMPLE DATA COLLECTION

TN and TP samples were collected downstream from USGS gaging stations at a frequency of once a month over the study period. Temporal changes in TN and TP concentrations were determined by the annual load output produced by the WRTDS models, and the concentrations were compared to conservation practices throughout the duration of the study. USGS streamflow gaging stations collected streamflow data at each



of the water-quality collection sites. Stage data are collected every 15 minutes using non-submersible pressure transducers and uploaded to the USGS National Water Information System (NWIS) database. Streamflow measurements are taken routinely by an Acoustic Doppler Current Profiler (ADCP) to develop and maintain a stage-streamflow relation for each site. This relation is used to compute streamflow from stage data.

Water quality samples are collected and processed using standard equal-width increment collection methods representative of the entire water column and analyzed at the USGS National Water Quality Laboratory according to published USGS laboratory methods in use during the time of the sample collection and analysis (Fishman, 1993; Patton and Kryskalla, 2003; EPA, 1993). Concentrations reported of nitrate plus nitrite, ammonia plus organic nitrogen, and total phosphorous were obtained from the USGS NWIS database. Total nitrogen is defined as the sum of nitrate plus nitrite and ammonia plus organic nitrogen, and only samples with concentrations for both constituents were used (Krempa, 2016)

### **2.3. WRTDS MODEL**

The product of the WRTDS model is a time series estimation of concentration and flux for the entire period of measurements. The first process is to compute these values from the original discharge data over the time period. The model was downloaded as an R Studio package from CRAN. This an open source program provided by the USGS. The WRTDS model is used to estimate concentration for every single day over the time period using average daily value of discharge for each day, and the time variable which represents that day. A matrix of regressions and the estimate for each day is determined

using linear interpolation of the results. The results of the regression matrix are three dimensional. Time in years is the first dimension, time in month (from 1 to 12) is the second dimension, and the discharge in equal log space is the range of measured discharge values is the third dimension. This interpolation from the three-dimensional matrix is used to estimate concentrations for each day of the study period. The error from in this interpolation for annual values is less than 1% in most cases. A possible range of values are included for concentrations that are reported as less than laboratory detection limits (Krempa, 2016). Flow-normalized TN and TP concentrations were estimated with WRTDS by using each daily discharge average for a single date during every year of the estimations period were equally likely to happen; therefore, multiple daily concentrations were estimated for each day. According to Hirsch and others (2010), the rationale for using a weighted regression is to provide a better fit to reality because data that are observed closer in time and discharge to the desired time and discharge have higher weights in the regression. The regression equation to estimate concentration is stated in Equation (1):

$$\ln(c) = \beta_0 + \beta_1 * t + \beta_2 \ln(Q) + \beta_3 * \sin(2\pi t) + \beta_4 * \cos(2\pi t) + \varepsilon \quad (1)$$

where  $\beta_0$ ,  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ , and  $\beta_4$  are regression coefficients,  $c$  is concentration,  $Q$  is discharge,  $t$  is time in years, and  $\varepsilon$  is model residuals error. In this case the residuals errors reported below USGS laboratory reporting values. The functional form of Equation (1) which is linear in time, linear in  $\ln(Q)$ , and sinusoidal on an annual period, does not imply that their coefficients apply throughout the entire domain of the data, but become useful approximation for describing relationships over a limited portion of the domain. An approximated weighted regression can estimate a value of  $c$  for any given combination of

$Q$  and  $t$ .  $Q_0$  defined as the discharge in cubic feet per second and  $t_0$  for which there is an estimation of  $c$ . Weights are made on each measured value and are given a relevance to the point of estimation ( $Q_0, t_0$ ). The relevance is defined by a distance from the measured value ( $Q_i, t_i$ ) and the point of estimation. Each of the  $\beta$  coefficient are found using a sample of the constituent concentration data and its corresponding weighted discharge data, measured at different times (Hirsch and others, 2010).

The WRTDS model makes estimations for concentrations and flux from flow normalization, which removes random variations in discharge data. Plotting observed data alone, does not always provide the most comprehensive assessment of the effectiveness of BMPs aimed at reducing TN and TP, because climate-driven streamflow quantities confuse the interpretation of chemical data for lotic water. According to Hirsch and others (2010), these methods help reduce bias in flux estimates, by reducing the chance of select, extremely high or low values which aren't representative of the overall health of the watershed, or when using limited data to interpolate between sampling periods. It is important to use methods where perceived trend is a result of changes occurring in the watershed, and how it responds to various hydrologic conditions, and not a result of a temporal tendency which emerged only periodically during the study. To better observe these conditions flow-normalized data is used (Hirsch, and others 2010).

Hirsch explains (2010) that flow-normalization (FN) eliminates the influence of the temporal pattern of discharge, by viewing the discharge on any given day as a random sample of the discharges that might have taken place on each day. Probability distribution of discharge data is used on each given day of year. FN uses measured discharge values for a given day, each being assigned an equal probability of happening in any given year.

The discharge value for any given day is one sample from the probability distribution of discharge for the given day of that year. For each day of the month, FN assumes all measured discharge values on that day over the study period are equally likely to happen. To compute the FN concentration for the day of the month, the model estimates all values of measured concentration samples using the WRTDS model with the time variable set to that day of the month, but with the discharge variable set to one of the measured discharged value for that day. The FN concentration is the mean of all estimated concentration values flow-normalized total nitrogen (FNTN) and flow-normalized total phosphorous (FNTP), and FN flux is the mean all flux values using the WRTDS methods (Hirsch, 2010).

The FN concentration and flux estimates can be summarized into a time series of averages. Flux, which is synonymous with load, is calculated for both sampled and FN concentrations by multiplying the concentration by its respective discharge value. This gives flux in units of kg/day, which can be converted to kg/month and so on. The resulting FN concentrations and flux change very little over time compared to the original concentrations and flux, because the random effects of discharge variation are removed. These results give a much more accurate depiction in what changes are occurring within the watershed, without bias from instantaneous data. The results from this model are meant to help quantify the occurrence of any changes and help project cooperators and stakeholders understand what trends are taking place within the watershed (Hirsch and others 2010). The results from the WRTDS model will help land investigators and project planners achieve water quality goals in the watershed regarding land-use and best management practices.

## 2.4. STATISTICAL ANALYSES

The effectiveness of BMPs were analyzed by two tail hypothesis tests using the sign test method, and data groups were split by the year that a significant BMP within the study area was implemented. A two-tail sign test was chosen because the water quality data needed to be determined significant whether nutrient concentrations increased or decreased within that window. For example, the first BMP implemented was MRBI in 2012, therefore all of the data from 2010 to 2012 was in one group of the sign test, and the other group was from 2012-2014. 2014 is the year of the next BMP, thus giving discrete windows for the two groups of the sign test. The short term independent site data that were collected over the study period ranges from 2010 - 2019, however to evaluate the effectiveness of each BMP, the data was divided into two groups: one set representing all data before the year a BMP was implemented and one set representing all data after the BMP was implemented. Any overlap in water quality effects or time lag within this analysis is taken into consideration, because the time periods for each BMP are only two year apart. At times it can take decades for water quality to improve. The results of the two-tailed sign test were determined by level of significance, being a P-value  $< 0.05$ . A P-value  $< 0.05$  indicates that 95% of the data compared in the two groups were significantly different. If shown a P-values  $< 0.05$ , concentrations have either shown an increase or decrease. A P-value  $> 0.05$  indicates no significant change in water quality (Dixon and Mood, 1946).

To determine the magnitude of significance for the two groups, the effect size was tested. The two necessary equations are stated as Equation (2) and Equation (3):

$$Spooled = \sqrt{\frac{(n_1-1)s_1^2 + (n_2-1)s_2^2}{n_1+n_2-2}} \quad (2)$$

$$d = \frac{\bar{x}_1 - \bar{x}_2}{Spooled} \quad (3)$$

First, the Spooled data are calculated amongst the two groups, then the difference in means are divided by the Spooled to find the effect size. In conjunction with a sign test, the effect size can show the magnitude and directs of which the data are changing. For this study, an effect size d-value  $> .020$  was considered significant (Lankens, 2013). A negative d-value would indicate mean values in the second group were large, indicating the nutrient concentration have significantly increased. A positive d-value would indicate the difference in mean values in the first group, before the BMP were significantly greater, indicating that water quality has improved over the discrete window.

All of the data for annual BMP analysis and seasonal variation were analyzed by box and whisker plots for both FN nutrient concentrations and sampled values. Box and whisker plots were chosen because they can show the entire range of data and where mean values change over time. All statistical analyses were carried out in R Studio, SYSTAT, and Excel.

## 2.5. SEASONAL ANALYSIS

Seasonal trends were divided up into four categories based on when of typical agricultural practices occur throughout the year. These dates were determined by accessing the University of Missouri's report (2000) which identifies typical agricultural activities and when those activities take place throughout the year. There are a number of

factors to consider such as applications of fertilizer, planting and harvest times (Fullhage, 2000). For the purpose of this study, seasonal trends throughout the year are identified in Table 2.1. Results from seasonal analysis were interpreted from the WRTDS model output data, and by box and whisker plots. The goal from this analysis is simply to determine the best windows throughout the year for sampling depending on what trends the operators of the study are looking for. Periods of high values can be observed through the use of box and whisker plots, as well as baseline mean values. The benefit of looking at these trends over a long range allow studies with a limited number of sampling windows or funding to prioritize when they will sample throughout the year. This results from these methods may allow for research groups to quickly determine the most optimal times to sample for nutrients depending on what the scope of their project is.

Table 2.1. Seasonal Timeline.

Season	Month
Pre	Jan Feb
Planting/Growing	Mar Apr May June
Harvest/Growing	July Aug Sep Oct
Post	Nov Dec

### 3. RESULTS

#### 3.1. THE EFFECTS OF BMP

Table 3.1 gives the results for the sign tests and effects size for all short-term independent sites over the study period. Medicine creek had an increase in FNTN concentrations over the MRBI and PAS BMPs and showed a significant decrease in FNTN by the MHWP. Muddy Creek varied as it had a decrease in FNTN concentrations initially after the first BMP, then increased from 2014-2016, and decreased in concentrations from 2016-2019. Hickory Branch and Locust Creek show a decrease in FNTN values over the study period. By the end of the study period and all sites show a significant reduction in FNTN values. This indicate that BMPs may have had an effect in reducing TN concentrations over this period of study

Table 3.1. Flow normalized total nitrogen.

Site Name	Site Number/ Station ID	Statistic	Flow Normalized Total Nitrogen		
			Mississippi River Basin Initiative	Planning Assistance to States	My Healthy Watershed Plan 2016
			(2010 -2012) vs (2012-2014)	(2012 -2014) vs (2014-2016)	(2014 -2016) vs (2016-2018)
Medicine Creek	2	P-value	0.44	0.219	0.026
	6900050	Effect Size	-0.011904242	-0.095303372	0.160204912
Muddy Creek	3	P-value	0.01	0.04	0.01
	6900640	Effect Size	0.250522743	-0.526730565	0.783311226
Hickory Branch	5	P-value	0.012	0.018	0.024
	6902995	Effect Size	-0.109427754	0.66537107	0.363690329
Locust Creek	6	P-value	0.04	0.032	0.028
	6901500	Effect Size	-0.276025872	0.24882666	0.807879512



Table 3.2 shows sign test results and effect size results for FNTTP over the study period. The data are interpreted as those in table 3.1. Medicine Creek shows an increase in FNTTP concentrations until 2016 when FNTTP concentrations decrease significantly. Muddy Creek and Hickory Branch both show significant decreases in FNTTP concentrations over the study period. In this study Locust Creek is the only site that shows a significant increase in FNTTP concentration. Locust Creek was identified a one of the focus areas by the PAS and still showed a significant increase in FNTTP concentrations over the study period. There may be signs of point source loading in Locust which are worth investigating for future studies.

Figures 3.1 - 3.8 show the WRTDS model outputs for both FNTN and FNTTP. The trends be seen from the model outputs, as well as the sampled concentrations over the study period. Notice the sample concentrations represented by blue dots show much greater variability than the FN concentrations line represented in orange. Monthly FN consistently peak in the month of May and drop to a low during the month of November.

Table 3.2. Flow normalized total phosphorous.

Site Name	Flow Normalized Total Phosphorous				
	Site Number/ Station ID	Statistic	Mississippi River Basin Initiative (2010-2012) vs (2012-2014)	Planning Assistance to States (2012-2014) vs (2014-2016)	My Healthy Watershed Plan (2014-2016) vs (2016-2019)
Medicine Creek	2	P-value	0.001	0.001	0.001
	6900050	Effect Size	-0.552427775	-0.60057871	0.306419793
Muddy Creek	3	P-value	0.304	0.689	0.549
	6900640	Effect Size	-0.303931248	0.154851593	0.461611639
Hickor Branch	5	P-value	0.001	0.001	0.001
	6902995	Effect Size	0.311715972	0.166006024	0.187191744
Locust Creek	6	P-value	0.753	0.005	0.01
	6901500	Effect Size	0.435569213	-0.266111577	-0.423591995

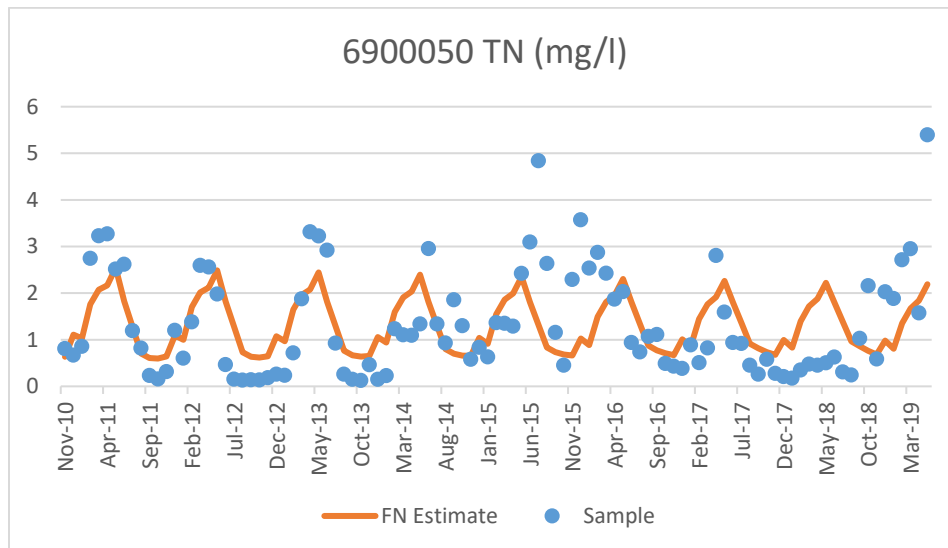


Figure 3.1. 6900050 Medicine Creek total nitrogen.

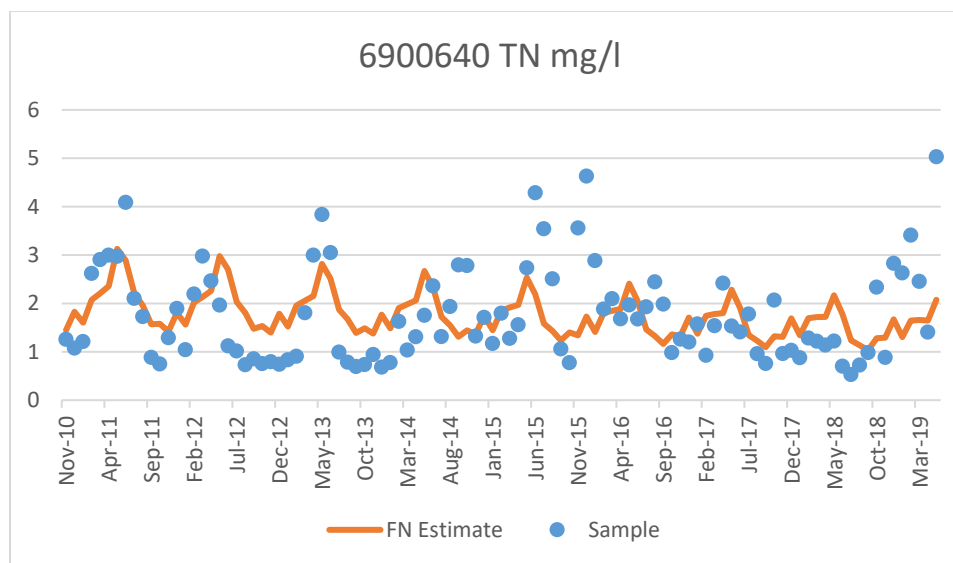


Figure 3.2. 6900640 Muddy Creek total nitrogen.

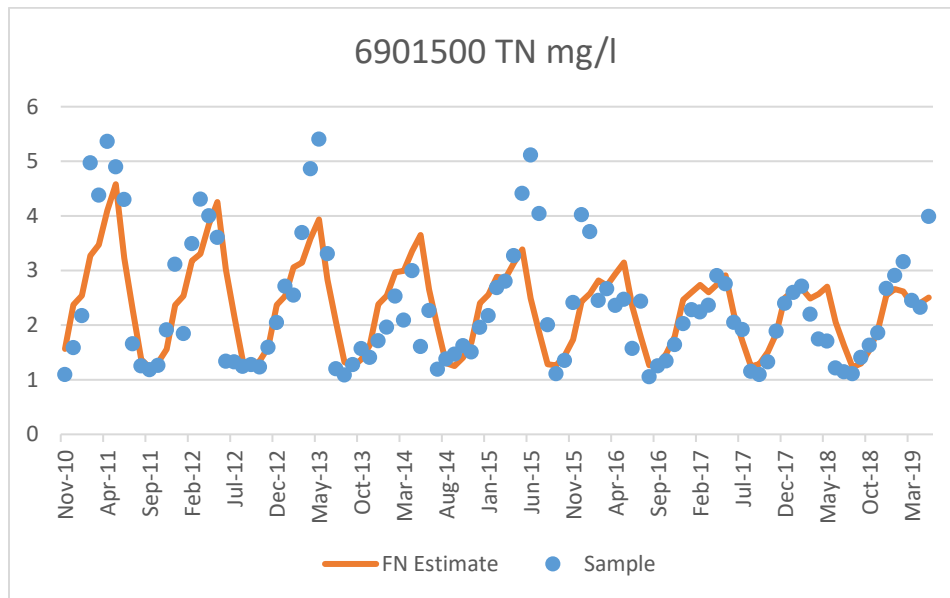


Figure 3.3. 6901500 Locust Creek total nitrogen.

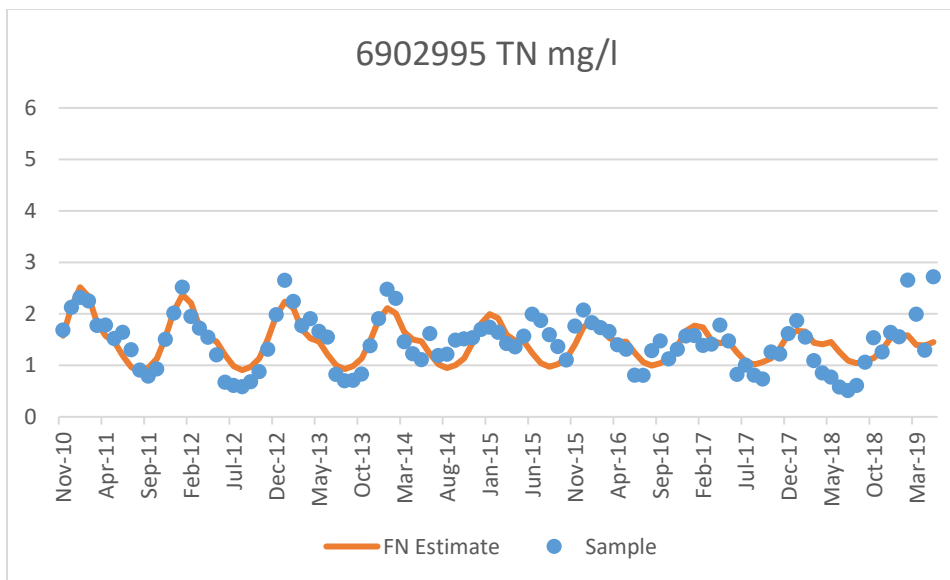


Figure 3.4. 6902995 Hickory Branch total nitrogen.

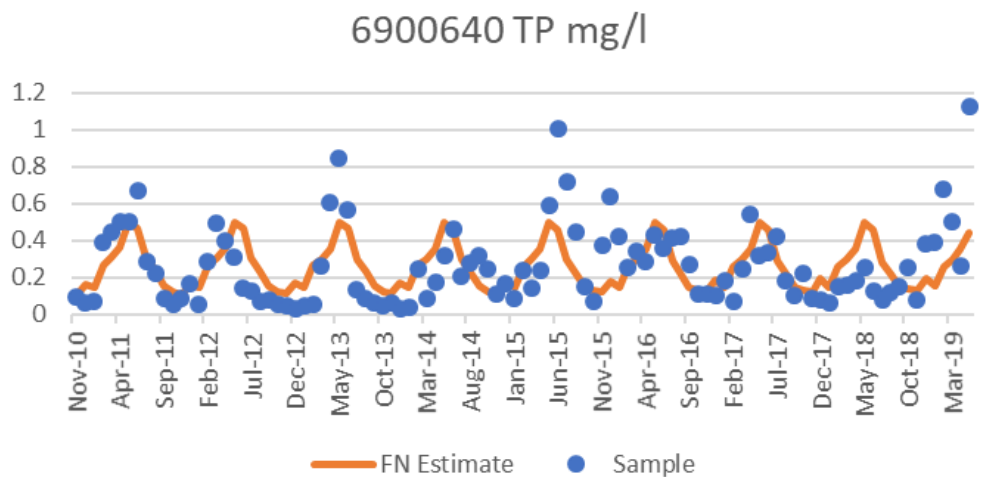


Figure 3.5. 6900640 Muddy Creek total phosphorous.

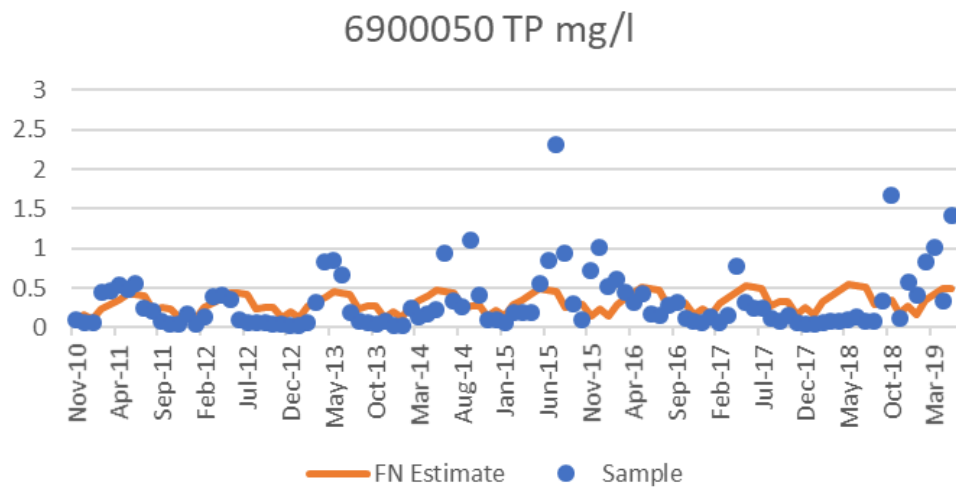


Figure 3.6. 6900050 Medicine Creek total phosphorous.

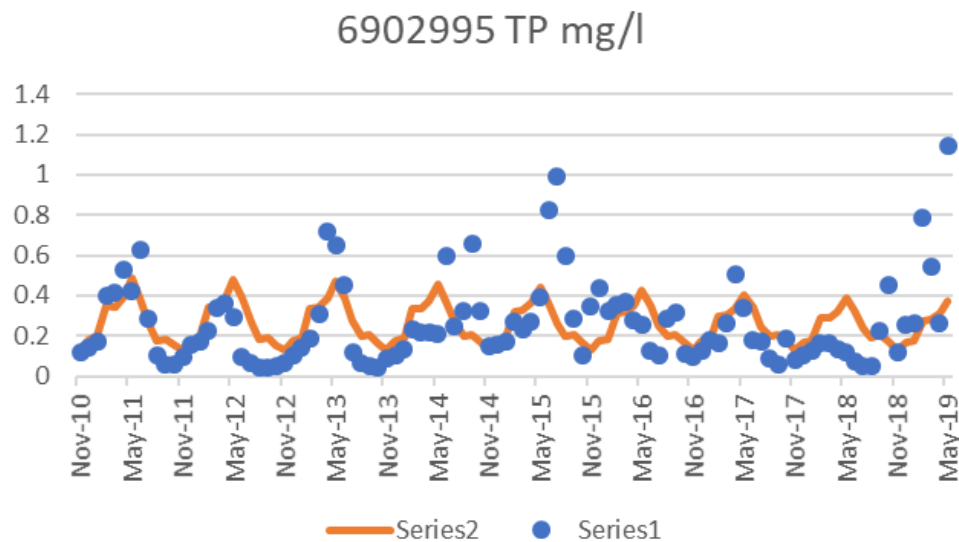


Figure 3.7. 6902995 Hickory Branch total phosphorous.

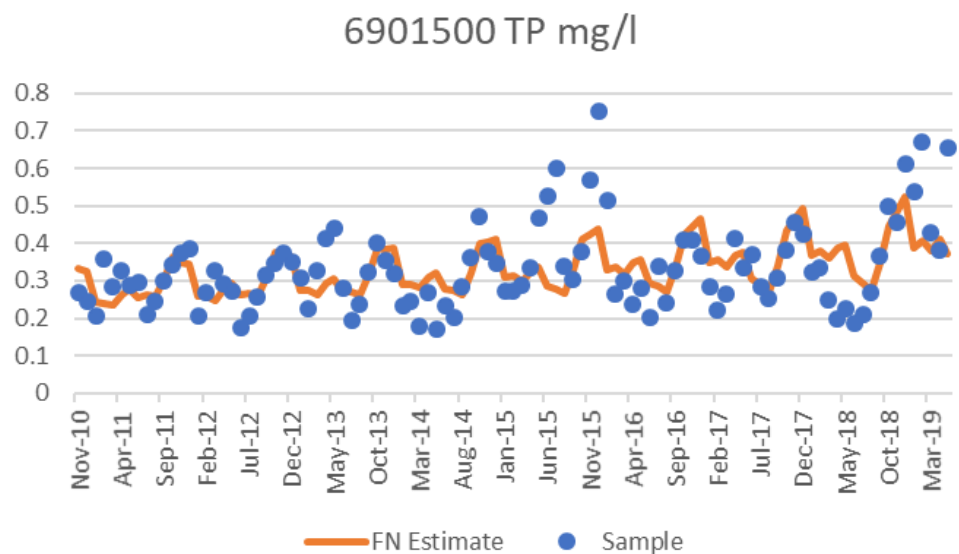


Figure 3.8. 6901500 Locust Creek total phosphorous.

Figure 3.9. shows box and whisker plot representing how mean values for TN and TP concentrations change throughout the study period. On the horizontal axis, each BMP

implanted over the study is represented as a discrete window in time. Plots for observed TN and TP concentrations vary over the study period, whereas the mean values for FNTN and TNTP, gradually decrease over time. This shows the observed values are much more variable than FN data. The trends show a positive result from BMP practices and the watershed as a whole is decreasing in nutrient concentrations gradually over time. A similar pattern can be seen the graphs in Figures 3.1-3.8.

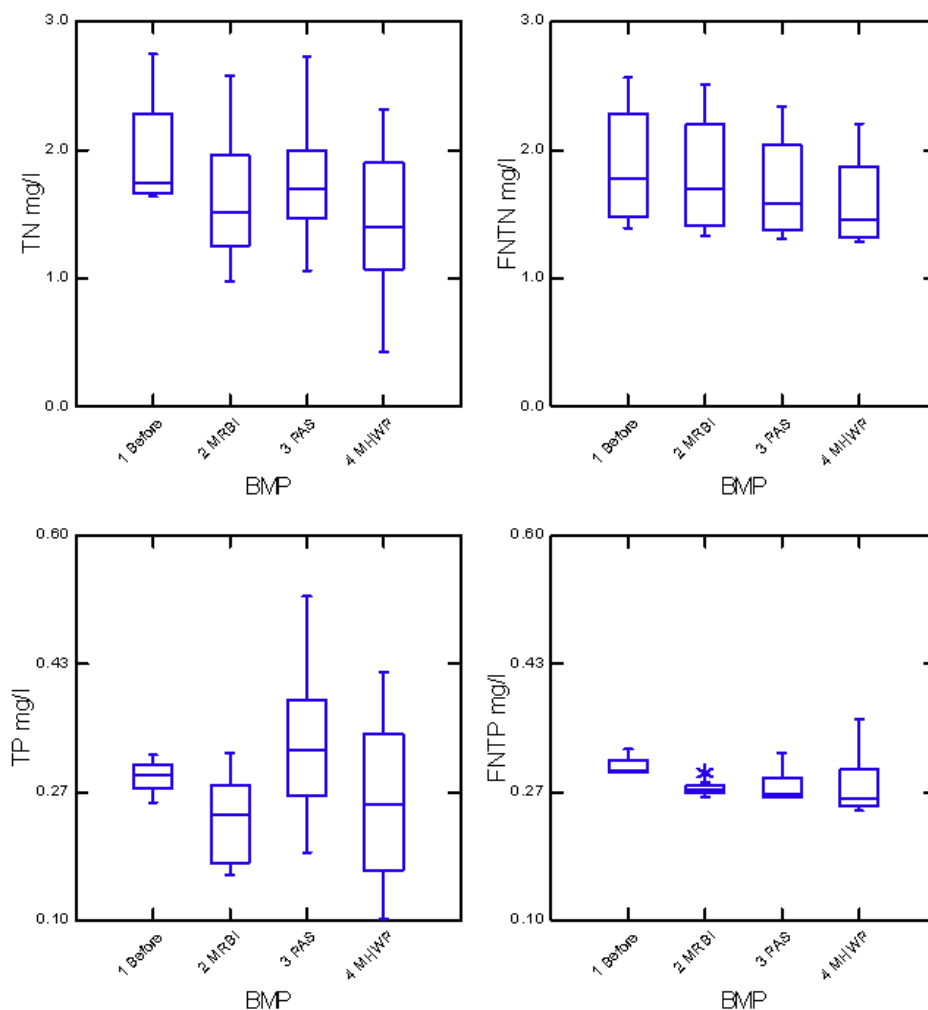


Figure 3.9. Comparative box and whisker plots which show how nutrient concentrations change with each BMP over the study period.

### 3.2. SEASONAL VARIATION

Seasonal variation for all sites are plotted in Figures 3.10 for FNTN values and in Figure 3.11 for FNTTP values. The seasonal trend for FNTN can be decreasing in concentration values for all sites. Concentration values for all sites for all years consistently peak in May. FNTTP values typically peak in May, except for Hickory branch which typically peak in November. Concentrations for FNTTP values vary by site. Hickory Branch and Medicine both show an increase over the study period, whereas all other sites steadily decline. There could be the possibility of point source loading to the streams with increased FNTTP concentrations. A more thorough analysis would have to be conducted to fully consider and identify specific sources of possible nutrient loading to streams.

Box and whisker plots in Figure 3.12 show the range of mean values in concentration for all sites. The horizontal axis shows a time period represented by the sampling window for each seasonal period. The planting season has the highest mean values for concentrations. This would help planners and investigators identify high values for the watershed to determine whether water quality impairment is still prevalent. The planting season would also give the greatest potential range of data for all cases. If planners and investigators wanted the most consistent bases average for all concentrations over the year, the best sample period would be in the pre-season for TN concentrations, and the best sample period would be the harvest season for TP concentrations. Baseline data are important to obtain for running models such as WRTDS because the user wants most of the data to not be flashy, or periods of extreme high and low values occur.

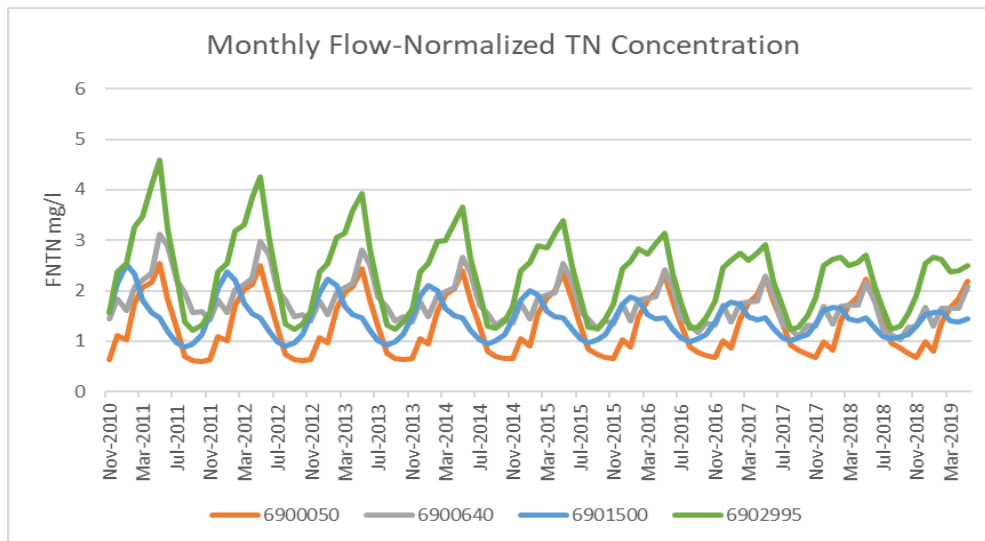


Figure 3.10. Monthly flow-normalized total nitrogen concentrations for all short-term sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek.

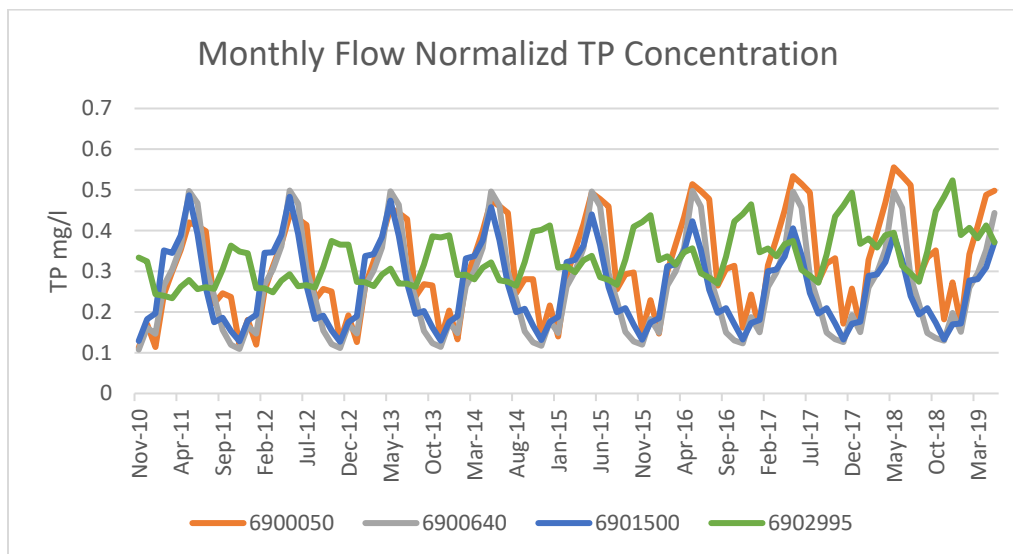


Figure 3.11. Monthly flow-normalized total phosphorous concentrations for all short-term sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek.



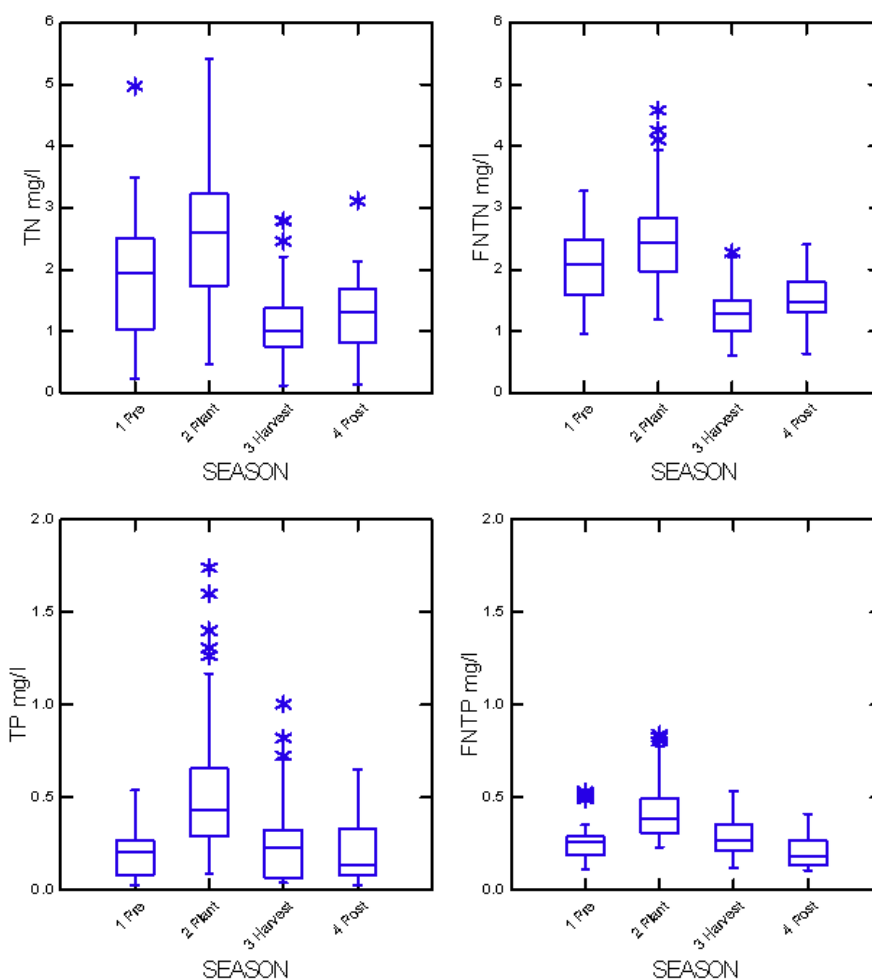


Figure 3.12. Seasonal box and whisker plots for concentrations in for all short-term sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek.

Figures 3.13 and 3.14 show the daily values by month of FN flux for both nitrate and phosphorous values over the study period. The peak time for flux values are consistent over the study period. Both nitrate and phosphorous flux values consistently decrease over the study period, except for Medicine Creek which show increase in flux values.

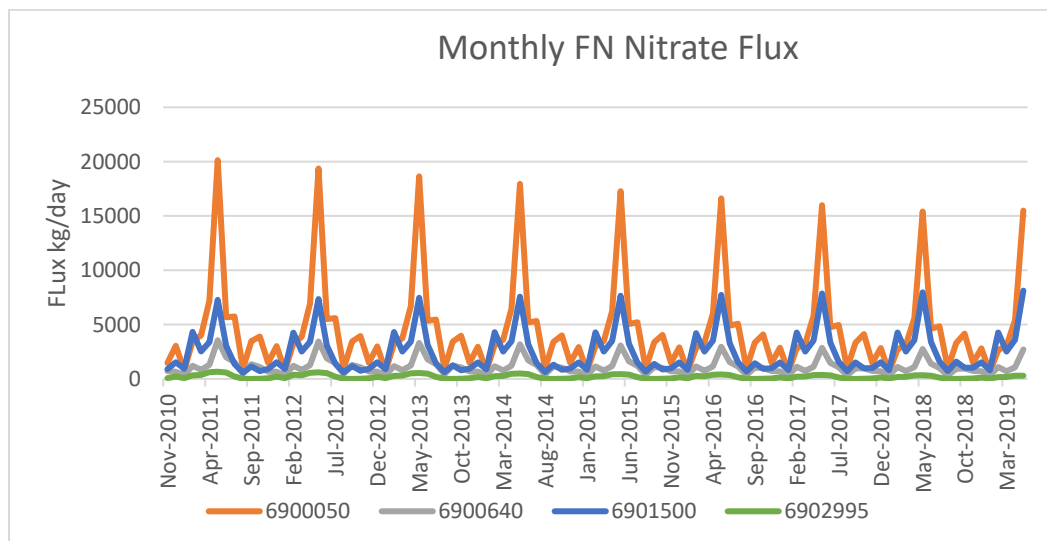


Figure 3.13. Monthly FN nitrate flux for all for all sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek.

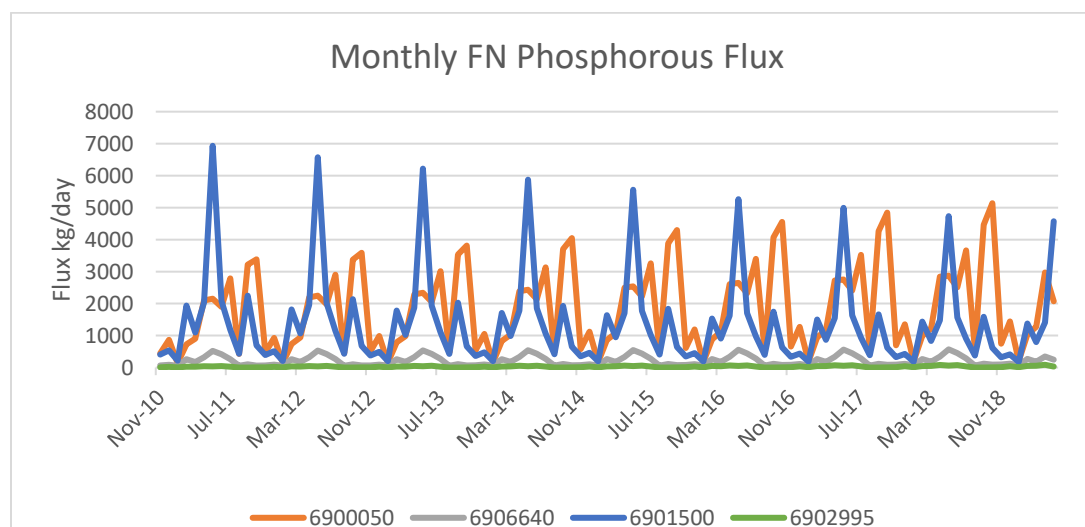


Figure 3.14. Monthly FN phosphate flux for all for all sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek.

### 3.3. LONG TERM TRENDS

The Figures 3.15 and 3.16 show the annual averages for FNTN and FNTN concentrations. Nutrient show a high concentration at the beginning of the study until

1985 when Crop Row Practices were introduced by the USDA. This showed a decline in nutrient concentrations shortly thereafter until the year 2001, when nutrient concentrations begin to rise. This rise may have resulted from a trend in conservation practices over that time, or a decrease in funding to farmers and planning. This trend also may have occurred from a recent population growth in cattle and hog numbers. During this time the EPA added the reaches of LGRW watershed to the impaired waters list for the first time. By 2010 all sites within the LGRW and Grand River Basin show improvements, except in the case of FNTN concentrations at Locust Creek show a significant increase. The two Missouri River Site follow the same trends as the LGRW until 2016 when FNTN and FNTP concentrations show significant increases.

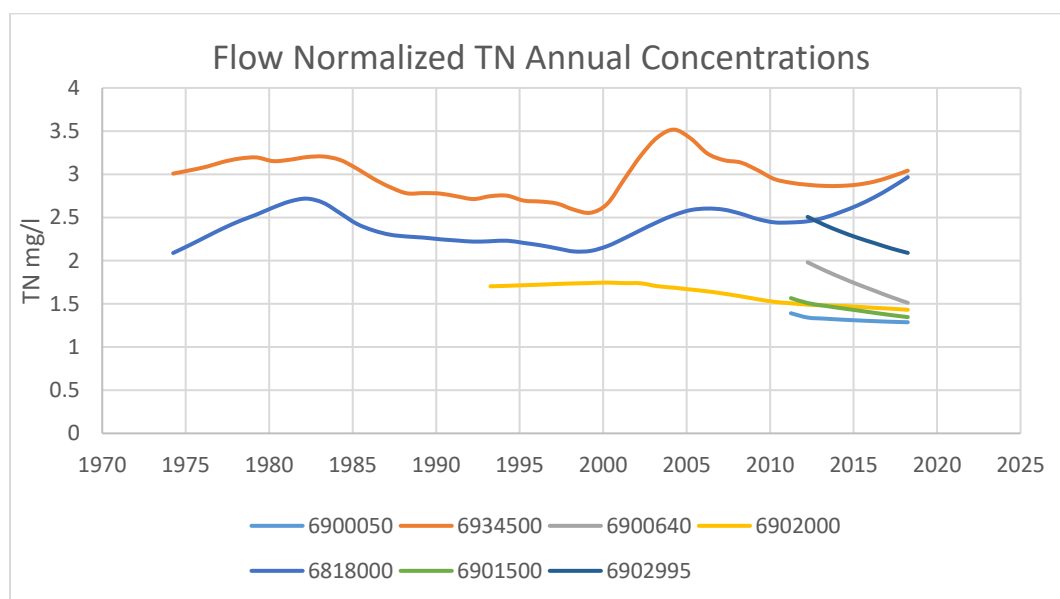


Figure 3.15. Flow normalized TN Annual concentrations for all sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek, 6818000, 6902000 Grand River, Missouri River St. Joseph and 6934500 Hermann.

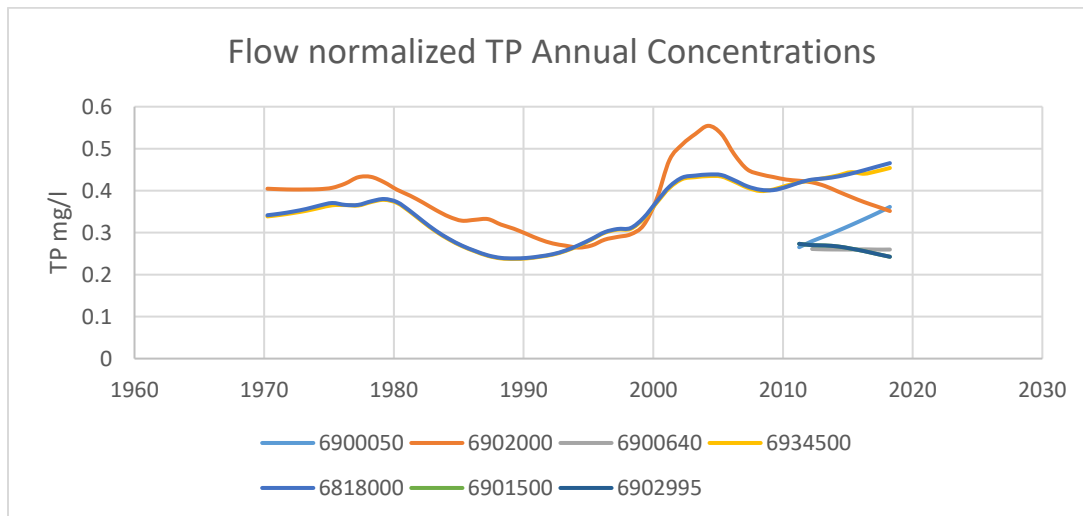


Figure 3.16. Flow normalized TP Annual concentrations for sites 6900050 Medicine Creek, 6900640 Muddy Creek, 6902995 Hickory Branch, 6901500 Locust Creek, 6818000, 6902000 Grand River, Missouri River St. Joseph and 6934500 Hermann.

#### 4. CONCLUSIONS

All short-term sites showed improvements in TN concentrations over the study period. Two long-term sites (6818000 and 69034500) Missouri River at St. Joseph and Missouri River at Hermann showed an increase in TN concentrations over the study period. With the LGRW discharging into the Missouri River between these two sites, and LGRW sites declining in Locust Creek showed higher concentrations in TP. Most effective BMPs stream banks stability projects, filter strips, and side dressing/ top dressing.

From the time overlap from BMPs, it is difficult to determine which BMPs are most effective. In this study it can be seen how all BMPs collaboratively effect the watershed over the study period. If a research group wanted to identify a specific BMP had a positive impact or not. The research group would have to find a particular project and isolate those two windows in time before and after the practice. This would have to planned years before and after that BMP project to effectively observe those changes in water quality trends over time. This study was not effective in identify which individual projects were effective.

This study was able to identify different sampling windows for seasonal variations. These samples windows would vary by locations throughout the country. Harvest times in Missouri vary by county and month typically. Project planners create their own windows, depending on preseason application of fertilizers, planting and harvest times for their region. What planners attempt to identify will vary by project.

Looking at entire watershed no matter how consistent the LULC category, the hydrological processes are complex. It is difficult to isolate individual events and practices within a small window of time, and limited funding. There are likely influences in addition to nutrient runoff from non-point agriculturally based sources. This may possibly include point sources from wastewater treatment plants, other waste management projects such as landfills and controlled animal waste operations.

A more thorough project should look at specific events and identify specific sources of loading. Krempa (2016) with the USGS performed a study looked at amount of fertilizers and estimates for animal manure in the area. The purpose of this study examined whether BMPs with an engineering, had a positive or negative influence on the selected streams and watershed as whole. It would be beneficial to perform higher resolution studies in the future. This would examine specific reaches of streams, which the effects of a particular BMP, or engineering project, could be evaluated with spatial and temporal relativity to that project.

## 5. RECOMMENDATIONS

Planners within the LGRW should continue implementing BMPs and monitoring over the next decade, until all sites shows decreases in FNTN and FNTP concentrations. The USGS MRBI project has already been approved for another three years of funding. Planners should continue looking at the big picture. Missouri River sites displayed worsening over this study period, while the LGRW is showed improvement. This indicates that large amounts of the nutrient load being carried by the Missouri River are coming from sites outside of the LGRW.

Regions planners should collaborate by region, not simply state by state. A regional effort is necessary to identify water quality trends in basins as large as the Mississippi and Missouri. Investigators should work collaboratively to identify other areas of concern, and focus efforts to improve the MRBI mission.

Figure 5.1 shows an ideal stretch of farmland which borders a stream. There is a buildup of earth and a continuous tree line of indigenous plants which stand between the area in which crops are grown and the stream. The earth build up helps prevent sheetwash runoff, a process which transports excess runoff directly to streams. The deep-rooted indigenous trees help stabilize stream banks, prevent soil erosion and help uptake excess nutrients before they enter water bodies.

It is important to consider by changing the landscape we are removing it from is natural state. These natural states have been held in a state of balance and equilibrium for thousands of years before modern agricultural practices began. Once the landscape is altered anthropogenically, the landscape must be maintained by all who depend on it.

Government and local planners must work together to maintain a balance between the demands from agricultural production, and what is sustainable for future generations.



Figure 5.1. Farmland with effective tree and earth barriers.



## BIBLIOGRAPHY

1. Caraco, N.F. and Cole, J.J., 1999, Human Impact on Nitrate Export – An Analysis Using Major World Rivers: *Ambio* v. 28, no. 2, p. 167-170
2. Creekmore, L.H., 1999, Algal Toxins, chap. 36 of Friend, Milton, and Franson, J.C., eds., *Field Manual of Wildlife diseases – General Field Procedures and Diseases of Birds* U.S. Geological Survey Information and Technology Report 1999-2001, p. 263-266
3. Dixon, W.J and Mood, M., 1946, The Statistical Sign Test, *Journal of the American Statistical Association*, 41:236, 557-566, DOI
4. Femmer, S.R., 2011, Algal Community Characteristics and response to Nitrogen and Phosphorus Concentration in Streams in the Ozark Plateaus, Southern Missouri, 1993-1995 and 2006-2007: U.S. Geological Survey Scientific Investigations Report 2011, p. 25
5. Fulhage C.D., 2000 Land Application Considerations for Animal Manure. EQ 202. MU Guide. MU Extension, University of Missouri-Columbia
6. Krempa, K.M., 2017 Temporal Changes in Nitrogen and Phosphorus Concentrations with Comparisons to Conservation Practices and Agricultural Activities in the Lower Grand River, Missouri and Iowa, and selected watersheds, 1969–2015
7. Lakens D., 2013, Calculating and reporting effect sizes to facilitate cumulative science: a practical primer for t-tests and ANOVAs. *Front Psychol.* 2013; 4:863. doi:10.3389/fpsyg.2013.00863
8. Missouri Department of Natural Resources (MDNR), 2014, The State of Our Missouri Waters – Lower Grand River Watershed, p. 3
9. Missouri Department of Natural Resources (MDNR), 2016, Healthy Watershed Plan – Lower Grand River Watershed, p. 1-20
10. Natural Resources Conservation Service [NRCS], variously dated (a), Mississippi River Basin Healthy Watersheds Initiative: U.S. Department of Agriculture, Natural Resources Conservation Service web page, accessed October 26, 2016, at <https://www.nrcs.usda.gov/wps/portal/nrcs/detailfull/national/home/?cid=stelprdb104820>
11. Natural Resources Conservation Service [NRCS], variously dated (b), NRCS conservation programs: U.S. Department of Agriculture, Natural Resources Conservation Service web page, available at <https://www.nrcs.usda.gov/wps/portal/nrcs/main/national/programs/>.

12. U.S. Army Corps of Engineers (USCOE), 1963. Report on survey for flood control, Grand River and tributaries, Missouri and Iowa. U.S. Army Engineer District, Kansas City, Missouri.
13. U.S. Department of Agriculture, Soil Conservation Service (USDA-SCS). 1982. The land and water resources of the northern Missouri River tributaries basin - Iowa and Missouri.
14. U.S. Department of Agriculture (USDA), 2017, Missouri Monthly Rainfall by County, p. 1-3
15. U.S. Environmental Protection Agency (EPA), variously dated, National Water Quality Inventory Report to Congress: U.S. Environmental Protection Agency web page, digital data accessed August 23, 2018, at <https://www.epa.com/waterdata/national-water-quality-inventory-report-congress>.

## VITA

Weston Scott Duley was born in Chicago, Illinois in 1988. In August of 2016 he received his bachelor's in science in Geology from the University of Missouri- Kansas City. Upon completion he further challenged himself and accomplished his Bachelor of Science in Geological Engineering from Missouri University of Science and Technology in May of 2017. During this time, he worked for the United States Geological Survey as a Hydrology student. In December 2019, Weston Duley received his Master of Science in Geological Engineering. He has accepted a Civil and Agricultural Engineer position with the National Resource Conservation Service in Portland, Oregon.