Summer 2018

Nutrient Transport and Storage in a Karst Spring-Reservoir System during Baseflow, Missouri Ozarks

Heather A. Moule
Missouri State University, Moule04@live.missouristate.edu

NUTRIENT TRANSPORT AND STORAGE IN A KARST SPRING-RESERVOIR SYSTEM DURING BASEFLOW, MISSOURI OZARKS

A Masters Thesis

Presented to

The Graduate College of

Missouri State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science, Geospatial Science

By

Heather A. Moule

August 2018

NUTRIENT TRANSPORT AND STORAGE IN A KARST SPRING-RESERVOIR SYSTEM DURING BASEFLOW, MISSOURI OZARKS

Geography, Geology, and Planning

Missouri State University, August 2018

Master of Science

Heather A. Moule

ABSTRACT

Urban and agricultural land uses are important sources of nitrogen and phosphorus which, if in excess, can cause eutrophication in lakes and rivers. There have been few studies of nutrient transport and storage in karst spring and reservoir connected stream systems draining the Missouri Ozarks. This study aims to link the baseflow nutrient contributions of Sanders Spring to downstream reservoir outflow and the Headwaters South Dry Sac River Watershed in Springfield, Missouri. Water samples were collected seasonally and analyzed for total nitrogen (TN), total phosphorus (TP), and several other water quality parameters. Discharge was also monitored to calculate water and nutrient budgets. Water did not flow over the dam during 65% of the study period, but baseflow from Sanders Spring may have still provided 46% of the total flow at the South Dry Sac River gage. Typically, TN and TP concentrations were higher at Sanders Spring compared to the reservoir outlet and the South Dry Sac River. However, TP concentrations increased significantly at the reservoir outlet during a high spring baseflow. Nearly 33% of baseflow from Sanders Spring is lost by seepage from the reservoir. Future work should include stormflow analysis to understand how the reservoir may be functioning as a source or sink of nutrients to the river and to better understand subsurface flow through the karst system.

KEYWORDS: water quality, reservoir, nutrients, karst, spring, phosphorus, nitrogen

This abstract is approved as to form and content

____

Robert Pavlowsky
Chairperson, Advisory Committee
Missouri State University

NUTRIENT TRANSPORT AND STORAGE IN A KARST SPRING-RESERVOIR SYSTEM DURING BASEFLOW, MISSOURI OZARKS

By

Heather A. Moule

A Masters Thesis
Submitted to the Graduate College
Of Missouri State University
In Partial Fulfillment of the Requirements
For the Degree of Master of Science, Geospatial Science

August 2018

Approved:

____
Robert Pavlowsky, PhD

____
Toby Dogwiler, PhD

____
Xiaomin Qiu, PhD

____
Julie Masterson, PhD: Dean, Graduate College

ACKNOWLEDGEMENTS

There are many people that I would like to express my utmost gratitude for. First, I want to thank Dr. Robert Pavlowsky for giving me this opportunity, the freedom to research what interests me, and the help to start and finish this project. I would also like to thank my committee members for their patience and guidance. I would like to specially thank Marc Owen for significant help with field work. I would like to thank Hannah Adams, Sarah Letarte, Joe Nash, and Katy Reminga for additional help with field work. I would also like to give a very special thanks to Kelly Rose, who helped me process my samples in the laboratory and spent countless hours helping and teaching me to use the equipment. I would also like to thank Megan Hente as well as any undergraduates who may have helped process some of my samples.

I would like to thank the Ozark Environmental and Water Resources Institute and the Graduate College at Missouri State University for providing the equipment I needed and funds to carry out my research. I would also like to thank the Watershed Committee of the Ozarks for letting me do my research at the Watershed Center.

Lastly, I would like to thank friends and family for all of the support during this journey. I want to give a special thanks to my mother who spent many phone calls listening to me de-stress and pushed me to continue. Finally, I would like to give a very special thanks to my significant other, Steven Baker. I would not have made it through without his love and support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1 – INTRODUCTION

Nitrogen (N) and phosphorus (P) are responsible for pollution in water bodies and around the world (Carpenter et al. 1998). The enrichment of nutrients, most notably N and P, in streams, lakes and reservoirs is called eutrophication and can result in increased algal growth often referred to as “blooms” (Sauer et al. 2008). The death and decomposition of the organic matter in these algal blooms can cause low oxygen and toxic conditions in aquatic ecosystems (Khan and Ansari 2005). In the United States, major nutrient sources include fertilizers for cropland, manure from pastures and rangelands, and urban runoff from construction and sewage (Carpenter et al. 1998). An estimated 86% of P contributions in many streams throughout the United States come from cropland and pastures while less than 15% may come from urban sources (Alexander et al. 2004). Nutrient budgets are useful management tools that help identify nutrient sources and sinks in surface water bodies (Swank and Waide 1988; Valiela and Costa 1988). A nutrient budget for N or P is calculated by taking the difference between load inputs and outputs for a daily, monthly, or yearly time frame. The result can be used to evaluate whether a watershed or water body is a net source or sink of nutrients (Howarth et al. 1996; Luu et al. 2012). The term “sink” is often used to describe the annual behavior of nutrients in water bodies, but will be used here to describe the short-term or daily behavior of nutrients.

Nutrients are transported to surface waters in overland flow or through infiltration and can be temporarily stored in the soil (Anderson et al. 2002). Since phosphorus is readily sorbed to soil particles, it can be transported with sediment and

later stored in reservoirs (EPA 1999). In karst landscapes, nutrients in surface water may be transported through sinkholes, through the subsurface, and re-enter streams at the surface through springs (Taylor and Greene 2008). However, urban development increases impervious area, decreases infiltration rates, and creates higher runoff potential (Shuster et al. 2005).

Karst Systems and Nutrient Transport

Karst topography is characterized by highly soluble rock such as limestone and dolomite and may include many springs, sinkholes, caves, and intermittent streams (Figure 1). In karst regions, groundwater and surface water are closely interconnected. After large conduits form from dissolution of carbonate rock, the water table may lower to a level with no conduits. In this case, conduits may only be activated during periods of high discharge or stormflow. Thus, flow through karst may be highly variable and hydrographs may show a quick response to precipitation events. The response of flow through a conduit-dominated subsurface to precipitation may be within 24 hours (Taylor and Greene 2008). Nutrients transported through conduits may be measured and observed as pulses in surface water (Peterson et al. 2002). Nutrients can be easily and rapidly transported through karst topography, especially where soil layers are thin (Dreiss 1989). Water that travels quickly through karst terrain has limited contact between microbes and substrate, so natural filtration and sorption rates may be reduced (Sauer et al. 2008).

Soil has a large influence on the transport and storage of nutrients. The characteristics of soil can help determine potential flow characteristics and paths of nutrients within the subsurface (Dahm et al. 1998). Soils rich in clay and silt have low

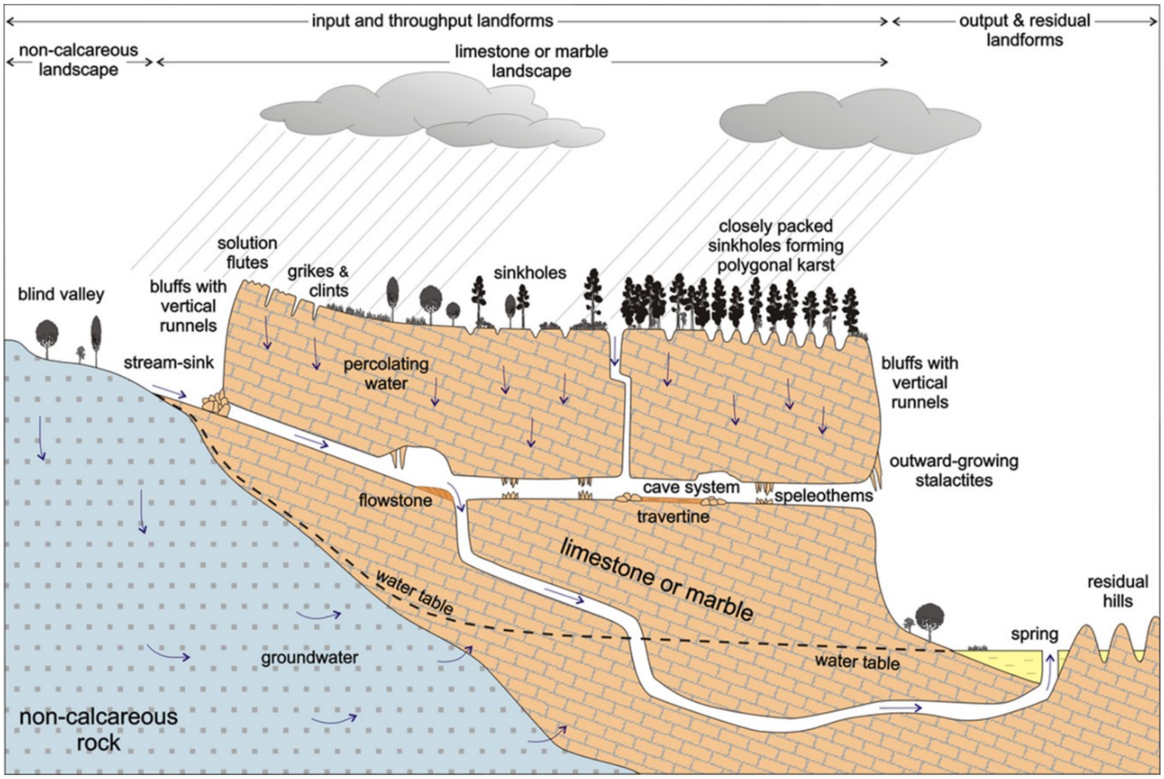


Figure 1. Karst topography (Kenny and Hayward, 2009)

infiltration rates which contribute to slow leaching of nutrients into groundwater. Clay and silt dominated soils have higher erosion rates which can contribute to additional P transport. Soils rich in sand have higher infiltration rates in which nutrients can travel more quickly (Correll et al. 1992). Nitrogen often enters soil in its organic form and is later converted into ammonium by bacteria where it can be stored temporarily. Ammonium cannot be mobilized through the soil column until it is converted into nitrate through nitrification. Nitrate may then leach into groundwater or get converted to its gas form through denitrification processes (Lamb et al. 2014). Because N does not easily sorb to soil and organic material, it is often transported through surface runoff in its dissolved form. Unlike N, P readily sorbs to soils and does not exist in a gaseous phase but can be

deposited through the atmosphere in its particulate phase (EPA 1999). During baseflow, nutrients may be temporarily stored in subsurface cavities until enough surface water infiltrates to slowly flush the nutrients into the groundwater system including springs.

Springs are often a major source of flow and nutrients to streams and rivers. During baseflow, when there is no contributing runoff, streams may retain larger amounts of N and P through biological uptake. In mid-latitude regions, discharge in is typically higher during winter and spring and much lower during summer and autumn. Consequently, nutrient export may be higher during spring and summer months. Springs typically export higher amounts of nutrients due to easier transport of flow through karst terrain. However, high discharge may limit microbial activity and uptake of nutrients due to reduced light from turbid water (Niyogi et al. 2010). Seasonal variation of spring nutrient concentrations is highly dependent on subsurface structure (Peterson et al. 2002). During baseflow, springs typically show little seasonal variation in nutrient concentrations. Concentrations of P may only vary about 0.04 mg/L or less, and concentrations of N may only vary around 4 mg/L or less (Hippe et al. 1994; Owen and Pavlowsky 2011).

Spring flow can be characterized by its flow path or how water moves through the subsurface. Flow through karst can be separated into two categories: diffuse and conduit flow (Figure 2). However, most flows are typically characterized somewhere in between these end members. <u>Diffuse flow</u> is indicative of a less mature karst system characterized by flow along many small interconnected openings from fractures and joints. <u>Conduit flow</u> is indicative of a more mature karst system characterized by flow along larger openings due to large scale dissolution. Water that flows through the smaller openings

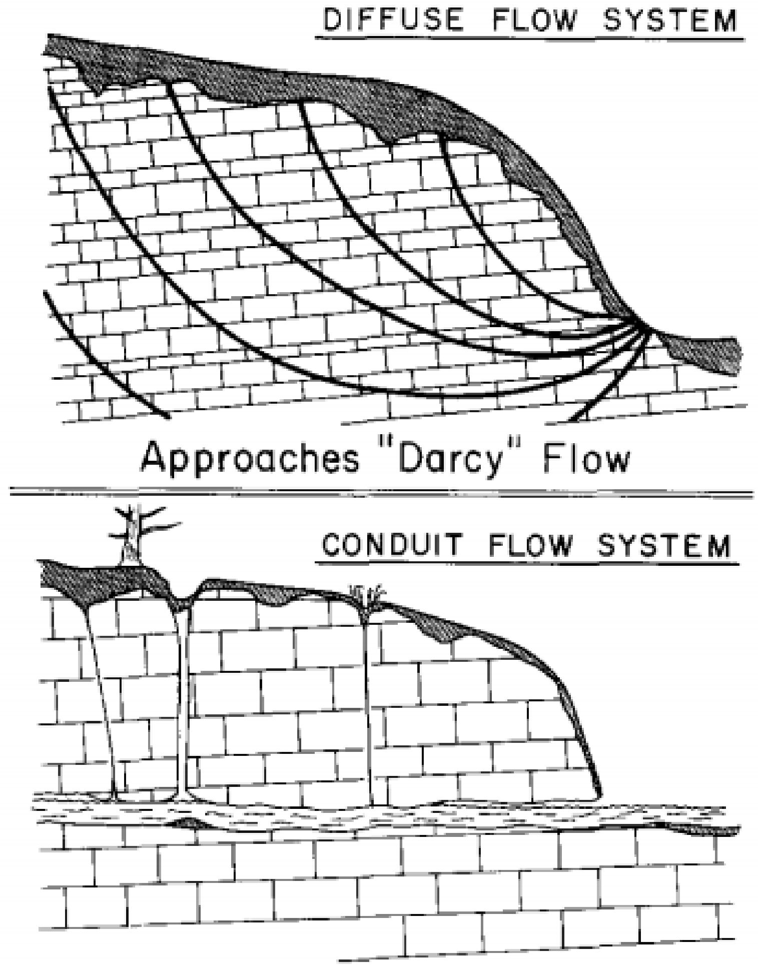


Figure 2. Diffuse and conduit flow (Shuster and White, 1971)

has a larger residence time in the subsurface which can be reflected by lower karst spring hydrograph peaks (Bonacci 1993). Thus, water has a longer time to reach chemical equilibrium with the subsurface materials (Wicks and Engeln 1997). This is reflected in little seasonal variation of water quality parameters such as specific conductivity (SC), temperature, and pH (Shuster and White 1971; Owen & Pavlowsky 2011). However, the presence of faults can complicate the characterization of spring flow and caution should

be used with interpretation (White 2003).

Physical properties of groundwater can indicate depth and source characteristics of spring flows. Surface water with relatively little thermal variation may indicate deeper groundwater sources (O'Driscoll and DeWalle 2006; Luhmann et al. 2011). Temporal variation in nutrient concentrations may also reflect subsurface flow paths. Diffuse groundwater flow to the surface may be characterized by little seasonal variation in N and P concentrations (Peterson et al. 2002; Kingsbury 2008; Huebsh et al. 2014). Water that flows through larger conduits has much less residence time. These conditions are reflected in "flashy" karst spring hydrographs with large peaks as well as relatively more chemical and temperature variation (Lerch et al. 2005). Conduit flow is reflected by larger temporal variations in temperature, pH, and SC. Larger spikes in nutrient concentrations may only be seen during higher discharge and stage when karst conduits become initiated (Bonacci 1993).

Impoundments and Nutrient Transport

There are an estimated 515,149 reservoirs, also called impoundments around the world. The number of small reservoirs (<0.1 km^2) have been underestimated and may make up as much as 86% of the total number of impoundments (Downing et al. 2006). Historically, reservoirs were built as way to meet growing water demands. Reservoirs and dams help manage irrigation and flooding and are common sources of drinking water and hydroelectric power. Consequences of damming include changes in nutrient budgets and cycling as well as oxygen and thermal conditions. Water storage is often described by its residence time, or average length of time, in the impoundment. The conversion of rivers

to reservoirs through the construction of dams can raise the residence time of water by a factor of 3, which significantly increases the potential for sediment and nutrient storage within reservoirs (Friedl and Wuest 2002). This reflects the necessity of calculating a water budget prior to calculating a nutrient budget (Winter 1981).

Sedimentation in reservoirs often plays a large role in nutrient concentrations (Kennedy and Walker, 1990). When sediment and particles settle in a reservoir, attached nutrients will also settle. Consequently, reservoirs often act as sinks for nutrients, particularly P (Friedl and Wuest 2002; Burford et al. 2012). However, reservoirs may become a source of P to downstream rivers when sediment is remobilized and when P is released due to changes in pH, temperature, or redox conditions (Nowlin et al. 2005; Christophoridis and Fytianos 2006; Powers et al. 2015). Reservoirs may be a sink for N through denitrification or burial in sediment (Howarth et al. 1996). Reservoir volume and depth may have a larger influence on N or algal concentrations than for P. In more shallow reservoirs, N may be mixed more readily than in deeper waters which is reflected by a negative correlation between N concentrations and volume (Burford et al. 2007). In other words, shallow lakes may be better sinks of N than deeper lakes. Sediment may be conducive to denitrification, especially in hypoxic or anoxic conditions (Harrison et al. 2009).

Release of P from sediment is often a result of variations in redox conditions and spatial stratification of P concentrations. Anoxic conditions have been correlated with "bursts" of nutrients released from sediment storage (Penn et al. 2000). Such conditions have been shown to occur during spring or summer when spikes in P are common (Kennedy and Walker 1990; Yurista et al. 2004; Matzinger et al. 2007). This timing of

pulses in P concentrations may also be due to mobilization of sediment from wind or rain events, which are typical in spring when lake turnover occurs (Correll 1999; Wetzel 2001). Spring turnover occurs when seasonal temperature-density changes cause complete vertical mixing of a lake or reservoir and often produces spikes in P concentrations in the water column (Davis and Bell 1998). In many lakes, there is a strong relationship between summer algal growth and TP concentrations during spring turnover (Dillon and Rigler 1974).

Several studies emphasize the need for more research on small reservoirs (Fairchild and Velinsky 2006; Ignatius and Rasmussen 2016). Historically, large reservoirs have been the sole focus of many water quality and quantity studies, despite the large number of small reservoirs. Compared to larger reservoirs, small reservoirs may have a higher capability of accreting and trapping sediments, shorter residence times, and stronger redox gradients. (Smith et al. 2002). Small reservoirs have also been shown to have high sediment trap efficiency. Many small reservoirs have trap efficiencies of up to 98% (Dendy 1974). This has important implications for P dynamics in reservoirs. Small reservoirs may account for 15% of the removal of total global N whereas large reservoirs account for only 5% (Wollheim et al. 2008). This difference is likely due to the significantly higher number of small reservoirs which emphasizes the importance of small reservoir studies and management.

Nutrient Budgets

Budgets for N and P are generally calculated by the difference between nutrient inputs and outputs for different transport pathways (Bosch and Allen 2008; Brown et al.

2011). Large differences in inputs and outputs may indicate sediment or biomass storage or losses by seepage. Additionally, modern nutrient budgets can be compared with past studies to determine the effect of land use change and development on N and P yields. In basins with spring-fed reservoirs and stream systems, P may be more significantly altered than N yield (Watson et al. 1979). The significance of P in these systems may be further exemplified by the role of internal P release from sediment in reservoirs. In one spring-fed lake, internal load of P from sediment release was nearly 33% of the total P input to the lake (Brown et al. 2011). In spring-fed streams, net uptake of nutrients may be higher during baseflow, while net export of nutrients may be higher during stormflow (Niyogi et al. 2009).

Although important, baseflow contributions of nutrients are infrequently studied. In karst, baseflow reflects increased groundwater connectivity to surface waters through springs and may show significant N contributions to streams and rivers (Pittman et al. 1997). Contributions of N through groundwater may be significant due to excess nitrate from urban drainage and agricultural practices (Janke et al. 2014; Nolan and Stoner 2000). Additionally, seepages/leakages of reservoirs and streams may contribute additional nutrients to baseflow (Hatch et al. 2006; Kumar et al. 2008). More specifically, there may be a connection between seepage of reservoirs and springs that are in close proximity (Ghobadi et al. 2005). This suggests that a simple estimation of seepage flow may be more accurate during baseflow.

Missouri Nutrient Problems

The Ozarks is a physiographic region encompassing parts of Arkansas, Missouri,

Kansas, and Oklahoma. Most of the Ozarks lies within Missouri and Arkansas where it extends from the Missouri River to the Arkansas Valley (King 1973). The Missouri Ozarks refers to the portion of the Ozarks that extends 9.4 million hectares south of the Missouri River (Hanberry et al. 2014). In the Ozarks, the major source of N and P enrichment is livestock and poultry manure. Beef cattle, in particular, supply a significantly larger amount of N and P than any other source. Therefore, the amount of nutrient contributions from cattle, poultry, and swine may vary from basin to basin depending on the major livestock in the region (Davis and Bell 1998).

Nutrient contributions to the Missouri River Basin are predominately from fertilizer and manure. Sediment mobilization is a source of P in much of the basin. Reservoirs and lakes retained as much as 16% of the N load and 33% of the P load of the basin (Brown et al. 2011). Additionally, wastewater treatment plants may provide a significant amount of nutrients. (Richards and Johnson 2002; Owen and Pavlowsky 2010). Missouri has many springs and reservoirs that may affect nutrient loads. Thus, it is important to monitor N and P contributions in spring-fed and reservoir-fed streams. During baseflow, most of the surface water comes from groundwater supplied by seeps and springs (Miller and Vandike 1997).

Total Maximum Daily Loads (TMDLs) are standards calculated to determine the amount of pollutant loads a water body can receive without becoming impaired, and TMDLs are used to manage surface water quality. Total nitrogen (TN) and total phosphorus (TP) concentrations are often the subject of TMDLs in the United States. However, TMDLs do not exist for many Missouri streams and lakes. For water bodies lacking TMDLs, ecoregion reference conditions for Missouri are used (MDNR 2010).

Reference conditions are concentrations that reflect minimal anthropogenic impact. Total nitrogen concentrations are referenced at 0.289 mg/L, and TP concentrations are referenced at 7 ug/L. However, actual target concentrations for many Missouri watersheds may be much higher. For EPA approved TMDLs that currently exist in Missouri, nutrient target concentrations range from no than 60 to 75 ug/L of TP and 1.0 to 1.5 mg/L of TN (MDNR 2001). In many Missouri Ozark streams, TN concentrations range from 0.15 mg/L to 11.7 mg/L, and TP concentrations range from 6 to 2030 ug/L (Table 1). These results reflect the variable nature of nutrient concentrations in streams draining karst regions. For most streams in southern Missouri, average concentrations of TN and TP have been significantly higher than ecoregion and TMDL recommended limits.

Ratios of N to P concentrations can reveal nutrient limitation in reservoirs. Nutrient limitation occurs when enough nitrogen or phosphorus is added to increase biological processes which can cause harmful algal blooms (Bolgrien et al. 2009). Changes in ratios can also indicate changes in nutrient concentrations. For example, algal biomass increase may show lower ratios which reflect a decrease of nitrogen concentrations due to denitrifying bacteria (Paerl et al. 2001). Phosphorus is often the limiting nutrient during summer when algal blooms are prominent (Havens 2003). Ratios of TN:TP are used in some Missouri TMDLs to evaluate and control large algal blooms. Ratios of TN:TP for the James River in southwest Missouri are evaluated using several published N limiting thresholds. TN:TP ratios less than 10 to 12 define N limitation and values greater than 17 to 20 define P limitation. Many stream monitoring sights in the nearby upper James River Basin are considered P limited (MDNR 2001).

Table 1. Nutrient concentrations in Ozark watersheds

Major Water Body	Location	Drainage Area (km^2)	Mean TN (mg/L)	Mean TP (ug/L)	Study
James River, Gasconade River, Big Piney River	Southwest to Central Missouri	38.3 - 1663.3	1.11 - 2.56*	14 - 65*	Smart et al. 1985
Wilsons Creek, Pearson Creek	Southwest Missouri	3.3 - 151	0.79 - 8.29[A]	<50 - 2030	Richards and Johnson, 2002
South Dry Sac River	Springfield, MO	0.5 - 12.7	2.0 - 2.8	36 - 65	Bowen, 2004
Spring River	Southeast Kansas, Southwest Missouri	47 - 5,410	1.17 - 3.50*[B]	350 - 205*	Chambers et al. 2005
Jordan Creek, Fassnight Creek	Southwest Missouri	7.2 - 50	0.77 - 2.98	28 - 176	Miller, 2006
White River, James River	Southwest Missouri, Northwest Arkansas	51 - 2,567	0.38 - 11.7	6 - 178	Borchelt, 2007
Current River	Southeast Missouri	0.98	0.32 - 4.17*	30 - 196*	Koirala, 2009
Niangua River	Southern MO	11 - 1,141	0.34 - 1.68	13 - 181	Owen and Pavlowsky, 2009
White River, Illinois River	Northwest Arkansas	59.6 - 1489.2	0.87-3.81	200 - 420	Bailey et al. 2012
South Fork Little Red River	North Central Arkansas	12 - 84	0.15 - 2.50*	10 - 150*	Austin, 2015

*Stormflow results included [A] Nitrite plus nitrate [B] Nitrate

Purpose and Objectives

There are relatively few studies on nutrient budgets in karst systems in the Ozarks. There are even fewer studies on nutrient retention and transport through spring-fed reservoirs. The primary focus of this study is centered around the VWMR within the Valley Water Mill Watershed (VWMW) in Springfield, MO. One previous study has measured nutrient concentrations at the reservoir after drainage, but no nutrient study has been done at the site during relatively normal conditions (Bowen 2004). During baseflow, a small spring located 200m above the reservoir, Sanders Spring, contributes most of the flow in the VWMW. The VWMW drains 32% of the upper south Dry Sac River above a USGS gage located below the reservoir. Potential leakages from the reservoir flow into the South Dry Sac River from a small spring and tributary. The purpose of this study is to quantify baseflow nutrient load contributions of a karst spring in a mixed-land use watershed to understand nutrient and water sources, human contributions to nutrient concentrations, and implications for future monitoring and nutrient management through the following objectives:

1. Monitor specific conductivity, pH, and water temperature to identify sources and potential flow paths of groundwater which will provide information on how nutrients are transported through the subsurface during baseflow;

2. Calculate monthly hydrologic budgets based on baseflow records from stream gage data, estimated leakages, and evaporation losses which will provide information on potential reservoir losses;

3. Monitor nutrient concentrations to determine seasonal and spatial variations; and

4. Calculate daily nutrient budgets for the Valley Water Mill Reservoir and South Dry Sac River to determine spring inputs, storage and remobilization in the reservoir, and the role of karst in controlling the transport and storage of nutrients

Hypotheses

Using previous literature and information on the study area, four main results are expected:

1. Specific conductivity, pH, and water temperature will show little seasonal variation, which may reflect a diffuse flow path during baseflow;

2. The reservoir will provide a sink for N for most of the year due to denitrification, uptake by algae, or sedimentation. In other words, N concentrations at Sanders Spring will be higher than at the reservoir during baseflow for much of the year;

3. The reservoir will provide a source of P during spring or summer due to remobilization from sediment during spring turnover; and

4. During baseflow, the spring will contribute a significant portion of flow to the river, but some of this will be lost to evaporation and seepage at the reservoir

Benefits

This study will improve our knowledge on baseflow nutrient transport and storage through a karst-spring reservoir system in the Ozarks. The results of this study will also aid in management of the VWMW through improved understanding of the transport and storage processes that contribute to eutrophication and algal blooms. Because much of the water from the South Dry Sac River ends up at Fulbright Spring, still used for some of the drinking water supply, the Watershed Committee of the Ozarks (WCO) continuously works to manage the streams and reservoir within the VWMW (WCO 2009). The WCO is a non-profit organization dedicated to improving water resources through education and management. The WCO runs the Watershed Center, located southeast of the reservoir, which is a source for many educational field trips and offers opportunities for many valuable lessons on stream chemistry, stream ecology, and

watershed science. The information produced by this study will be used to aid these educational and management programs.

CHAPTER 2 - STUDY AREA

The VWMW is a subwatershed located in Springfield, MO within the Headwaters South Dry Sac Watershed (HW-SDSW) in Greene County, MO (Figure 3). Springfield, MO has population of over 165,000 (U.S. Census Bureau 2010). The VWMW drains 12.7 km^2 of northern Springfield near the major intersection of I-44 and US-65. The HW-SDSW has a drainage area of 39.8 km^2. The focus of this study will be on the northern tip of the VWMW near the Valley Water Mill Reservoir (VWMR). Three main springs contribute flow to this area. Shotgun Spring is located on the South Dry Sac River just above the VWMR confluence. Jarrett Spring flow arises beneath the east side of the reservoir below the water surface. Sanders Spring is the main contributor of flow in the VWMW during baseflow. The water in the VWMW flows into the reservoir, over the spillway, and into the South Dry Sac River.

Geology and Soils

The Headwaters South Dry Sac Watershed and VWMW both drain karst topography (Figure 4). The major surficial geologic formations within the VWMW are of Mississippian age (Wright Water Engineers 1995). The Burlington-Keokuk Limestone is the shallowest and most prominent formation in Greene County. The Burlington-Keokuk Limestone marks the start of the Springfield Plateau Aquifer and many of the spring and sinkhole systems are developed here. The Burlington-Keokuk is composed of around 155 to 270 feet of limestone and chert. Below the Burlington-Keokuk lies the Elsey and Pierson Formations which are primarily cherty limestone. The last geologic unit in the Springfield Plateau Aquifer is the Northview Formation which is composed of siltstone

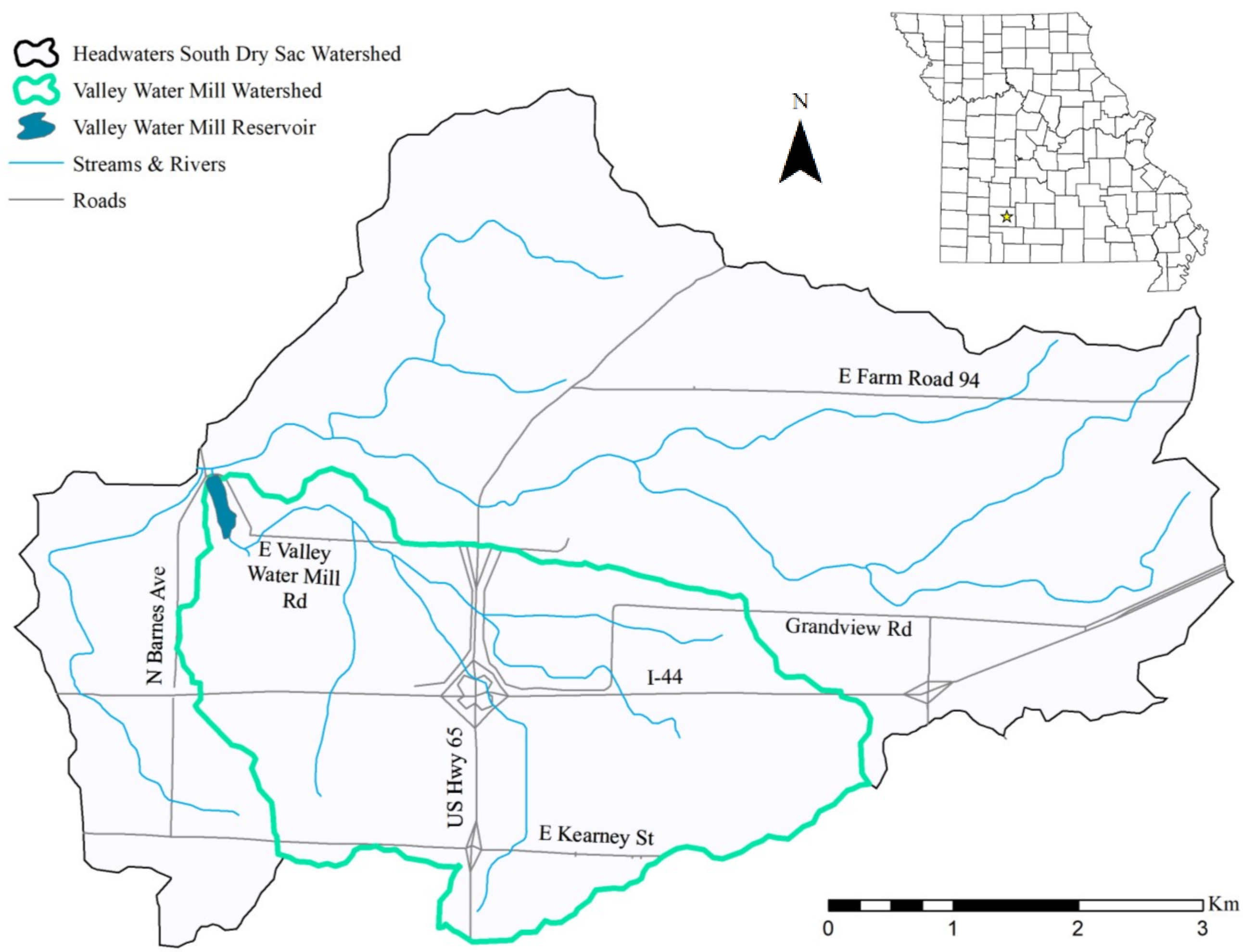


Figure 3. Valley Water Mill Watershed within the Headwaters South Dry Sac Watershed

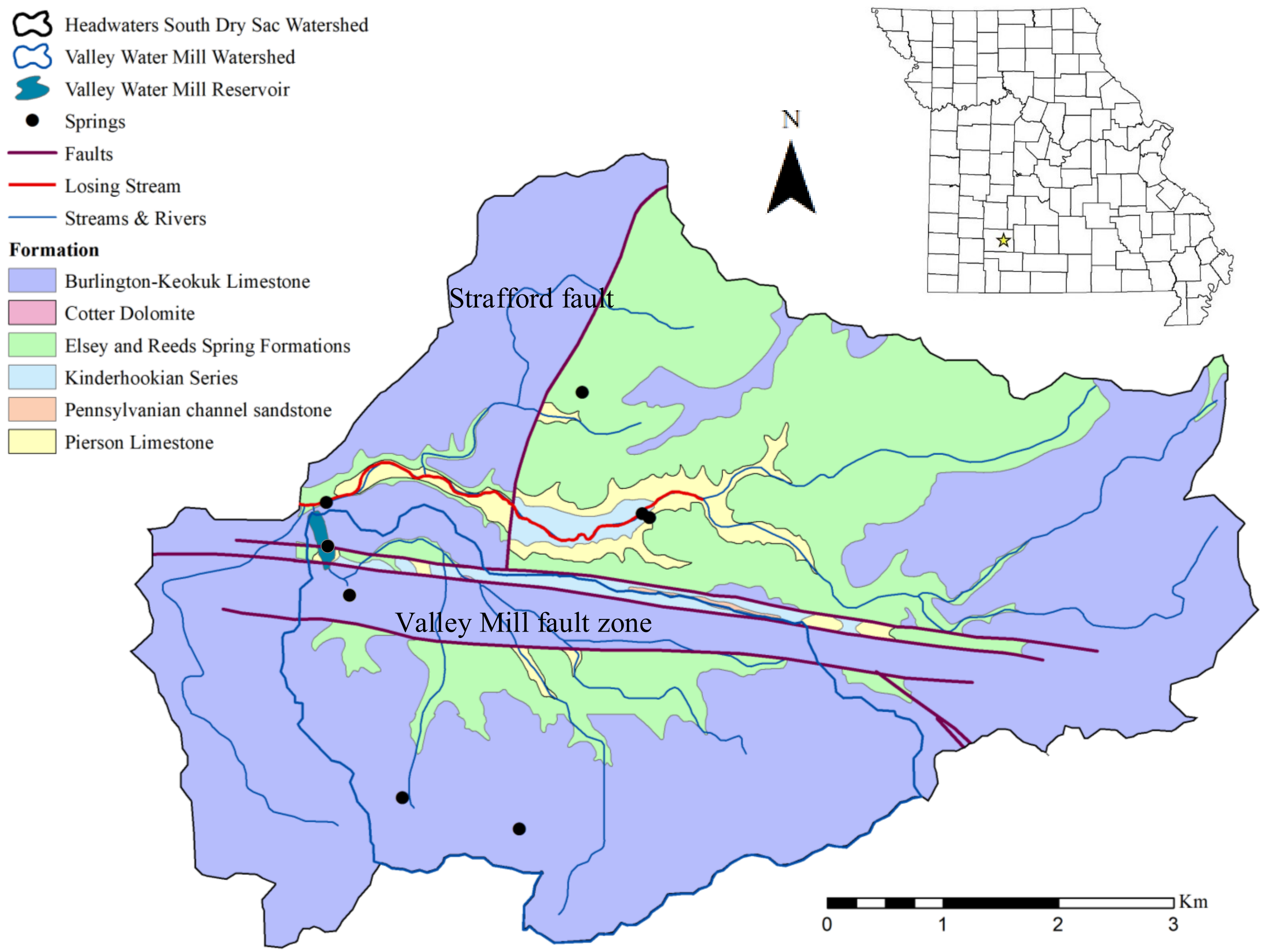


Figure 4. Geology of the study area

and shale. Below these Mississippian aged formations lie the Ozark Confining Layer and the Ozark Aquifer in which the Devonian and Ordovician aged formations are likely too deep to contribute to the spring systems in the VWMW (Bullard et al. 2001). The major faults within the watersheds include the Strafford fault and the Valley Mill fault zone. The Strafford fault runs north and east across the South Dry Sac River. Two fault lines running east-west comprise the Valley Mills Horst (Wright Water Engineers 1995).

The HW-SDSW and VWMW are both characterized by silty and loamy soils on adjacent hillslopes. The primary soils near the VWMW and reservoir are gravelly silt loams. Silty loams dominate much of the watershed uplands and valley bottoms. The main soil components near Sanders Spring and the VWMR include Goss, Wilderness, and Waben series. These are characterized as well drained with gentle to moderate slopes. The main soil components near the South Dry Sac River include Needleye, Winnipeg, and Goss series profile which are made up of loess over residuum and characterized as well drained with gentle slopes (Hughes 1982).

The main soil series within the watersheds can be classified by their hydrologic group using Soil Survey Geographic Database (SSURGO) data (Figure 5). Hydrologic groups A, B, C, and D describe the infiltration rate of the soil when saturated. Hydrologic group A defines soils as having high infiltration rates with low runoff potential and includes well drained gravelly sands. Group D defines soils as having very slow infiltration rates with high runoff potential and includes clays. If a region has varying infiltration rates that depend on its drainage, it is given two groups. The first letter in combined groups refers to drained soils, while the second letter refers to undrained soils (Soil Survey Staff 2018). Many of the soils within the VWMW have moderate

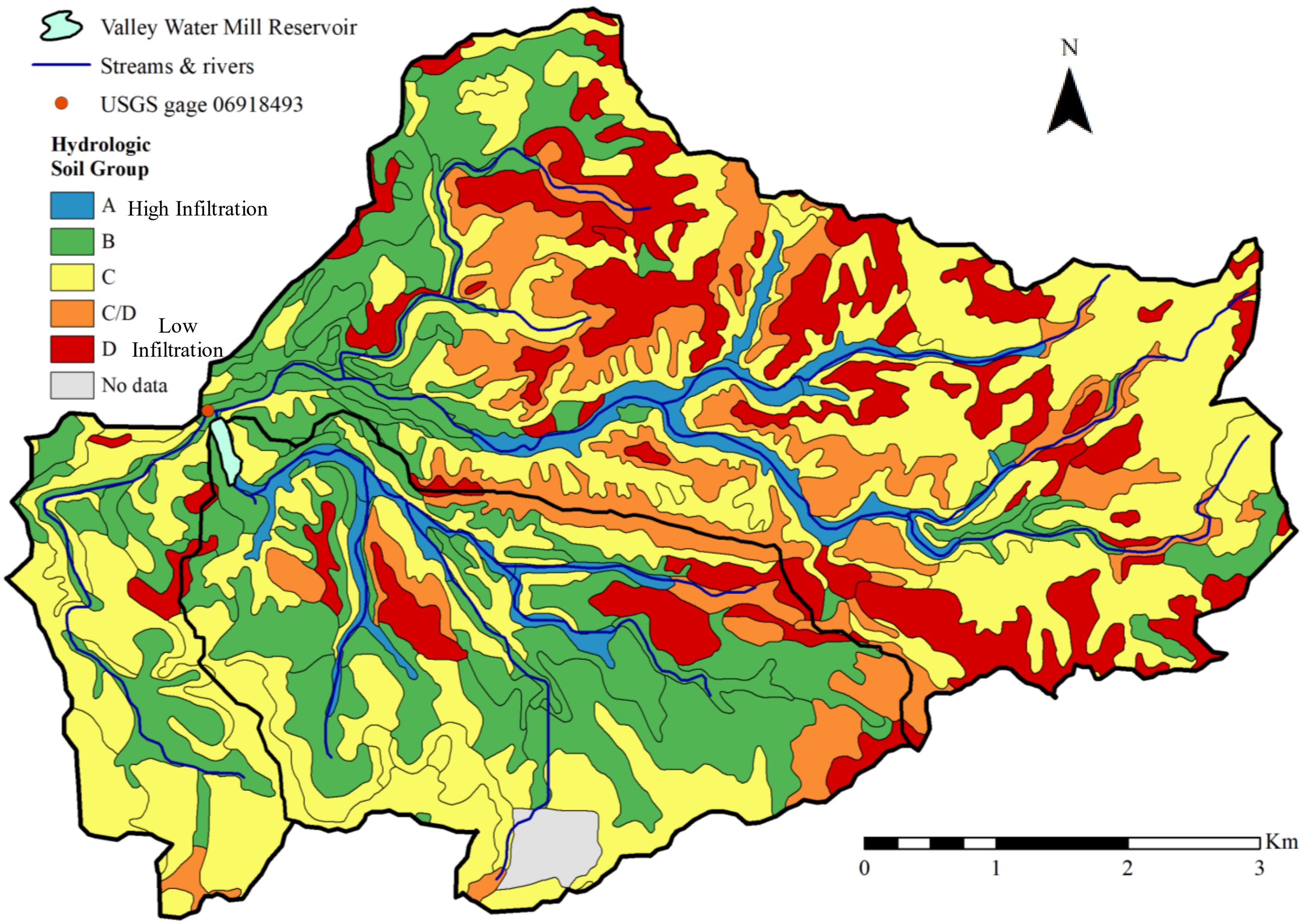


Figure 5. Hydrologic soil groups

infiltration rates (Table 2). A higher runoff potential makes the watershed more vulnerable to nutrient pollution. The drainage area of Grandview Tributary is primarily made up of group C which consists of soils with moderate infiltration rates. The VWMW has soils with moderate to slow infiltration rates while the area draining the upper South Dry Sac River has a wider range of soil types.

Climate

The climate of Springfield, MO is classified as humid subtropical which is characterized by variable precipitation, hot humid summers, and drier winters. Based on Springfield Weather Service Office Airport, MO US (USW00013995) NOAA 30-year climate normals from 1981-2010, the average temperature in Springfield is 13.5°C (Arguez et al. 2010). Average temperatures are 1.6°C in winter, 13.1°C in spring, 24.7°C in summer, and 14.2°C in fall. Total annual precipitation averages at 1,157 mm and annual snowfall averages at 432 mm. Average precipitation is 204 mm in winter, 331 mm

Table 2. Hydrologic soil group distribution

		% Total Drainage Area				
	Drainage Area (km^2)	A	B	C	C/D	D
Grandview Tributary	4.6	0.0	28.5	66.0	2.0	3.5
VWMW	12.7	5.0	40.0	32.0	11.0	8.0
Upper SDS	22.5	5.0	16.0	41.0	16.0	21.0
HW-SDSW	39.8	8.0	24.0	41.0	12.0	15.0

in spring, 307 mm in Summer, and 315 mm in fall.

Hydrology

The VWMW consists mainly of a system of connected springs, ephemeral streams, a dammed reservoir, and a gaining and losing river. The watershed is fed primarily by Sanders Spring and drains approximately 12.7 km^2 into the South Dry Sac River. The hydrologic system of the VWMW is connected to Fulbright Spring. Historically, Fulbright Spring has been a drinking water source for Greene County. Much of the water that recharges Fulbright Spring has been traced through a swallow hole in the South Dry Sac River just below the VWMR (Wright Water Engineers 1995).

Sanders Spring. Sanders Spring is the major source of groundwater to the VWMW during baseflow. Dye tracing has linked flow at Sanders Spring from several sinkholes in Springfield (Wright Water Engineers 1995). Water from Sanders Spring flows into a small perennial spring before reaching the VWMR (Figure 6, 7, and 8). Just upstream Sanders Spring, a small ephemeral tributary (FR102) contributes flow through a 3-box culvert during stormflow and periods of higher baseflow. In the past, average flow from Sander Spring was estimated to be 0.34 m^3 during baseflow and 0.91 m^3 during stormflow. During baseflow, nutrients in the VWMW come primarily from Sanders Spring (Bowen 2004).

Valley Water Mill Reservoir. The VWMR has an approximate surface area of 0.06 km^2 and drains over its dam, through a culvert and into the South Dry Sac River (Figure 9, 10, and 11). The dimensions of the reservoir are an average width of 105 m and a length of 505 m. The reservoir has the potential to store 149,536 m^3 with an average

Figure 6. Sanders Spring

Figure 7. Downstream view of channel formed by Sanders Spring

Figure 8. Valley Water Mill Reservoir inlet

Figure 9. Valley Water Mill Reservoir

Figure 10. Valley Water Mill Reservoir dam overflow

Figure 11. Valley Water Mill Reservoir spillway and culvert

depth of 2.6 m and a maximum depth of 6.1 m. The elongated shape of the VWMR is typical for most reservoirs. The major source of water to the VWMR during baseflow is Sanders Spring, and the reservoir may act as a trap or sink for much of the nutrients and sediment coming from the spring. Sedimentation rates in the reservoir range from 2 to 4.5 cm/yr after the year 2000. However, past sedimentation rates vary and reached as low as 0.3 cm/yr from 1978 to 2000. In 1969 and 2002, the reservoir was drained and removed of sediment (Licher 2003). Jarrett Spring also contributes flow to the reservoir, but its contribution is likely negligible. In 2002, estimated average discharge from the reservoir was 0.40 m^3/s during baseflow and 2.5 m^3/s during stormflow (Bowen 2004). Under high enough discharge and stage, water flows over the dam and into the South Dry Sac River.

South Dry Sac River. The South Dry Sac River (SDSR) is largely controlled by the karst geology where it is characterized by many sinkholes and springs. The river alternately gains and loses along its channel within the Headwaters South Dry Sac Watershed (Figure 12). The headwaters of the river closest to the VWMR are typically perennial. The SDSR discharge is monitored by a USGS gage (USGS 06918493 South Fork Dry Sac River near Springfield, MO) that was installed in 1996. Stage data started being measured in 2007 (USGS 2018). The USGS gage marks the outlet of the Headwaters South Dry Sac Watershed and has a drainage area of 39.8 km^2. From 1997 through 2017, average monthly discharge was highest in March, April, and May (Figure 13). Peak discharge reached 103 m^3/s on April 25, 2011. During the sample period, peak discharge reached 54.9 m^3/s on April 29, 2017. In 2002, average baseflow at the gage was estimated at 0.37 m^3/s and average stormflow was estimated at 3.6 m^3/s (Bowen 2004). Along with the VWMR, Grandview tributary and Shotgun Spring also provide

Figure 12. South Dry Sac River above the Valley Water Mill

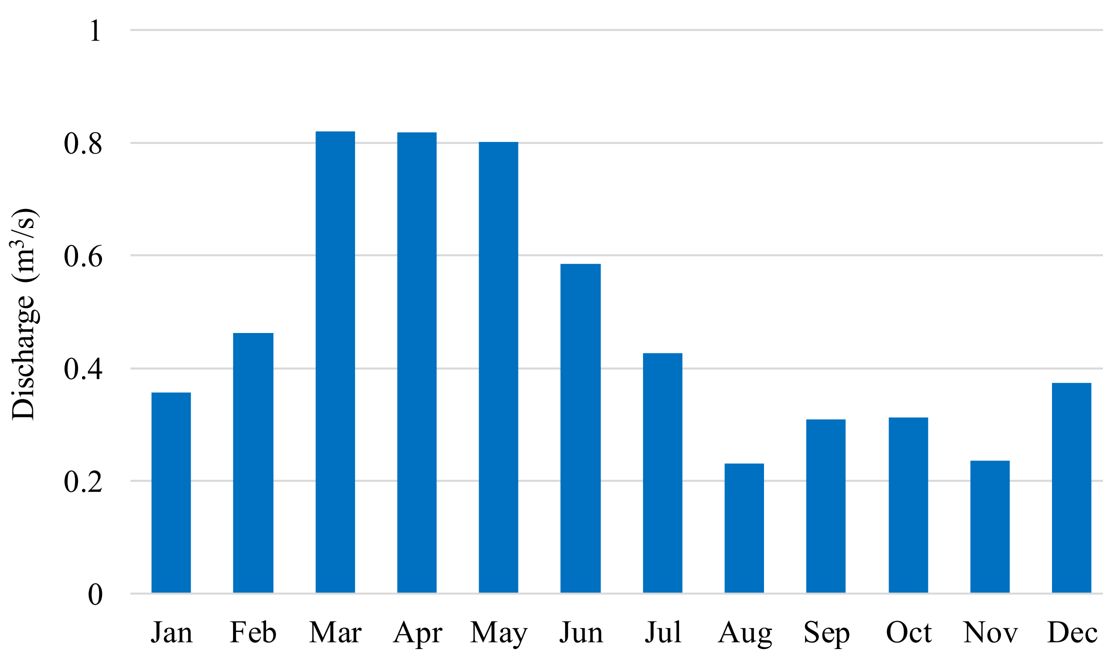


Figure 13. Average monthly discharge for the South Dry Sac River

discharge to the headwaters of the South Dry Sac River. The contributions of the tributary and spring are likely negligible throughout the year.

Leakage Contributions. Leakages around the dam outlet are apparent in the VWMW. Leakage is caused by seepage of water into the bed and embankment near the spillway and backwater flow in karst conduits due to the higher water table caused by the dam. It is likely that much of the leakage from the reservoir is released to the South Dry Sac River. One pathway may be through Grandview Tributary (Figure 14). Grandview tributary is dry for most of its upstream reach, but water re-emerges near the VWMR. Another pathway is likely through Shotgun Spring just above the reservoir on the South Dry Sac River (Figure 15). Additionally, there is variation in the amount of leakage that can be observed near the spillway of the dam. Water can be seen emerging from the ground and flowing through the culvert into the South Dry Sac River (Figure 16). This flow is often too small to measure accurately.

Land Use and Land Cover

Both the HW-SDSW and the VWMW have mixed land use and land cover (Figure 17). The region was initially used by the Osage tribe from around the 1700s to the 1800s until white settlers arrived in the 1830s. The dominant land use was largely agriculture until industrialization began in the 1990s. In the mid-1800s, the VWMR was initially built to be used as a grist mill. It was later used to supply drinking water to Springfield, and in in 1899 when it was purchased by the Springfield Water Company (Licher 2003).

According to data from the National Land Cover Database (NLCD), the VWMW

Figure 14. Grandview tributary

Figure 15. Shotgun Spring

Figure 16. Valley Water Mill Reservoir seepage

is dominated by urban land use (Homer et al. 2015). Land use and land cover for the VWMW is 59.2% urban, 23.6% agriculture, 15.6% forest, and 1.6% other. Urban land use includes open space as well as low, medium and high development from the NLCD classification system. Agriculture includes pasture/hay and cultivated crops. Forest includes deciduous, evergreen and mixed. All other classifications fit into the other category.

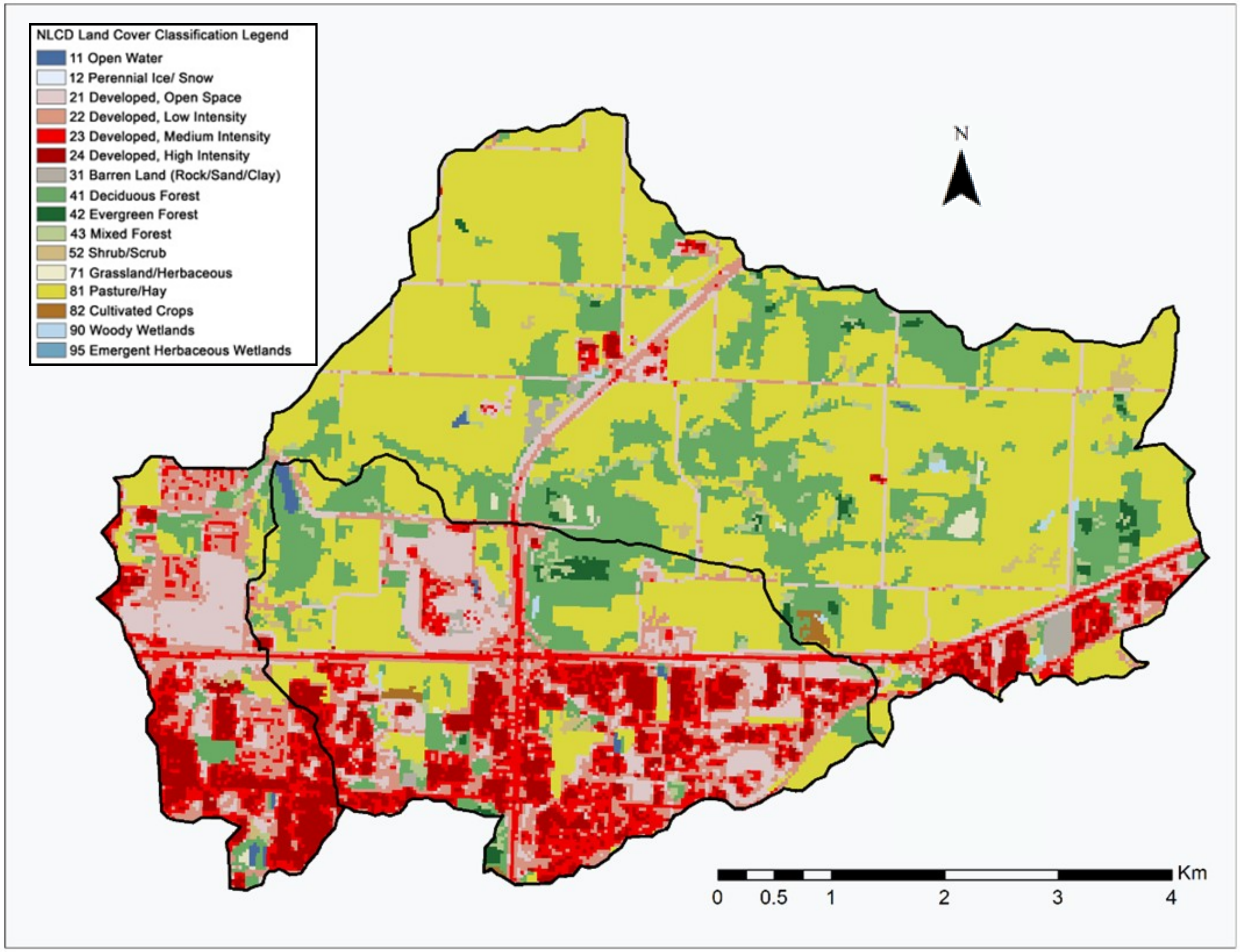


Figure 17. NLCD land cover of study area

CHAPTER 3 – METHODS

Continuous stage gage, water quality, and discharge data was collected at monitoring sites throughout the HW-SDSW and VWMW depending on base flow conditions (Figure 18; Table 3). 7 water sampling runs were completed from April 7, 2017 to January 19, 2018 (Table 4). Data from stage gages was collected and monitored from March 1, 2017 to March 1, 2018. Stage and survey data collected at the installed stage gages were used to create rating curves to estimate daily discharge. Percent difference was calculated to compare measured discharge with estimated discharge.

Sanders Spring (SS1) is located just upstream from a small tributary (FR-102). A continuous stage gage was installed at FR-102. A continuous stage gage was also installed further downstream at SS2 to be able to estimate flow at SS1. Water from SS1 and FR-102 flows through a reservoir inlet (SS3) and over a dam located at RD. A continuous stage gage was installed at RD to be able to estimate discharge over the dam. Field discharge measurements at RD include both flow over the dam and estimated seepage near the spillway. Discharge was estimated for seepage on October 27, 2017. Water at RD flows over the dam at high stage and flows through a boxed culvert into the South Dry Sac River. A USGS gage at SDS2 monitors flow from RD and upstream headwaters of the South Dry Sac River (SDS1). Shotgun Spring (L1), located above RD, and Grandview Tributary (L2), located below RD, are potential reservoir leakages to the South Dry Sac River. Discharge measurements were collected at 2 supplemental sites: SDS0 and SDS3 during one sampling event to evaluate any significant difference between flow upstream and downstream of monitoring sites.

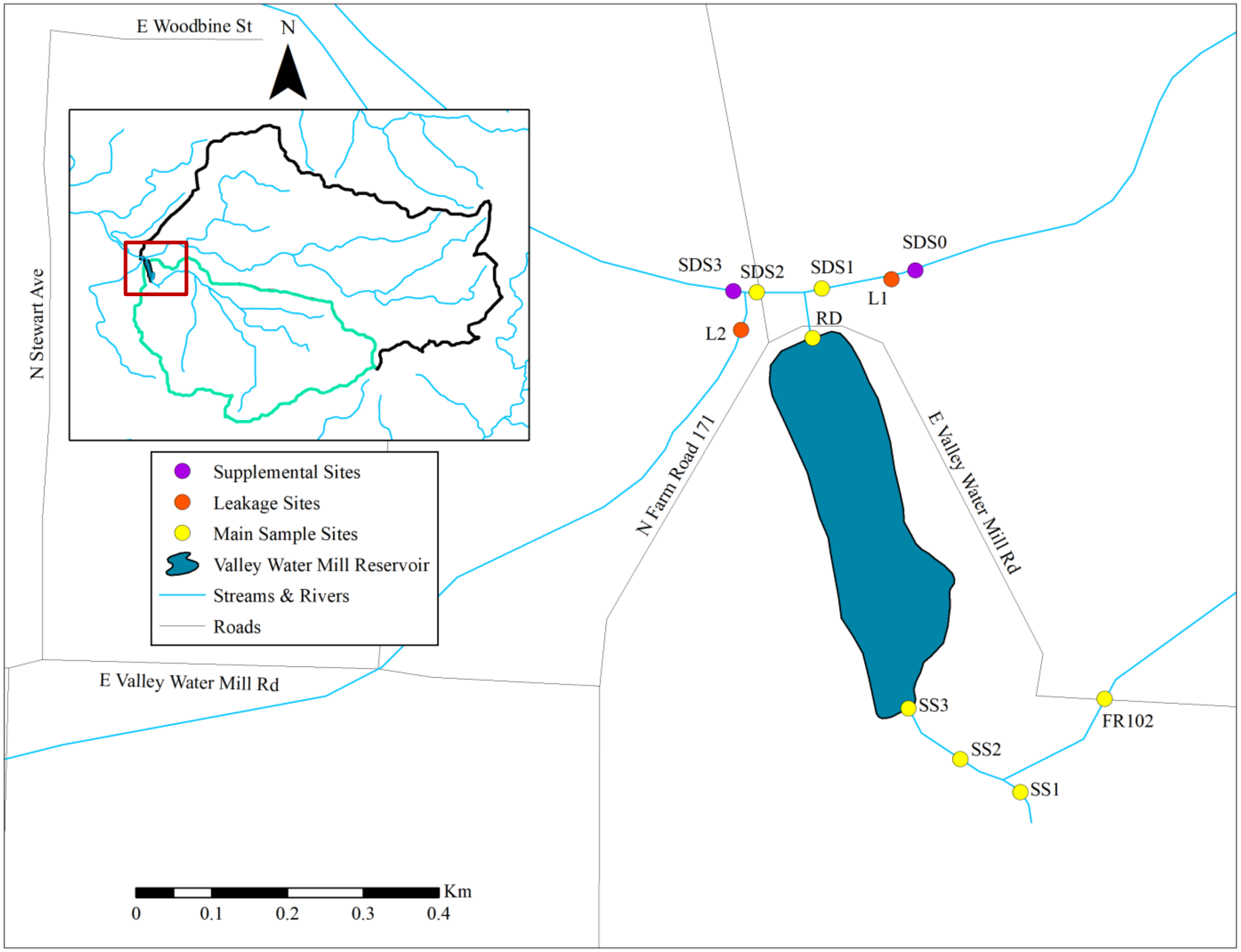


Figure 18. Sample site locations

Table 3. Monitoring sites and collected data

Site	Longitude	Latitude	Stage Gage	Water Samples Collected	Discharge Measured
SS1	-93.2453	37.2603		✓	✓
FR-102	-93.2438	37.2615	✓	✓	✓
SS2	-93.2461	37.2606	✓	✓	✓
SS3	-93.2468	37.2611		✓	✓
SDS0	-93.2467	37.2667			✓
L1	-93.2472	37.2664			✓
SDS1	-93.2486	37.2662		✓	✓
RD	-93.2487	37.2656	✓		✓
SDS2	-93.2495	37.2664		✓	✓
L2	-93.2498	37.2662			✓
SDS3	-93.2495	37.2663			✓

Table 4. Collected water samples

		# of Samples							
Date	SDS2 Average Daily Q (m^3/s)	FR-102	SS1	SS2	SS3	RD	SDS1	SDS2	Total
4/7/2017	1.24	2	2	2	4	4	2	2	18
6/9/2017	0.31	0	6	6	12	6	6	12	48
7/13/2017	0.12	0	12	6	6	6	6	12	48
10/27/2017	0.18	0	2	4	2	2	4	2	16
11/17/2017	0.10	0	4	2	2	2	4	2	16
12/15/2017	0.05	0	2	4	2	4	2	2	16
1/19/2018	0.08	0	2	2	4	0	4	2	14

Samples were collected for analysis of TN, total suspended solids (TSS), and chloride (Cl) as well as field duplicates for quality control checks. Levels of pH, dissolved oxygen (DO), SC, and temperature were measured in the field using a YSI meter. Geographic Information Systems (GIS) was used to create study area maps. The statistical programming language R was used for creating plots of various water quality parameters and discharge measurements. All field and laboratory methods followed Ozarks Environmental Water Resources Institute's (OEWRI) standard operating procedures (SOP). Most of the SOPs are based off standard EPA methods and can be found on the OEWRI web page at https://oewri.missouristate.edu/58411.htm.

Field Methods

Sampling. At each site, water samples were collected in 500 mL plastic bottles twice during each meteorological season by using a depth-integrated sampler. Grab samples were taken when stage was too low for the sampler. On June and July sample dates, water was collected three times throughout the day to ensure there was little diurnal variation of concentrations. Two duplicate samples were collected for two randomly chosen sites during each sample date for quality control. Stream temperature, SC, DO, and pH were collected at each sample site using a YSI Professional Plus Handheld Multiparameter Meter. Sample bottles were stored on ice in a cooler shortly after their collection and returned to be refrigerated. Discharge measurements were measured using a flow meter at stream gage locations and directly downstream the dam when baseflow is high enough for water to flow. Measurements were taken following OEWRI's SOP for the SonTek/YSI FlowTracker.

Continuous Stage Gages. Staff gages and Solinst leveloggers were installed at sites FR-102 (tributary), SS2 (spring-stream gage), and RD (reservoir) using PVC electrical conduits (Figure 19). Leveloggers were used to measure temperature and stage data at 15-minute intervals. A Solinst barologger was installed near the spring-stream gage to more accurately compensate for atmospheric pressure. Data from loggers were collected and downloaded periodically using an optical reader and laptop. Cross-section surveys were done using a Topcon total station at each gage to help develop rating curves to monitor stream discharge.

Laboratory Methods

Samples were brought back to the laboratory immediately after collection. Each Water bottles for TN and TP analysis were treated with 2 mL sulfuric acid and all samples were returned to a refrigerator for storage. Samples were tested for Cl, TSS, TN, and TP within their respective holding times. All laboratory procedures follow OEWRI SOPs.

Chloride (Cl). Concentrations of chloride were measured within 28 days using the Accumet Excel XL25 and XL250 dual channel pH/ion meters. These instruments have a detection limit of 0.1 mg/L. Instruments were calibrated before each use with standard chloride concentrations. Water samples were mixed with ionic strength adjuster for use with an ion selective electrode to ensure maximum accuracy and reproducibility. Quality control was carried out using laboratory blanks and duplicates.

Total Suspended Solids (TSS). Procedures for measuring TSS followed EPA method 160.2 (EPA 1983). Measurements of TSS were done within 7 days of sample

collection. Water samples were filtered through pre-rinsed 0.45 μm filters, dried in an oven at 105°C, and weighed. The concentration of TSS was calculated using the following equation:

$$TSS = \frac{(A - B)}{V},$$

where TSS is total suspended solids (mg/L), A is the mass of the filter + dried residue (mg), B is the mass of the dry filter or tare weight (mg), and V is the volume of sample filtered (L). The detection limit for this procedure is 0.5 mg/L for a 1-L sample. Measurements of below 0.5 mg/L were given values of 0 mg/L.

Total Nitrogen (TN). Concentrations of TN were measured within 28 days of sample collection with the Genesys 10S UV-Vis spectrophotometer. Procedures were derived from EPA laboratory analysis methods (EPA 1987). The upper and lower detection limits for this instrument is 0.1 mg/L to 5 mg/L, respectively. Concentrations larger than the detection limit require dilution of the sample. Several laboratory duplicates, and blanks were prepared for quality control. After samples were prepped and mixed with an alkaline persulfate oxidizing solution they were heated in an autoclave, converting various N compounds to nitrate. The samples were then neutralized with hydrochloric acid and their absorbance could be measured in wavelengths using the spectrophotometer. Absorbance data is then used to estimate TN in mg/L using second derivatives.

Total Phosphorus (TP). Measurements of TP were also measured within 28 days using the Genesys 10S UV-Vis spectrophotometer. Procedures followed EPA method 365.2 (EPA 1983). The lower and upper detection limits for TP is 0.01 mg/L to 0.5 mg/L, respectively. Concentrations above the upper detection limit require dilution. Samples

Figure 19. Continuous stage gages installed at sites FR-102, SS2, and RD

were digested with persulfate to convert all forms of P to orthophosphate. The orthophosphate was then analyzed based on the reaction with the reagent. Several laboratory duplicates and blanks were prepared for quality control.

Computer Methods

Geographic Information System (GIS). Study area and sample site maps were made in ArcMap version 10.5. Watersheds were delineated using flow direction and flow accumulation maps developed from a Digital Elevation Model (DEM) as well as pour points. The sampling location at the VWMR (RD) was used as the pour point for the VWMW delineation. The sampling location at the South Dry Sac River USGS gage (SDS-USGS) was used as the pour point for the Headwaters South Dry Sac Watershed. Sample site point features were created using a combination of GPS data and aerial imagery. DEMs, roads, county boundaries, SSURGO soil data, hydrological networks and spring data were acquired from the Missouri Spatial Data Information Service (MSDIS) website from the University of Missouri at www.msdis.missouri.edu. Data for land cover maps was acquired from the National Land Cover Data Base (Homer et al. 2015). Soil data was acquired using the USDA Web Soil Survey (Soil Survey Staff 2018).

Estimated Discharge. Stream discharge was estimated using Manning's equation. Manning's Equation is a function of velocity and area and can be calculated using the following formula:

$$Q = VA = \frac{1}{n} A R^{2/3} S^{1/2},$$

where Q is discharge (m^3/s), V is velocity (m/s), A is channel flow area (m^2/s) R is hydraulic radius (m), S is water surface slope (m/m) and n is Manning's roughness coefficient (Ward et al. 2016). Manning's roughness coefficient was chosen based on channel bed material, channel bank material, and stage. Cross-sectional data was entered into Intelisolve Hydraflow Express 2006 software to obtain channel flow area and hydraulic radius variables. The variables were then used in Manning's Equation to estimate discharge.

Rating Curves. Rating curves were made using cross section, stage, and weir data (Appendix A). Manning's discharge and stage values were derived from Hydraflow Express. Traditional rating curves use measured stage and discharge and require many stream gage readings at various water levels. Manning's equation uses hydraulic radius and water surface slope which can account for varying hydrologic conditions. So, using a rating curve based on Manning's estimated discharge is more accurate (Leonard et al. 2000). In Excel, Manning's roughness coefficients and slopes were adjusted to better fit field measured discharge and stage. Then, equations derived from these rating curves were used to calculate discharge. Relative percent differences were calculated to compare estimated discharge with field measured discharge by using the equation: (Measured Q – Estimated Q)/Measured Q * 100 (Appendix B).

The rating curve for the FR-102 tributary required significantly different Manning's roughness coefficients for various stage to account for sediment and debris buildup within two out of three cells of the boxed culverts. For low stage, a value of 0.013 was used for cement in the main cell of the culvert. A value of 0.800 was used for stage at which water would fill the other cells. The rating curve for Sanders Spring was

broken up into three segments to provide better accuracy for significant changes in stage during April. The Manning's roughness coefficients used for Sanders Spring ranged from 0.03 for low stage to 0.10 for floodplain stage. The rating curve for the VWMR was created by using HEC-1 modeled discharge values from a hydrology report done by Wilson Hydro and provided by OEWRI. Discharge values were given for various water surface elevations at the dam. Elevation was corrected for the height of the bottom of the stage gage installed at the dam to the top of the weir. Stage was also corrected by adding the difference between the maximum stage observed and the stage recorded by the levelogger (on that observed day). This helped in getting an accurate rating curve when compared with field measurements. Using the power functions from the adjusted rating curves, discharge was estimated for various stage that was collected for each gage.

Baseflow Separation. Using the estimated discharge from the rating curves and the USGS gage discharge, baseflow was separated from stormflow at each gage to understand the sensitivity of the watershed to precipitation events (Appendix C). Discharge was averaged from 15-minute to daily increments to use with the USGS Groundwater Toolbox which can be found at https://water.usgs.gov/ogw/gwtoolbox. The USGS Groundwater Toolbox has several research-supported baseflow separation methods to choose from (Barlow et al. 2014; Barlow et al. 2017). The Eckhardt filter is a two-parameter filter method useful for separating continuous baseflow (more than one event). The USGS Groundwater toolbox calculates the necessary parameters for you based on regression equations created by Eckhardt. The automatic baseflow separation methods have limitations when using daily discharge data, but they are suitable for general analysis (Partington et al. 2012).

Water Budgets. Monthly water budgets were calculated for the sample period. Modified from Skrobialowski and Focazio (1997), a simple water budget can be calculated using the following equation:

$$Input - Output = \Delta Storage,$$

where input is equal to discharge to the reservoir, output is reservoir outflow, evaporation and leakages, and Δstorage is equal to estimated change of storage in the reservoir. Any precipitation can be ignored because discharge is measured during baseflow.

Evaporation rates for the VWMR can be reasonably estimated using the following equation:

$$PET = \left[0.55\left(\frac{D}{12}\right)^2\left(\frac{SVD}{100}\right)\right]2.54,$$

where PET is potential evapotranspiration in cm/day, D is hours of daylight, and SVD is saturated vapor density at mean air temperature in g/m^3 (Hamon 1961; Winter et al. 1995). Hours of daylight were acquired from the United States Naval Observatory (USNO 2018). SVD values were acquired from Hamon (1961). Monthly average evaporation rates were estimated by multiplying the number of days in each month by the average daily evaporation rates. Evaporation volume was estimated by converting the evaporation rate to meters and multiplying it by the surface area of the reservoir.

Leakages from the VWMR were estimated by measuring discharge at Grandview Tributary and Shotgun Spring when there was no water flowing over the dam. For sample days when discharge was not measured at these locations, an average was taken for both leakage sites. Units of discharge were converted from m^3 to meters by dividing by drainage area to obtain volumes.

Nutrient and Sediment Budgets. Nutrient loads must be calculated before a nutrient budget can be made. Nutrient loads were calculated by multiplying discharge (ft^3/s) by nutrient concentration (mg/L) and a conversion unit. The conversion unit of 2.45 converts feet to meters and seconds to days to obtain daily loads in kg/day (MDEQ 2008). Nutrient loads at SDS2 may be equal to the sum of loads at RD and SDS1 due to estimation of discharge at SDS1. Discharge at SDS1 was estimated for each sample day by taking the difference of discharge at SDS2 and the discharge at RD if water was flowing over the dam. When there was no flow over the dam, loads were given a value of 0 kg/day. TSS loads were estimated for measurements below detection limit by multiplying discharge by detection limit (0.5 mg/L) and the conversion unit of 2.45.

Nutrient budgets can be calculated by a simple mass balance equation very similar to a water balance. For lakes and reservoirs, nutrient budgets include known inflows to lakes and known outflows (Frink 1967). For the VWMR, spring flow will be the input and reservoir outflow will be the output. If the reservoir is not flowing over the dam, the nutrient load for the reservoir is simply zero, and it can be assumed that most of the nutrients coming into the lake are either being stored in lake sediments or leaving the system through leakage, atmospheric deposition or metabolized by bacteria or plants. A positive balance in the nutrient budget will indicate that more nutrients were going into the reservoir than was being exported. In other words, the reservoir may be acting as a sink for nutrients. A negative balance indicates that more nutrients were leaving the reservoir than it was receiving. In this case, the reservoir may be acting as a source of nutrient.

CHAPTER 4 – RESULTS

Weather and Climate

During the study period from March 1, 2017 to March 1, 2018, Springfield had a wetter spring and drier fall compared to the past 30 years (Figure 20). The average total annual precipitation in the past was 1,157 mm (Arguez et al. 2010). The total annual precipitation in Springfield was 1,337 mm based on daily summary data from the USW00013995 NOAA station. Precipitation was greatest in spring and summer months.

Monthly precipitation peaked at 306 mm in April and dropped to low of 9 mm in November. Compared to the past 30-year climatic normals, Springfield received significantly more precipitation in spring months and significantly less precipitation in

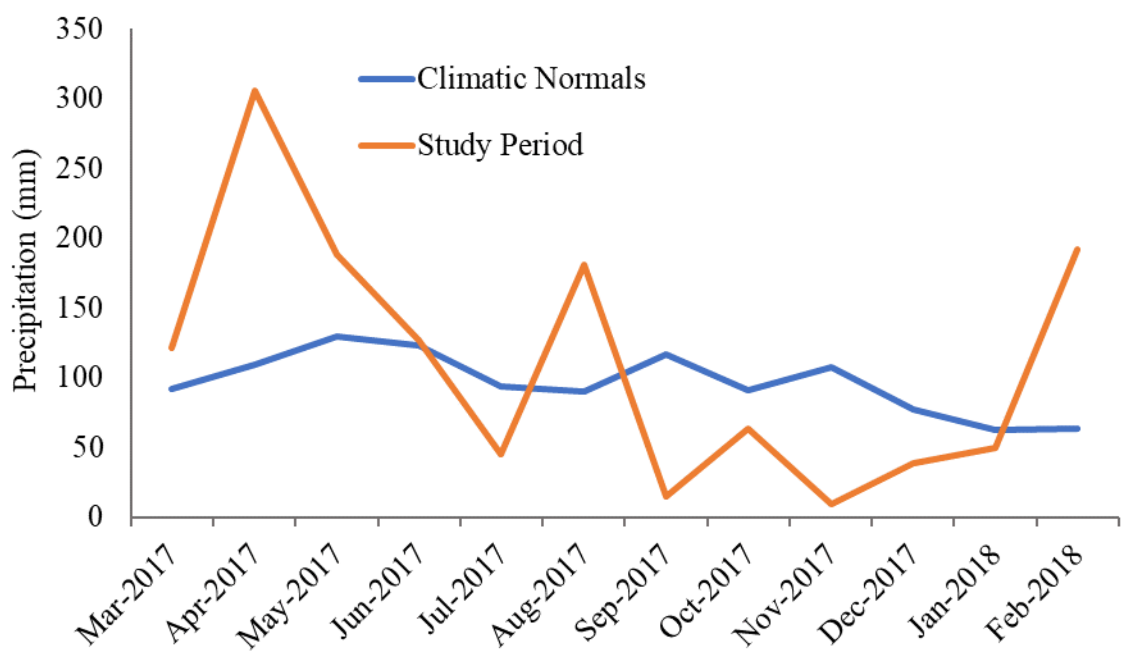


Figure 20. Past and present monthly precipitation

fall and winter months. Significantly less snowfall occurred than in the past. Compared to the annual snowfall average of 432 mm, a total of 5 mm of snow fell during the study period with 5 days of snowfall recorded: 0.1 mm on March 14, 2017; 1.8 mm on December 23, 2017; 0.5 mm on January 14, 2018; 2.2 mm on January 15, 2018; and 0.9 mm on February 4, 2018.

During the study period, temperatures were slightly warmer in spring, fall, and winter months than in past years (Figure 21). Average temperatures were only slightly cooler during August. The average temperature in August for the past 30 years was 25.4°C and during the study period the average temperature was 22.8°C (Arguez et al. 2010). Overall, temperatures during the study period were around 0.9°C warmer than past averages.

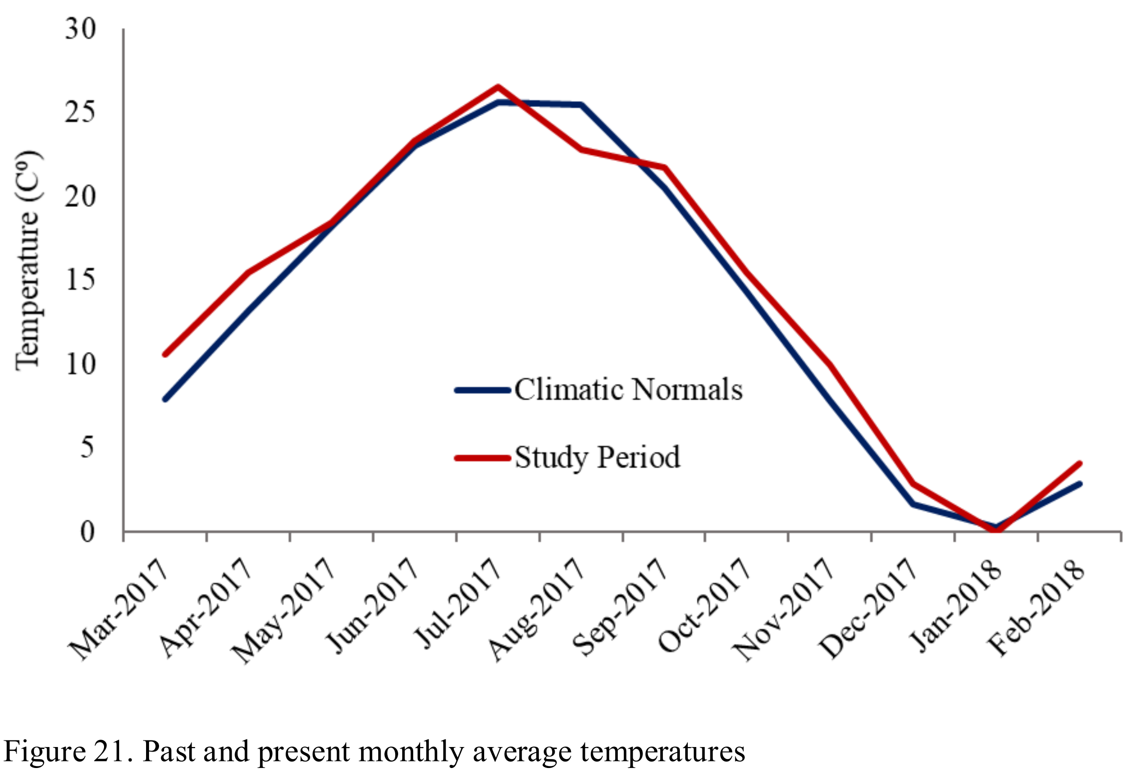


Figure 21. Past and present monthly average temperatures

Hydrology

Estimated Flow. Only one sample and discharge measurement for site FR102 was taken in April during the sample period. This tributary was dry during sample events for the remainder of the study period and was not very sensitive to precipitation events (Fig 22 and 23). Events with less than 40 mm of rain seemed to have little effect on baseflow. No flow occurred at the tributary for most of June through mid-February. Stormflow (total flow) was highest at 0.40 m^3/s in late April of 2017 and had an average of 0.006 m^3/s

Figure 22. Tributary (FR102) main channel

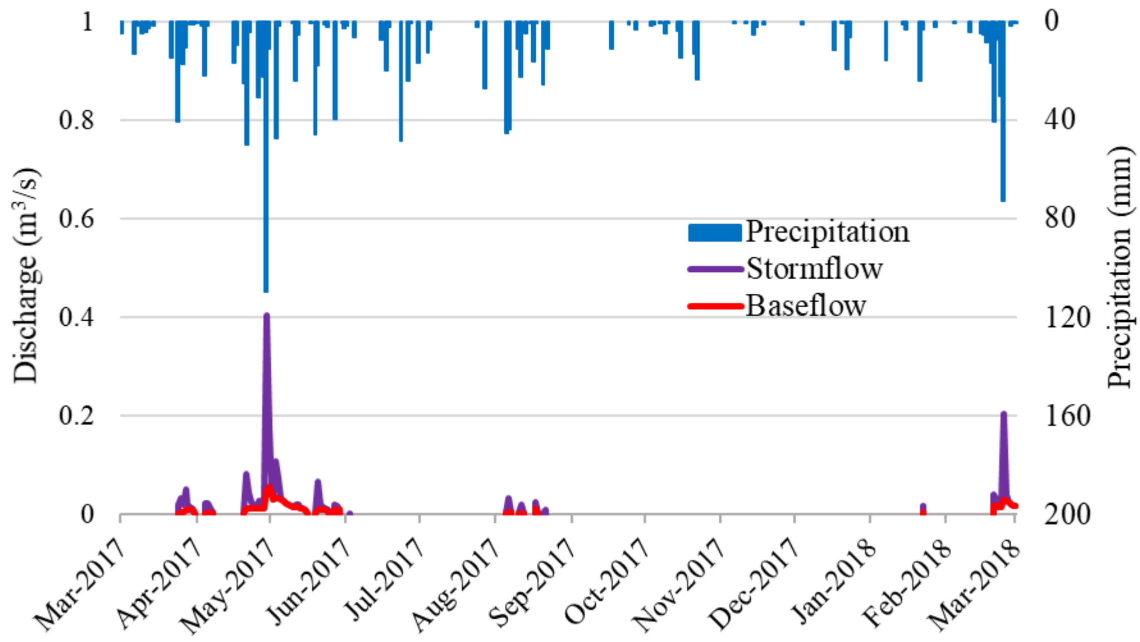


Figure 23. Hydrograph for FR102

during the study period. Baseflow was highest at 0.06 m^3/s in late April of 2017 and had an average of 0.003 m^3/s during the study period.

Sanders Spring flowed the entire year with a minimum total flow of 0.008 m^3/s in January. Total flow reached a maximum of 4.42 m^3/s in late April and had an average of 0.31 m^3/s during the study period. Baseflow reached 1.06 m^3/s and had an average of 0.21 m^3/s during the study period. Total flow at Sanders Spring was relatively more sensitive to precipitation events, although baseflow was very low from September through February and made up a significant portion of total flow (Figure 24). Rain events with less than 30 mm had little effect on baseflow unless there were several consecutive days with rain.

Flow over the dam occurred very infrequently during baseflow conditions (Figure 25). Daily baseflow at the reservoir reached a max of 0.89 m^3/s and had an average of

0.12 m^3/s. Rain events less than 40 mm had little influence on dam overflow unless there was sustained precipitation. The VWMR only flows over the dam when stage reaches 0.74 m. This was the stage determined after correcting for the height from the bottom of the levelogger (dam gage) with the elevation at the top of the weir. This is consistent with observations made in the field (Appendix D). Stage recorded as 0.00 was due to dry conditions near the dam or ice. Total flow was more responsive than the spring during large rain events. Maximum total flow was 6.66 m^3/s and had an average of 0.31 m^3/s.

The South Dry Sac River had a similar hydrograph to the other sites (Figure 26). Precipitation events with less than 40 mm of rainfall appeared to have little effect on discharge. However, total flow at SDS2 was up to 5 times higher than other sites

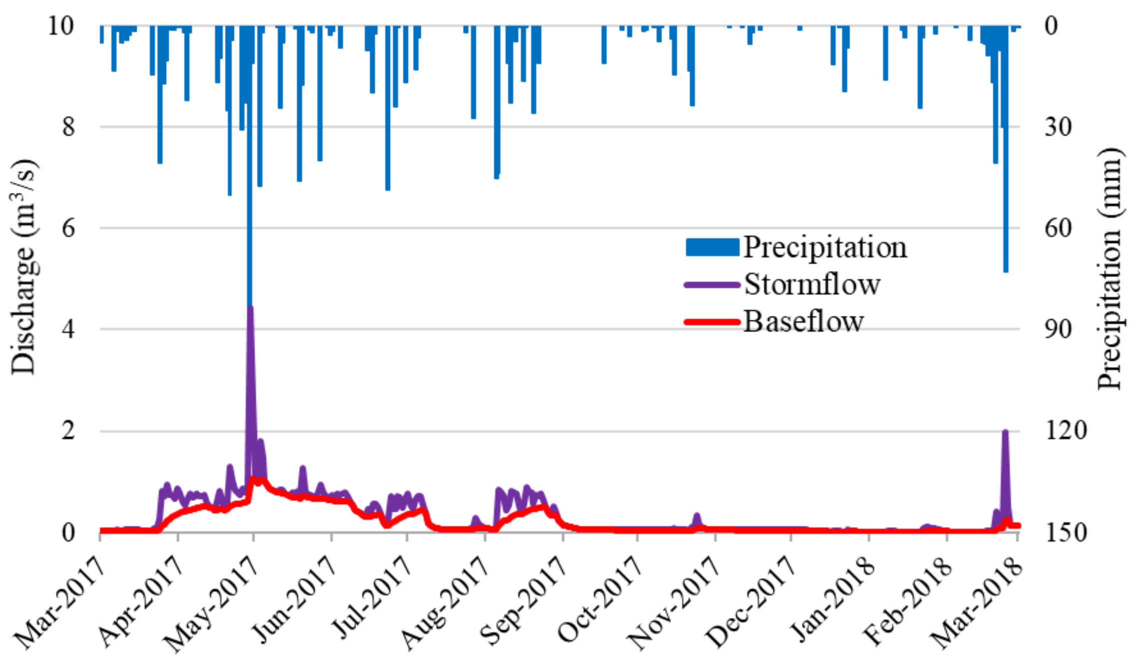


Figure 24. Hydrograph for SS2

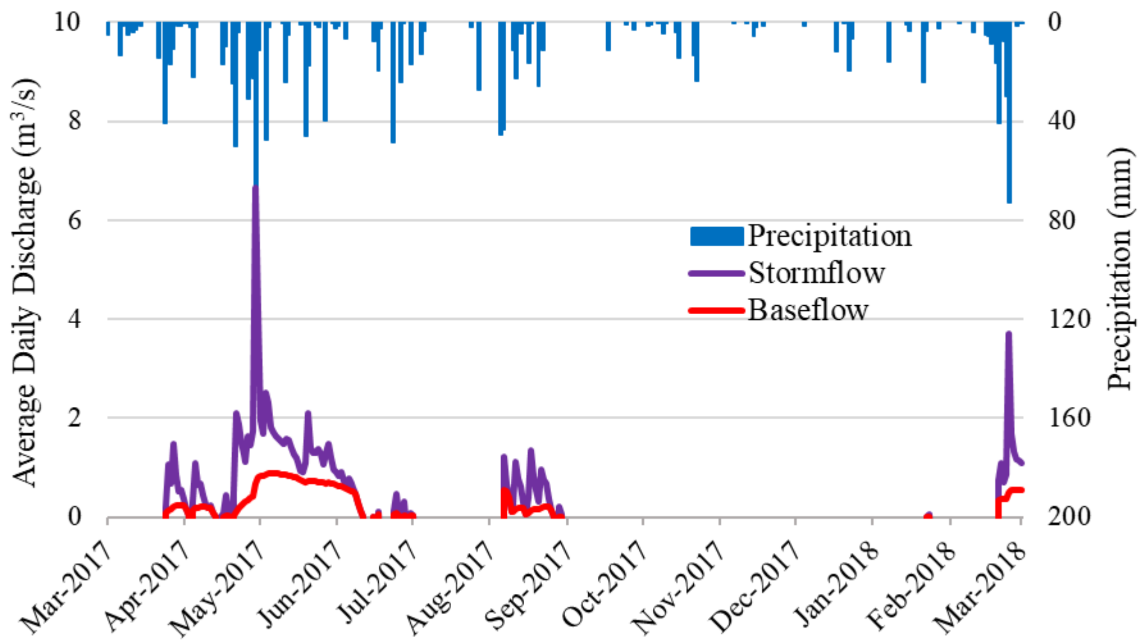


Figure 25. Hydrograph for RD

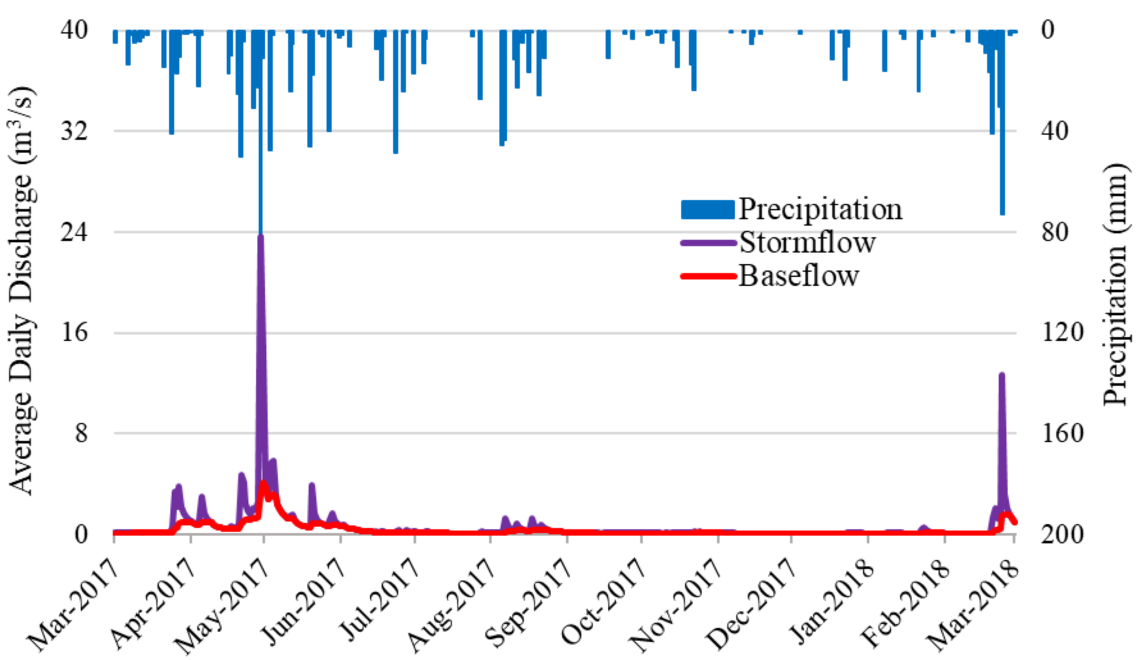


Figure 26. Hydrograph for SDS2

during larger rain events. Total flow reached a maximum daily average of 23.67 m^3/s and had an average of 0.63 m^3/s. Baseflow sustained flow in the river during much of the study period. Baseflow reached a maximum daily average of 4.12 m^3/s and had an average baseflow of 0.35 m^3/s which was close to the average at Sanders Spring.

The gages at FR-102, SS2, RD, and SDS2 each appeared to have very similar response times to storm events (Figure 27). Discharge at FR-102 was multiplied by 40 and discharge at SS2 and RD was multiplied by 5 to show scale. Peak discharge at each site had a short lag time of 13-14 hours after storm events (Appendix E). FR-102 and SS2 responded very similarly. Additionally, RD and SDS2 also responded very similarly.

Measured Discharge. Discharge was measured in the field to adjust and evaluate rating curves. Calculated discharge values were relatively close to measured discharge

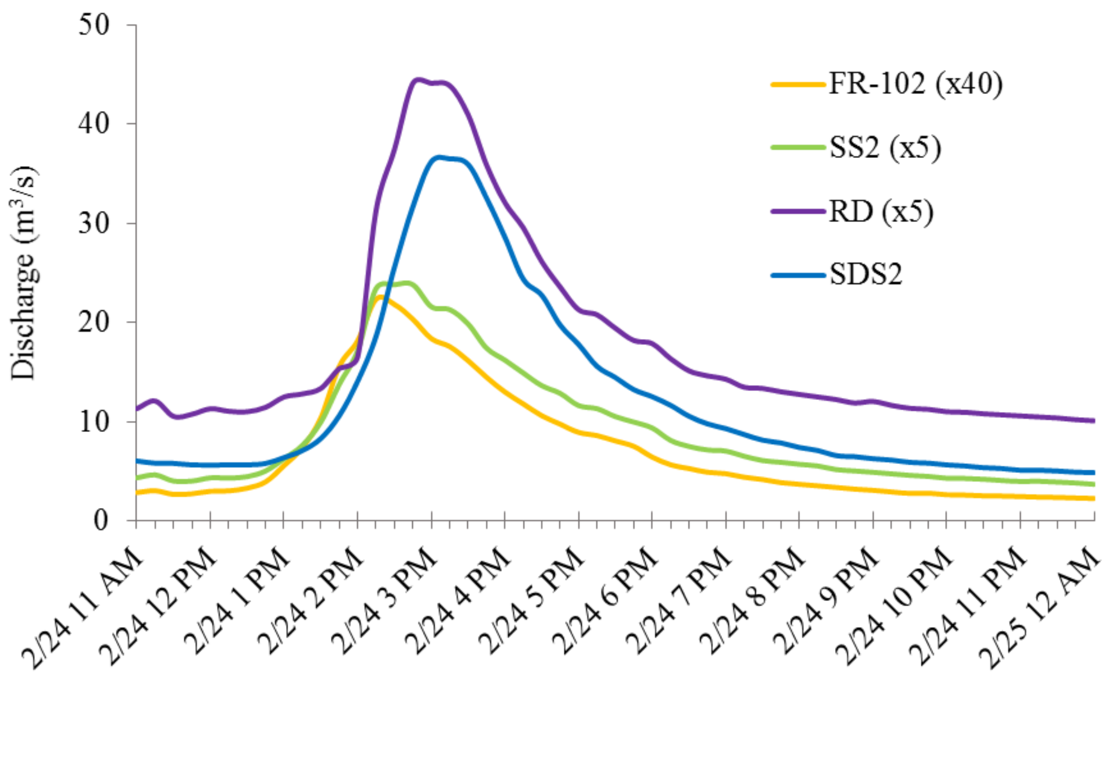


Figure 27. Storm event response for FR-102, SS2, RD, and SDS2; Discharge was amplified for scale

values across most sites. The rating curve for SS2 (spring gage) had a large percent difference for stage less than 0.26 m. The field measured discharge for FR102 was 0.008 m^3/s with a stage of 0.29 m on April 7, 2017. Estimated discharge using the rating curve is 0.009 m^3/s. The percent difference is 11%. It is important to note that the rating curve for the reservoir gage gives negative values for flows below 0.7 m of stage which were converted to 0.00 m^3/s. Measured discharge on October 27, 2017 was for leakage from the reservoir and was a rough estimation, because flow was too low to measure with the flow meter. Average discharge for L1 (Shotgun Spring) was 0.004 m^3/s and 0.0121 m^3/s for L2 (Grandview Tributary) making a total average of 0.03 m^3/s for leakages (Appendix F). These leakages may contribute some of these nutrients downstream from the dam. Additionally, discharge measured at SDS0 and SDS3 in December showed little difference which may reflect temporal variability in leakages from the reservoir.

Baseflow Contributions. Baseflow contributions at SS2 were high for much of the study period except during months with significant storm events (Table 5). Conversely, baseflow contributions at SS2 were lowest in February and March at 36% and 40% of stormflow, respectively. Baseflow contributions at FR-102 remained low when the tributary was flowing. Baseflow contributions to stormflow were slightly higher at RD in May and June but remained low during most of the sample period.

Reservoir Losses. Loss from the reservoir was estimated by taking the difference between inflows and total outflows from the VWMW (Table 6). A negative value indicates a potential net loss from the reservoir; outflow is greater than inflow. A positive value indicates that there is a potential net gain at the reservoir; inflow is greater than

Table 5. Baseflow contributions to total flow

Month	SS2		FR102		RD + Leakage	
	Total (m^3/s)	Baseflow %	Total (m^3/s)	Baseflow %	Total (m^3/s)	Baseflow %
Mar-17	0.24	40	0.01	34	0.24	26
Apr-17	0.92	60	0.60	1	0.99	19
May-17	0.87	87	0.28	4	1.48	53
Jun-17	0.53	72	0.00	No flow	0.27	64
Jul-17	0.20	72	0.00	No flow	0.03	4
Aug-17	0.52	60	0.00	25	0.42	31
Sep-17	0.06	93	0.00	No flow	0.03	0
Oct-17	0.07	70	0.00	No flow	0.03	0
Nov-17	0.05	86	0.00	No flow	0.03	0
Dec-17	0.03	81	0.00	No flow	0.03	0
Jan-18	0.03	54	0.00	33	0.03	1
Feb-18	0.16	36	0.02	47	0.47	31

Table 6. Monthly average water budget during baseflow

Month	Inflow (m^3/s)	Outflow (m^3/s)				Net Gain/Loss (m^3/s)
	SS2	RD	Leakage	ET	Total	
Mar-17	0.084	0.063	0.030	0.010	0.103	-0.020
Apr-17	0.525	0.185	0.030	0.016	0.231	+0.295
May-17	0.770	0.777	0.030	0.022	0.828	-0.058
Jun-17	0.390	0.172	0.030	0.030	0.231	+0.158
Jul-17	0.155	0.001	0.030	0.035	0.066	+0.089
Aug-17	0.306	0.130	0.030	0.025	0.185	+0.120
Sep-17	0.061	0.000	0.030	0.020	0.050	+0.011
Oct-17	0.049	0.000	0.030	0.012	0.042	+0.007
Nov-17	0.045	0.000	0.030	0.007	0.037	+0.009
Dec-17	0.029	0.000	0.030	0.004	0.034	-0.005
Jan-18	0.018	0.000	0.030	0.004	0.034	-0.016
Feb-18	0.052	0.147	0.030	0.006	0.182	-0.130

outflow. Some of this value may be error, so caution in interpretation is necessary. A net loss may be due to evaporation or reservoir leakage and a net gain may be due to rainfall or groundwater seepage. There was a net loss during March, May, and December of 2017 as well as in January and February of 2018. During the rest of the study period, the reservoir experienced a net gain. Spring flow contribution was greatest during April and May. Differences between inflows and outflows were greatest during most months with higher spring inflow (Figure 28).

The South Dry Sac River below the reservoir has a large baseflow contribution during summer and fall months with a maximum of 95% baseflow in November (Table 7). Baseflow contributes the lowest amount of stormflow in late winter and spring months with a minimum of 38% in February. Potential baseflow contributions of SS2 flow to total flow at SDS2 are highest in June and July which is likely overestimated due to evaporation losses at the reservoir. On average, baseflow contributions from SS2 were 46% of total flow at SDS2.

Water Quality

Triplicate sampling runs were completed on June 9, 2017 and July 13, 2017 to determine whether there was significant variation in water quality during daylight hours of sample days (Appendix G). Coefficient of variation (CV) results showed little daytime variation, so single sampling continued. In January, water at the reservoir was frozen, so measurements were not taken. The CVs for all water quality parameters except TSS were less than 30%. Most samples had CVs less than 10%. However, TSS showed very high CVs for all sites which is likely due to very small concentrations measured during much

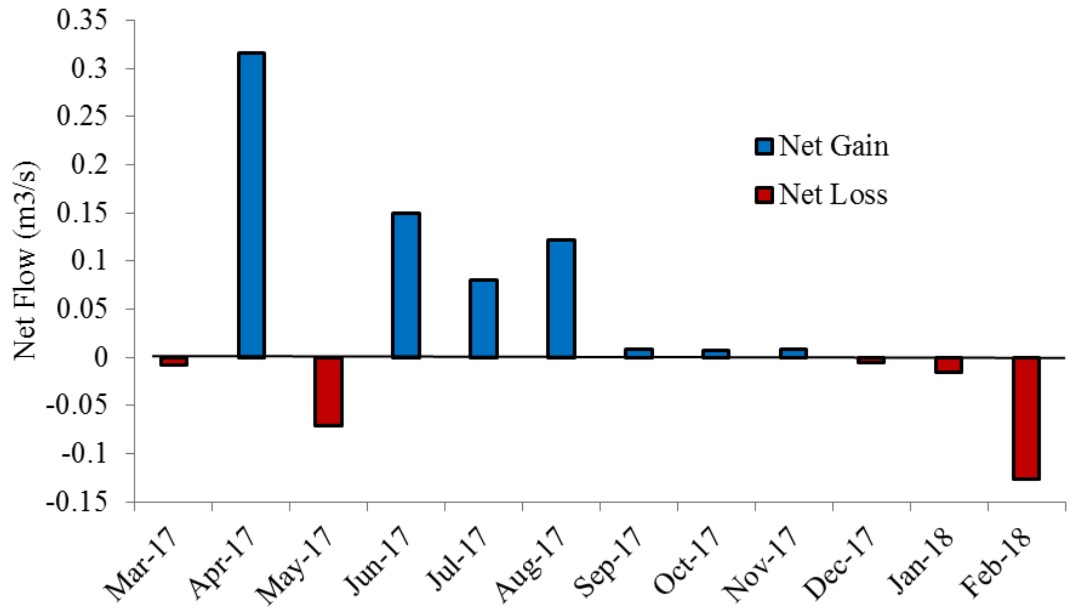


Figure 28. Monthly average net flow during baseflow

Table 7. Discharge at SDS2

Month	SDS2		SS2 Baseflow Contributions (%)
	Total (m^3/s)	Baseflow %	
Mar-17	0.70	46	12
Apr-17	2.70	40	20
May-17	1.64	78	44
Jun-17	0.31	89	119
Jul-17	0.14	84	106
Aug-17	0.45	61	67
Sep-17	0.13	91	47
Oct-17	0.15	75	33
Nov-17	0.09	95	50
Dec-17	0.08	69	35
Jan-18	0.14	66	13
Feb-18	1.04	36	5

of the sample period. Therefore, samples collected for this study were considered representative for the days of collection. General water quality chemistry including temperature, DO, pH, SC, and Cl can be found in Appendix H. Field measured discharge, TN, TSS, and TP concentrations as well as calculated loads for TN, TSS, and TP can be found in Appendix I.

Temperature. Temperatures at Sanders Spring showed little seasonal variation (Figure 29). Temperatures ranged from 14.2°C to 16.2°C and had a CV of 5% at SS1. Compared to Sanders Spring, the VWMR showed the more seasonal variation with values ranging from 5.5°C to 27.4°C and a CV of 50%. This reflects much more influence of air temperatures on water temperatures. The South Dry Sac River also appeared to have more seasonal variation with a CV of 40%. The clear difference between the water temperatures in the reservoir and river compared to the water from the spring indicate that temperatures may reflect the influence of both air temperatures and subsurface structure.

DO, pH, SC, and CL. Across all sites, DO concentrations appeared to increase from fall to winter sample dates (Figure 30). When water temperatures were low, DO concentrations were high and when water temperatures where high, DO concentrations were low. This pattern is typical and reflects the expected inverse relationship between water temperature and DO. Increased air temperature increases microbial activity which results in lower DO (Sanchez et al. 2006). Concentrations of DO were the most variable at RD with a CV of 33% and the least variable near SS1 with a CV of 8% which reflects the lack of influence of air temperature on water flowing out of the spring.

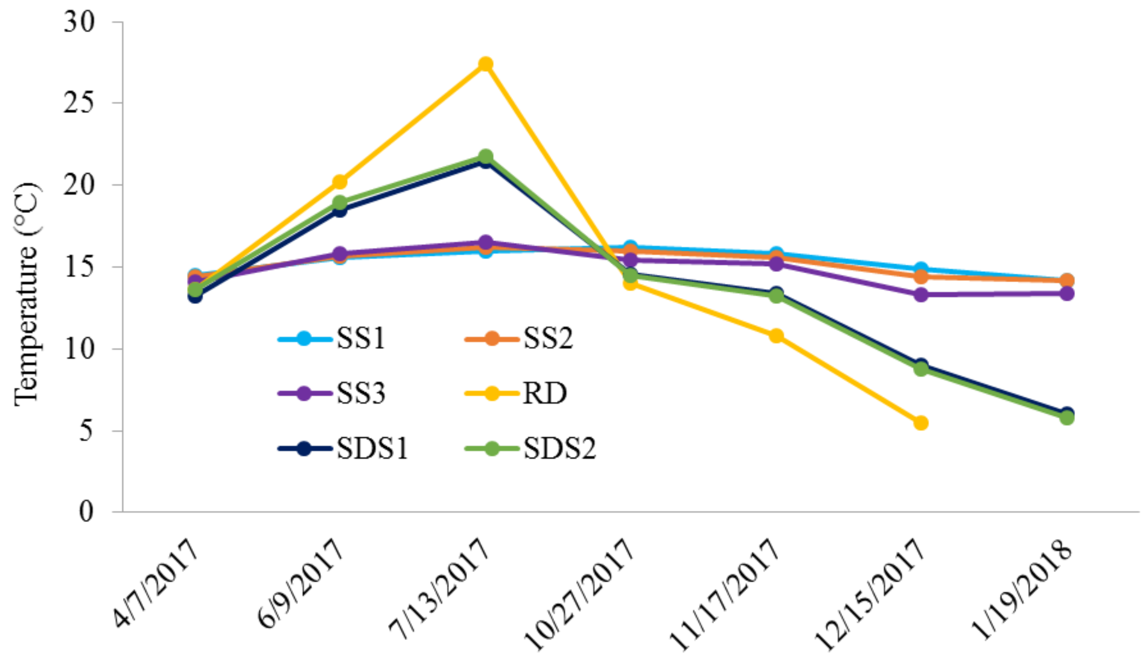


Figure 29. Temporal variation of water temperature

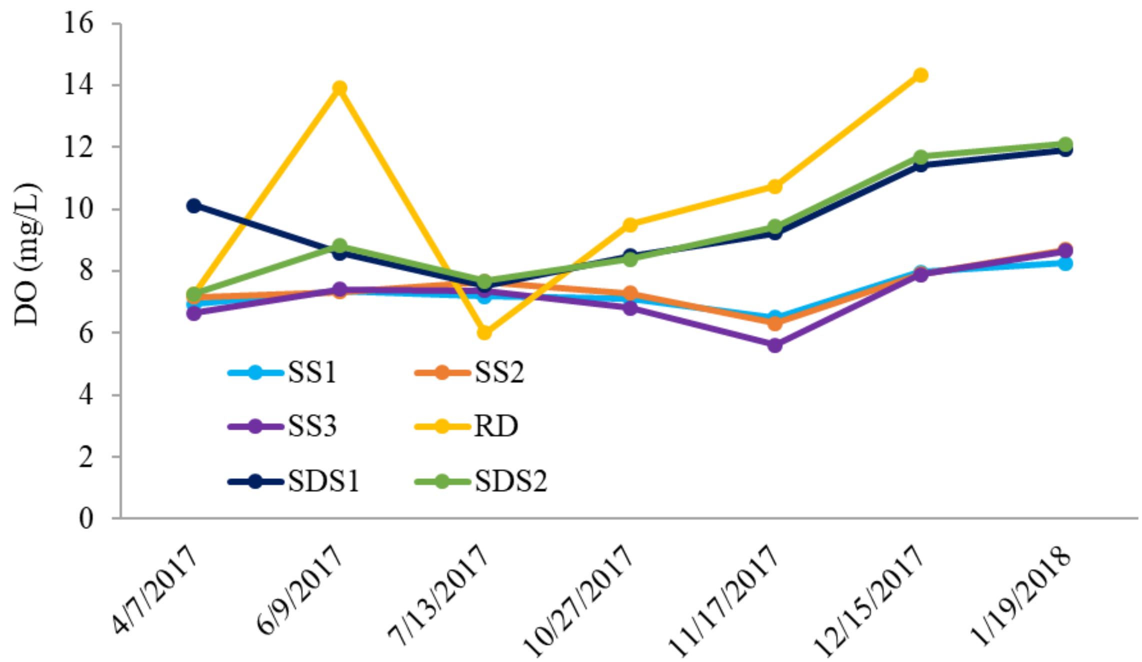


Figure 30. Temporal variation of DO concentrations

There was little seasonal variation of pH at each sample site (Figure 31). The pH of surface water can indicate alkalinity which has implications for residence time in the subsurface, particularly in karst regions. Neutral values of pH suggest slightly acidic rainwater has had time to equilibrate with calcium carbonate (Shuster and White, 1971). Values of CVs ranged from 1.1 to 3.7% across all sites. This indicates that water remained neutral in the study area. Values of pH at SS1 were lower in April which likely reflects that water moves more quickly through the subsurface during periods of higher rainfall.

During the study period, values of SC showed relatively little seasonal variation at Sanders Spring (Figure 32). Values of SC at SS1 are generally around 100 uS/cm higher than at SDS2, which is expected. Specific Conductivity has been shown to reflect

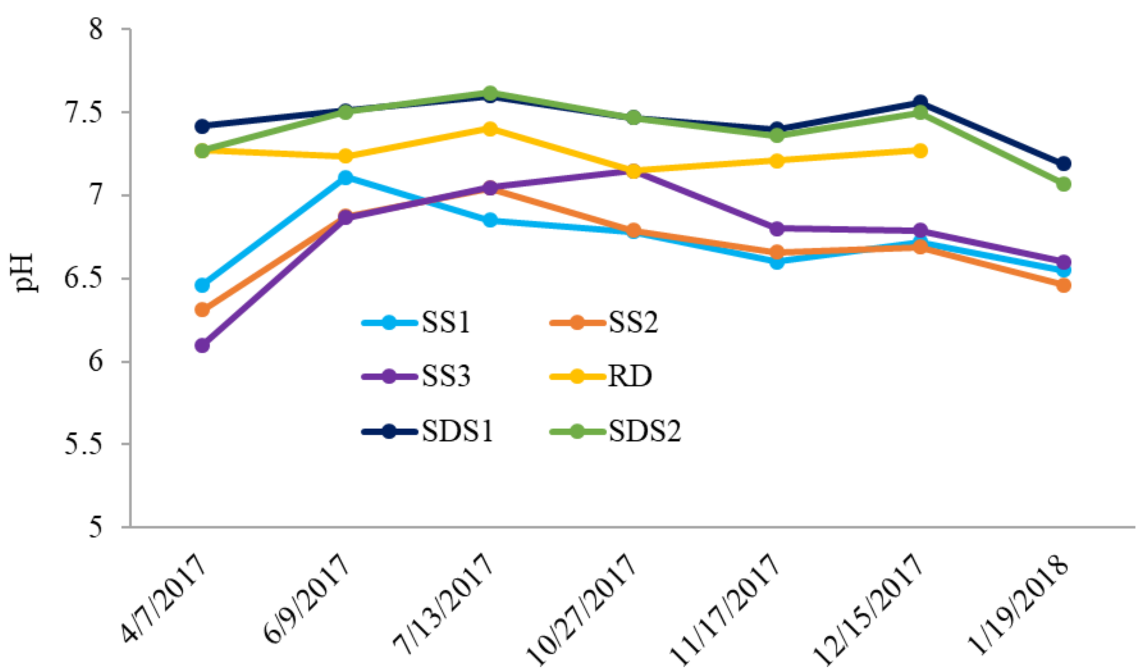


Figure 31. Temporal variation of pH levels

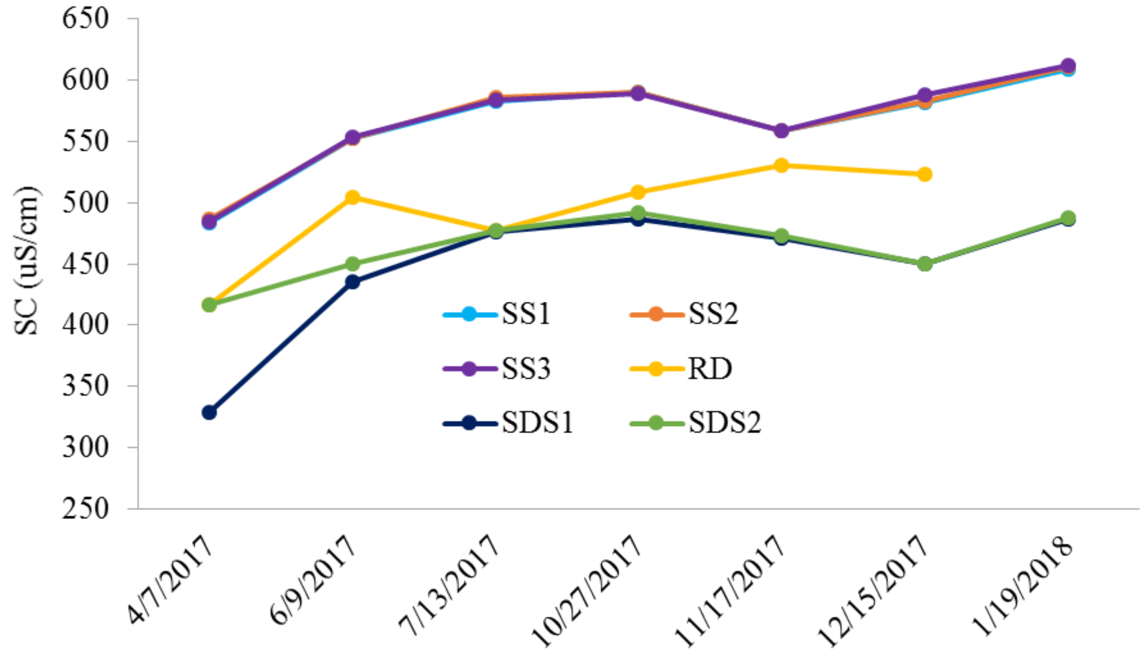


Figure 32. Temporal variation of SC concentrations

hardness and values of SC are typically higher in groundwater than in surface water (Shuster and White 1971). The SC at SS1 showed little variation during the study period with a CV of 7%. The SC at SDS2 was only slightly higher at 12.5%.

Chloride showed some temporal variation, with values being highest during April and January sample dates (Figure 33). Chloride sources include agricultural chemicals, sewage, and road salts used for de-icing (Panno et al. 2006). Chloride values peaked at 63.7 mg/L at RD in April and 65.5 mg/L at SS3 in January. Chloride was never below 20 mg/L during the sample period, and CVs only ranged from 14.4% at SS2 to 23.3% at RD, suggesting little seasonal variation. Chloride concentrations were highest at SS1, SS2, and SS3 for much of the study period, which may explain higher SC at those sites as well.

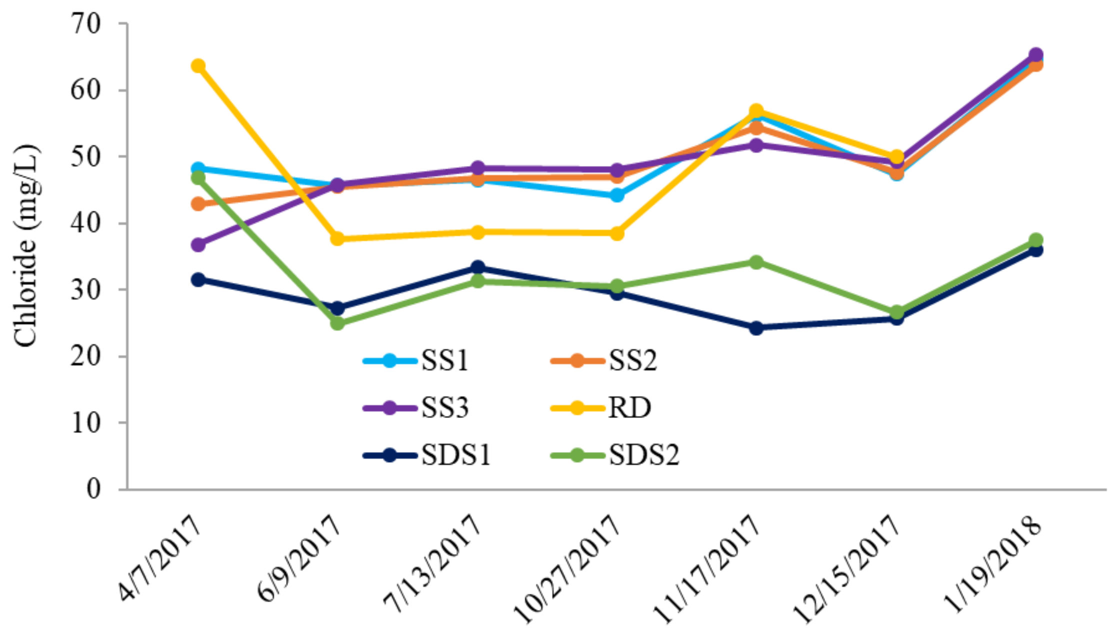


Figure 33. Temporal variation of chloride concentrations

Total Nitrogen. Total nitrogen concentrations were most variable during the study period at the reservoir and South Dry Sac River sites (Figure 34). At RD, the CV for TN was 34.0% while SDS1 and SDS2 had a CV of 32.8% and 25.7%, respectively. Concentrations of TN were lower at RD compared to SS1 during much of the sample period. Total nitrogen concentrations were lowest at RD compared to SS1 during the July sample date. Concentrations of TN increased during sample dates after July, consistent with disappearance of the summer algal bloom in the reservoir during fall and winter months.

Total nitrogen was highly variable across sites within the HW-SDSW (Figure 35). From Sanders Spring to the South Dry Sac River, TN concentrations were much less variable for most sample dates. In December, there was a steady decrease in TN concentration across the sites. For most sample dates, TN was lower at the VWMR than

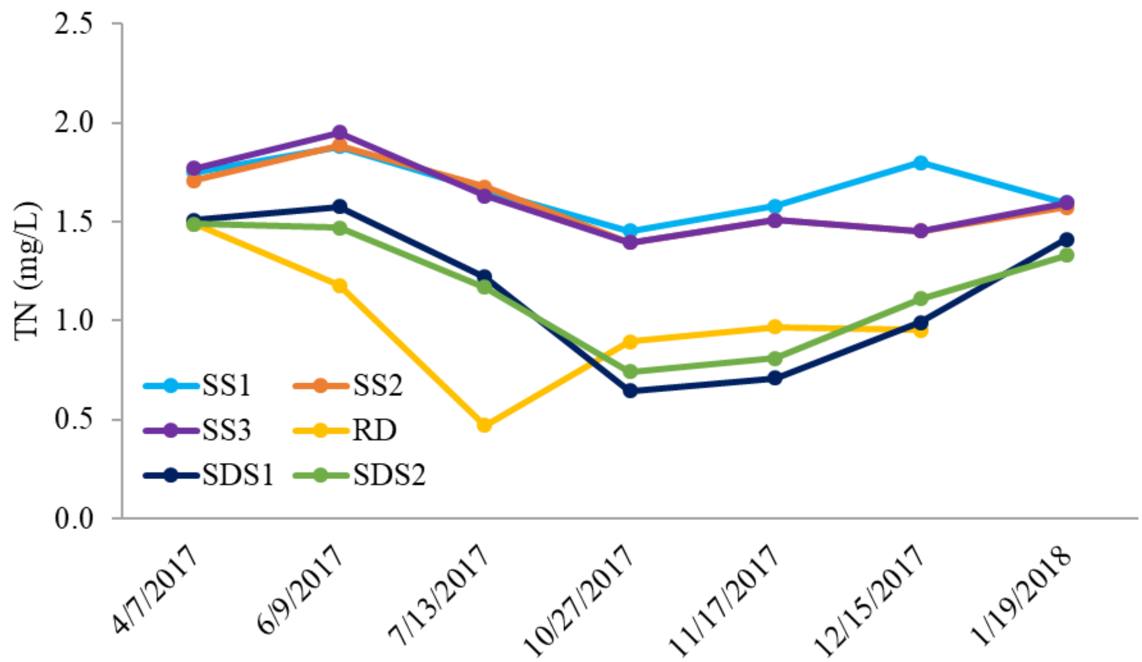


Figure 34. Temporal variation of TN concentrations

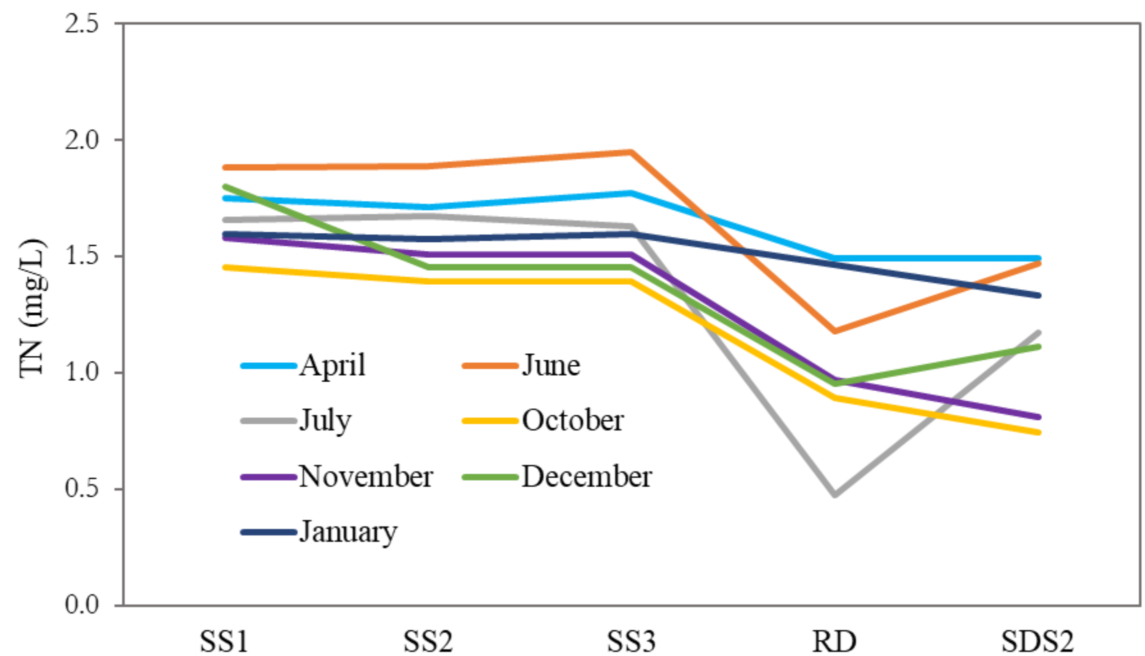


Figure 35. Spatial variation of TN concentrations

at any other site. At the sample site below the reservoir, SDS2, TN is higher in concentration than at SDS1 above the reservoir. In fall months, the South Dry Sac River is lower in TN. Across all sites, TN reaches a maximum of 2.0 mg/L, a minimum of 0.5 mg/L, and an average of 1.4 mg/L. TN is consistently highest at the spring.

Total Suspended Solids and Total Phosphorus. Concentrations of TSS were highest during the sample dates in spring and winter months (Figure 36). At most sites, TSS concentrations were highest during the April sample date. The CV of TSS concentrations were above 83% at all sites and highest at SDS2 at 224%. Much of the variation was likely due to the extremely low TSS concentrations during most of the sample dates. Concentrations of TSS were under the detection limit for most of sample dates at SDS2 except in April. This suggests that TSS concentrations may largely depend on discharge within the HW-SDSW.

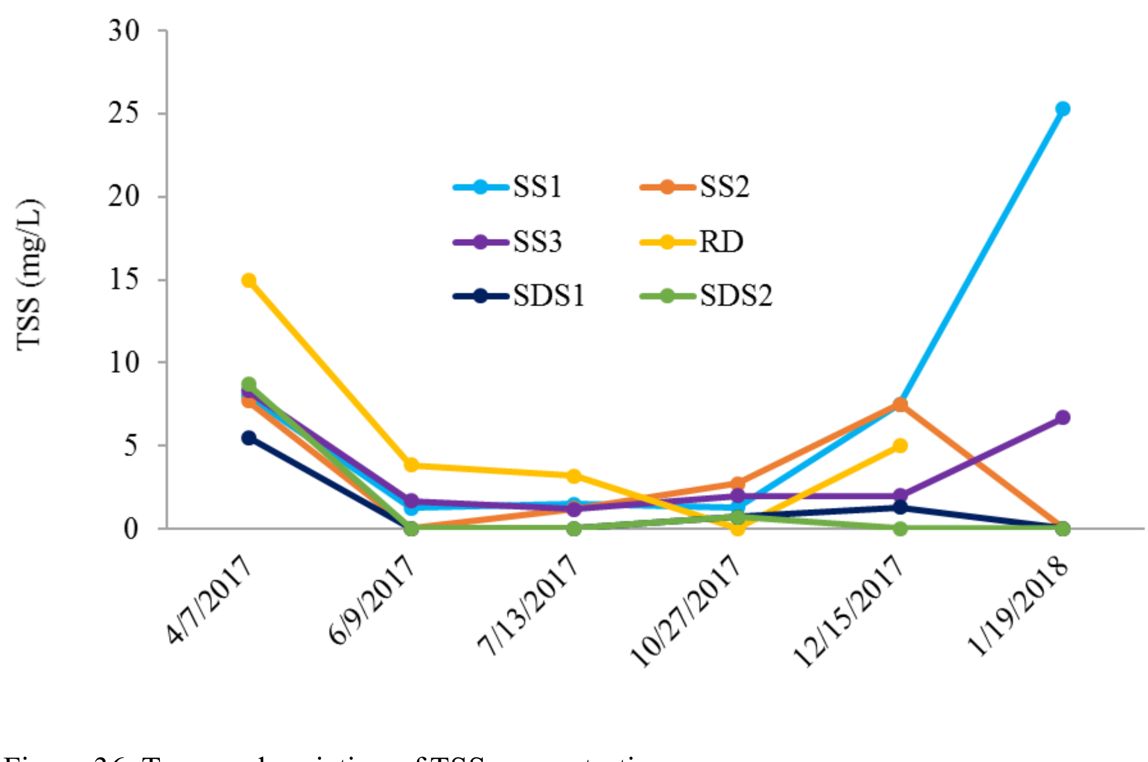


Figure 36. Temporal variation of TSS concentrations

Total phosphorus concentrations showed slightly similar seasonal variation to TSS at most sample sites (Figure 37). Total phosphorus concentrations were slightly higher during spring and winter sample dates. This likely reflects the relationship of TP with TSS and suggests that TP transport is dependent on TSS transport. Concentrations reached 105 ug/L at RD during the sample date in April but remained below 20 ug/L during the rest of the sample period.

Total phosphorus concentrations were much more variable across the study area during spring and winter sample dates (Figure 38). In winter months, TP concentrations steadily decreased from Sanders Spring to the South Dry Sac River. During the January sample date, TP peaked at the Sanders Spring gage (SS2) but remained low at sites upstream and downstream. This could be a result of human error from stirring up sediment during sampling. However, TSS concentrations likely would have also

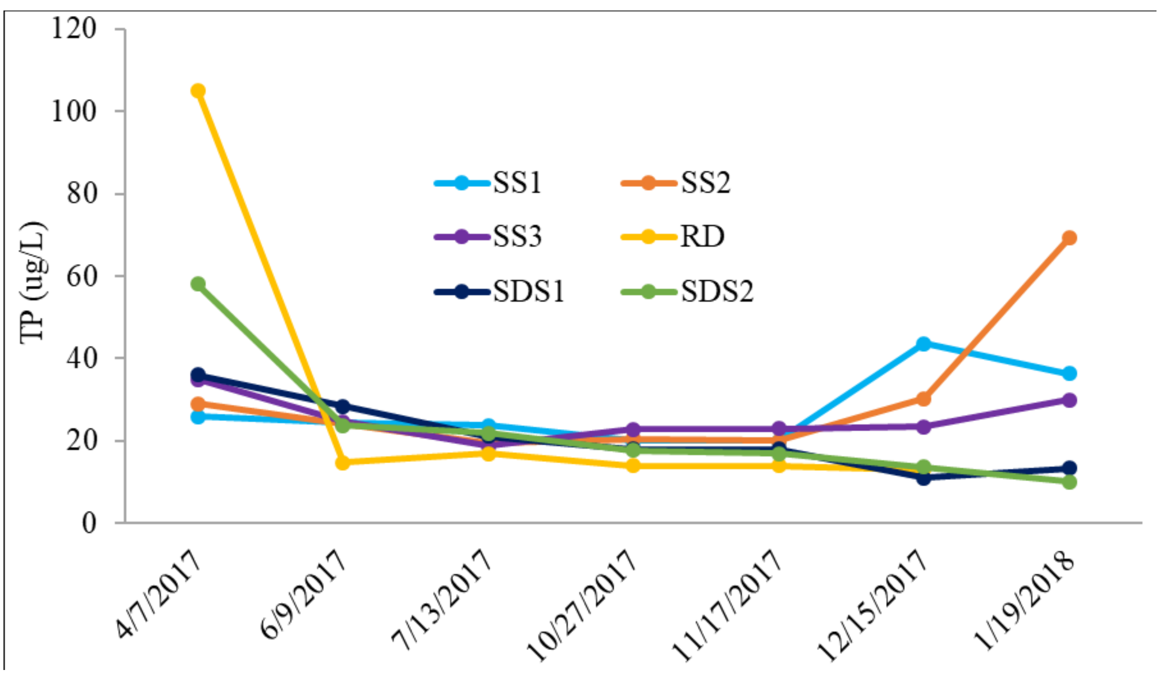


Figure 37. Temporal variation of TP concentrations

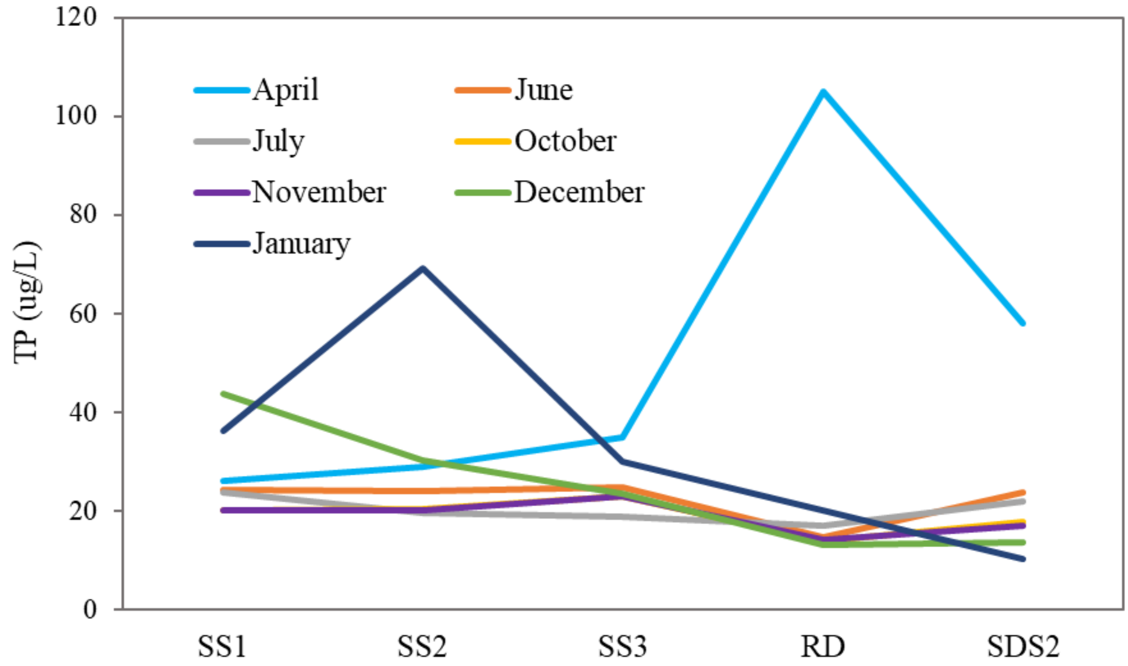


Figure 38. Spatial variation of TP concentrations

increased and this was not the case (Figure 39).

Concentrations of TSS peak significantly at Sanders Spring (SS1) during the January sample date. which could indicate a pulse of sediment that settles downstream. This could explain why TP is higher at SS2 as TP is released from the sediment and transported downstream. During April's sample date, TP also spikes at the VWMR (RD). This is consistent with TSS spiking in April as well. Phosphorus was likely being released from sediment in the VWMR as a result of spring turnover. For the rest of the sample period, the reservoir acts as a sink for P being transported downstream from Sanders Spring. From Sanders Spring to the VWMR, average concentrations of P were 30 ug/L. This decreased to an average of 20 ug/L at the South Dry Sac River sample sites.

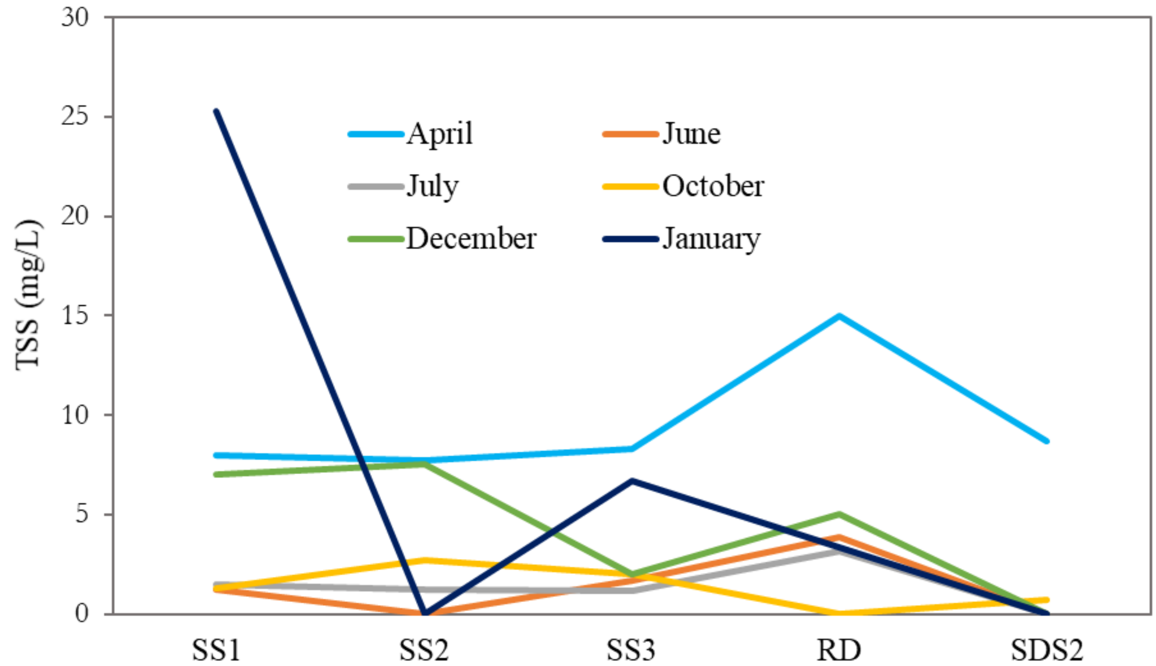


Figure 39. Spatial variation of TSS concentrations

Ratios of water quality concentrations and temperatures can indicate change between sample sites. Ratios with a value of 1 indicate no change; greater than 1 indicate higher downstream values; less than 1 indicate lower downstream values. Ratios between 1.0 and 1.2 and between 1.0 and 0.8 indicate small changes. Ratios between 1.2 and 1.4 and between 0.8 and 0.6 indicate moderate changes. Ratios outside of these ranges indicate significant change between sample sites. There were almost no significant changes between SS3 and SS1 for most water quality parameters (Figure 40). Concentrations of TSS and TP showed the largest changes.

TSS concentrations were significantly lower downstream from Sanders Spring during winter sampling dates and higher during June and October sampling dates. This variation in TSS is likely due to such low concentrations during much of the sample

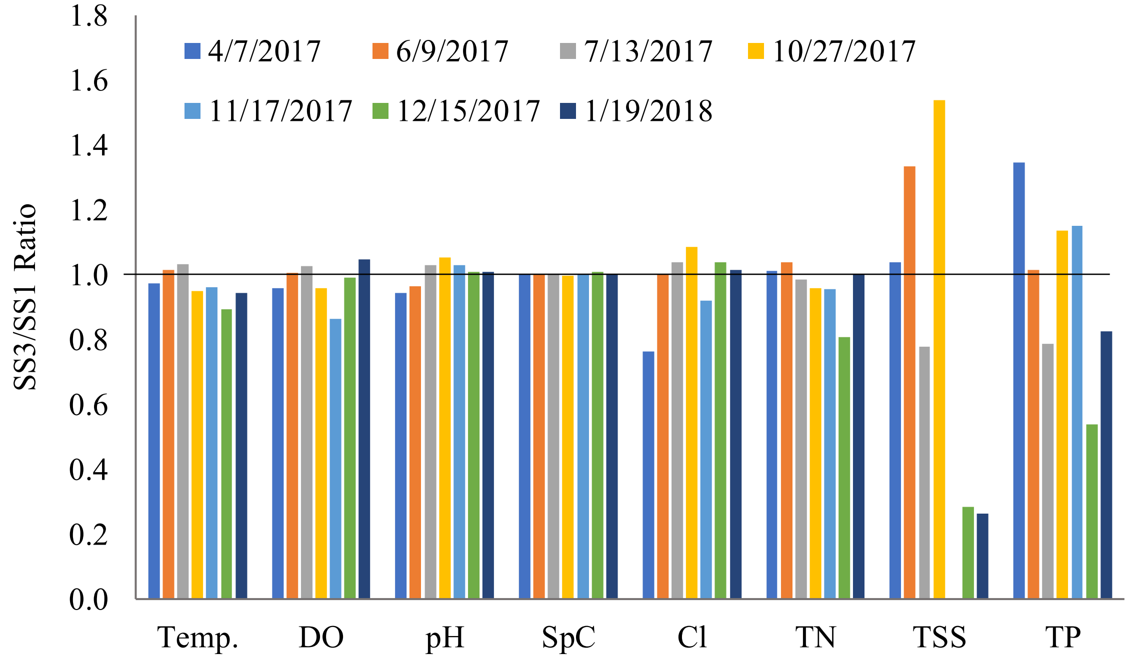


Figure 40. Ratios of water quality parameters for SS3 and SS1

period. Concentrations of TP showed moderate changes with a decrease downstream during later sampling dates.

Ratios of pH, SC, and Cl show little change between RD and SS3 during most of the sample period (Figure 41). Temperature and TN values show moderate change except in July, when TN concentrations are significantly lower at RD. Temperature changes vary seasonally. The greatest change between temperatures occur during summer and winter sample times. This reflects the consistent temperatures at Sanders Spring and the sensitivity of water temperatures at the VWMR to air temperatures. Changes are significant for DO, TSS, and TP between RD and SS2. This reflects the biological and chemical processes occurring in the reservoir.

Water quality changes very little between SDS2 and SDS1 for much of the year

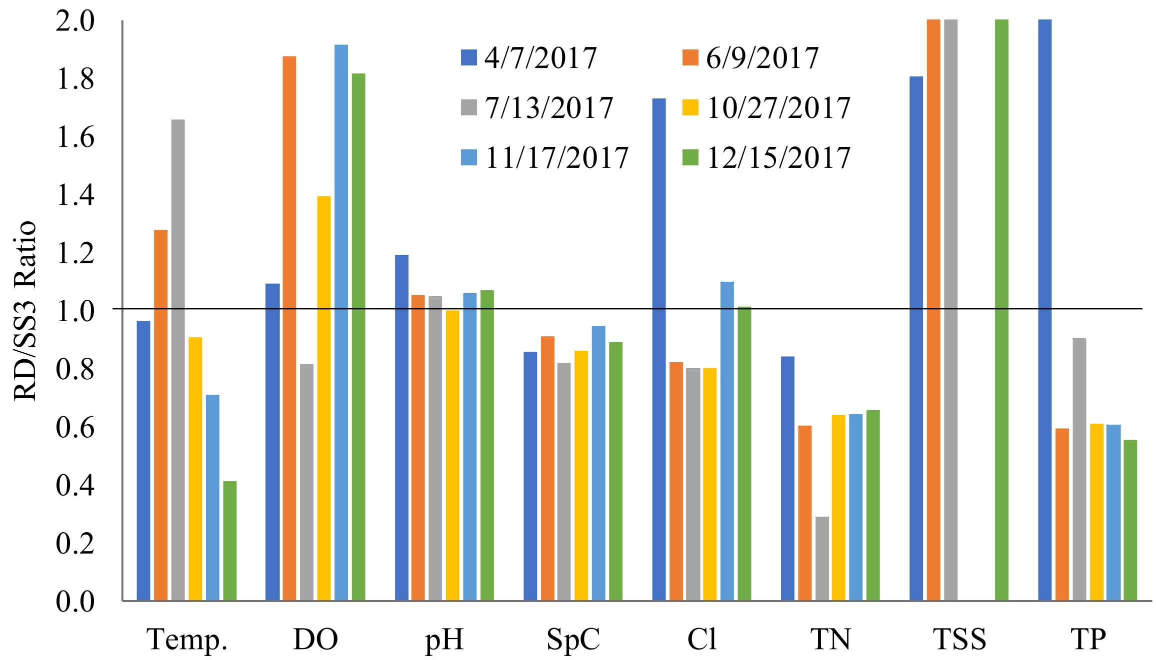


Figure 41. Ratios of water quality parameters for RD and SS3

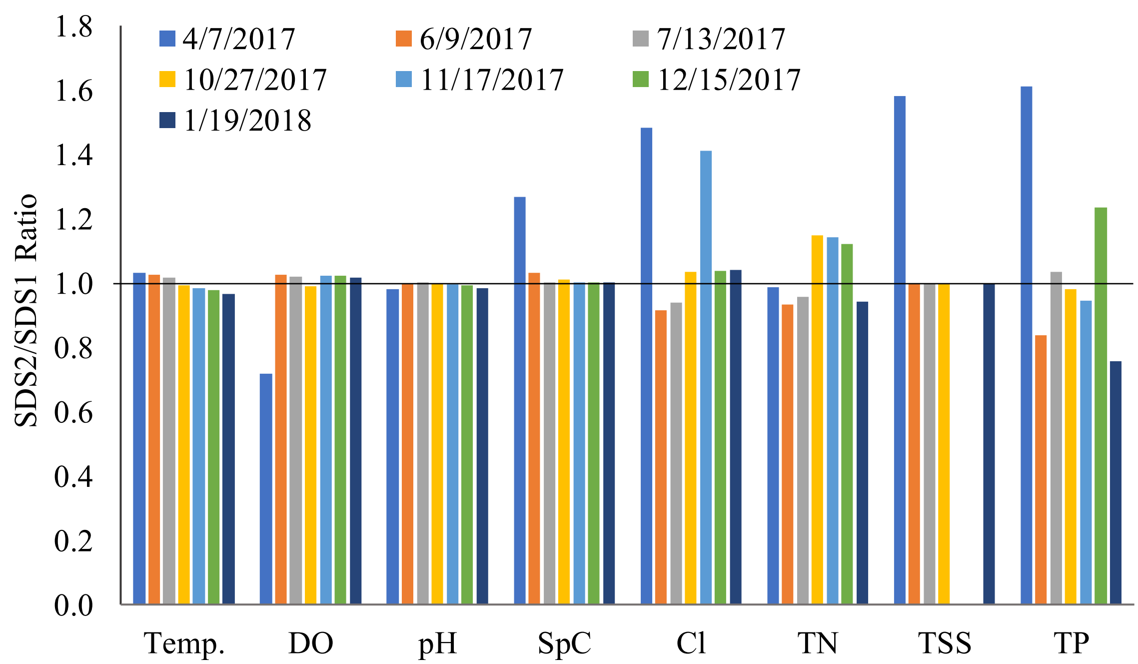


Figure 42. Ratios of water quality parameters for SDS2 and SDS1

significant. In April, DO was lower downstream during the sample time. Concentrations of SC, Cl, TSS and TP were all significantly higher below the reservoir. This suggests that RD may be a source of nutrients to the South Dry Sac River during April. Temperature and pH showed almost no change for the entire sample period.

TN:TP ratios for the VWMR reflect the conditions and limiting nutrient during each sample date. During the April sample date, N was the limiting nutrient of the reservoir (Table 8). Little to no algae was observed during sample dates in spring and winter months and significant algal biomass was observed during summer months (Figure 43, 44, and 45). Phosphorus was the limiting nutrient of the reservoir and reached a high of 79.9 during June's sample date, which reflects when algal blooms were observed. During the July sample date, the reservoir was co-limited, which may reflect N fixation by bacteria when algal blooms reached their peak growth.

Sanders Spring Contributions

Temperature and pH values showed little variability for Sanders Spring during the sample period (Figure 46). Specific Conductivity had a large range of values (484-609 uS/cm) but remained relatively stable after spring months. The low SC in April is likely a result of the high discharge during that month. Baseflow was much higher than usual when sites were sampled in April. The CV for each of these variables were below 10%. The average temperature at Sanders Spring was warm with at 15.31°C. These steady temperatures suggest water at Sanders Spring is from deeper sources rather than water from the surface. Water at Sanders Spring was slightly acidic but close to neutral with an average pH of 6.72.

Table 8. TN:TP ratios for Valley Water Mill Reservoir

Sample Month	TN:TP
April	14.2
June	79.9
July	27.7
October	64.0
November	69.3
December	73.0

Figure 43. Algal conditions of the Valley Water Mill Reservoir in March 2018

Figure 44. Algal conditions of the Valley Water Mill Reservoir in June 2018

Figure 45. Algal conditions of the Valley Water Mill Reservoir in October 2018

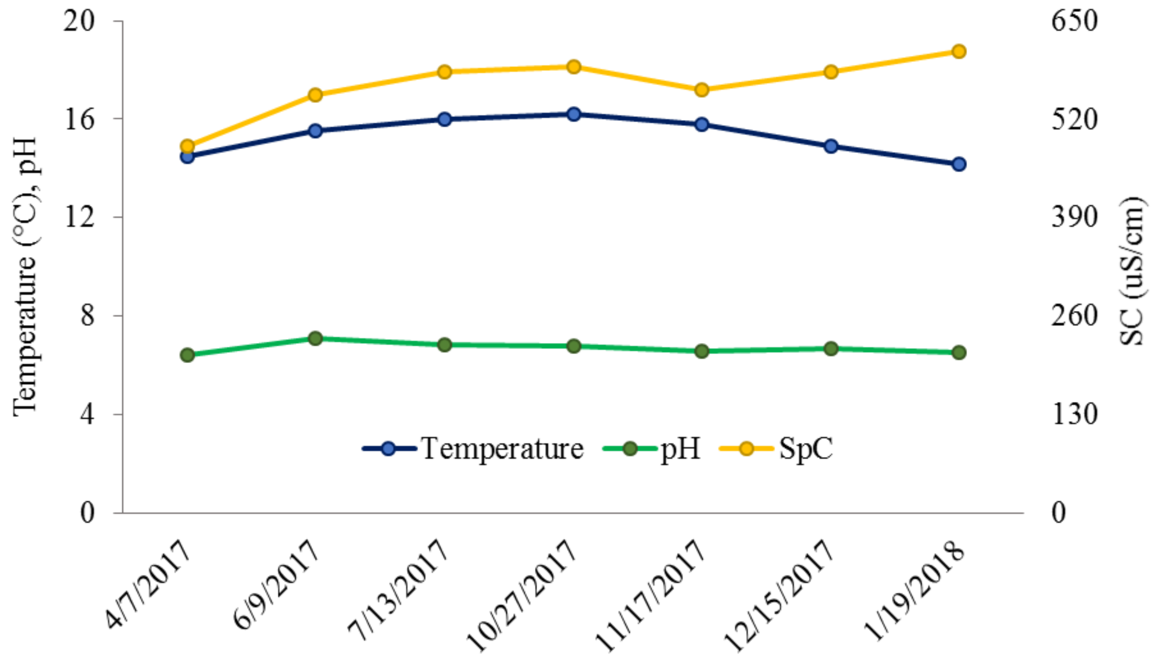


Figure 46. Temperature, pH, and SC at SS1

Concentrations of TN and TP also lacked seasonal variability and did not appear to vary with discharge (Figure 47). Discharge was multiplied by two for scale. The average TN and TP concentrations at SS1 were 1.67 mg/L and 27.74 ug/L, respectively. The average TSS concentration was 7.39 mg/L. The CV for TN was 8.72% and the CV for TP was 32.13%. The CV for TSS was much higher at 125.57%. Discharge was highly variable with a CV of 125.50%. The lack of variation in water quality suggests flow from Sanders Spring was diffuse and not controlled by conduits during baseflow.

Basic nutrient budgets for the VWMR may show how much nutrients from Sanders Spring were either stored within sediment or taken up by algae or microbes in the reservoir during the days sampled. It is important to note that some of the load may be lost to seepage from the reservoir. Positive values indicate total load from SS2 stored at RD and negative values indicate total potential load that was exported to SDS2. Total

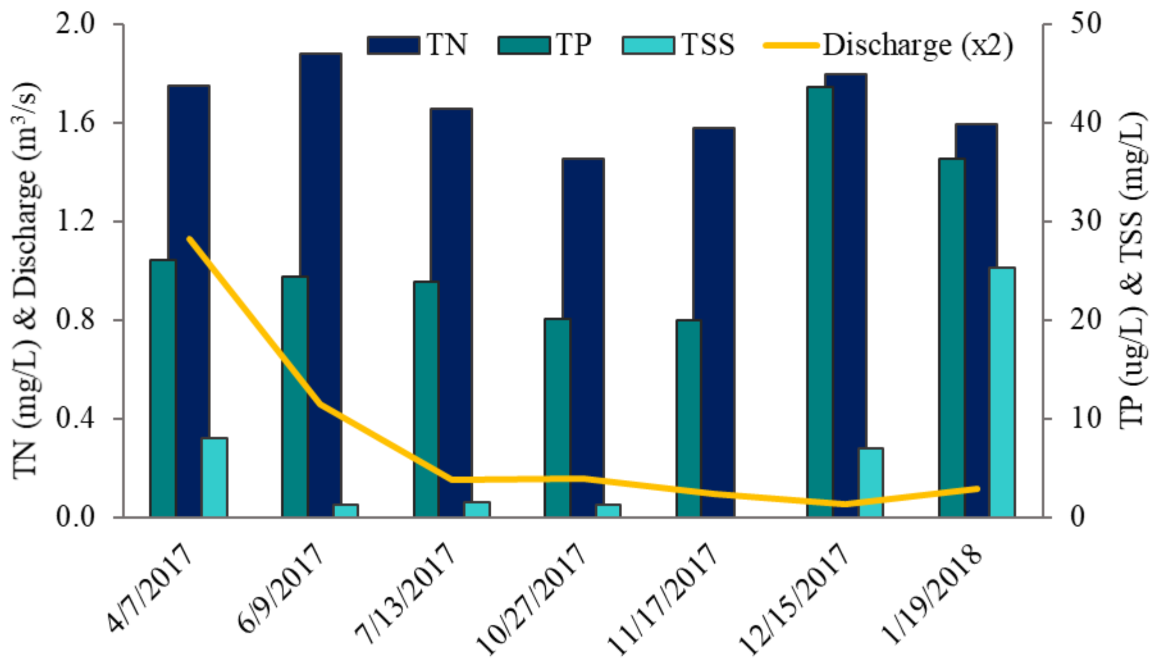


Figure 47. Discharge, TN, TP, and TSS concentrations at SS1

nitrogen loads were stored at the reservoir during each sample date (Table 9). Storage of TN was highest during June with a net value of 24.15 kg/day. Storage of TN was lowest in December with a value of 4.19 kg/day. Potential SS2 contributions of TN load to SDS2 were significant during much of the sample period. Total phosphorus loads from SS2 were also stored at RD during much of the sample period except in April, when TP loads at RD were significantly higher (Table 10). Contributions of TP loads from SS2 to SDS2 were much lower than for TN except in winter months. Total phosphorus loads at SS2 during sample dates in December and January were significantly higher than at SDS2. Similar to TP, TSS loads were significantly higher at RD during the sample date in April (Table 11).

Table 9. SS2 contributions of TN loads

Date	SS2 (kg/day)	RD (kg/day)	Reservoir Storage (Input-Output)	SDS2 (kg/day)	SS2 Contributions (% of SDS2)
4/7/2017	85.46	74.47	10.99	89.00	96
6/9/2017	37.74	13.59	24.15	39.57	95
7/13/2017	10.93	0.00	10.93	12.38	88
10/27/2017	9.64	3.17	6.46	12.62	76
11/17/2017	6.30	0.00	6.30	7.17	88
12/15/2017	4.19	0.00	4.19	4.62	91
1/19/2018	7.77	0.00	7.77	9.00	86

Table 10. SS2 contributions of TP loads

Date	SS2 (kg/day)	RD (kg/day)	Reservoir Storage (Input-Output)	SDS2 (kg/day)	SS2 Contributions (% of SDS2)
4/7/2017	1.27	10.45	-9.18	2.12	60
6/9/2017	0.48	0.17	0.31	0.64	75
7/13/2017	0.16	0.00	0.16	0.23	68
10/27/2017	0.13	0.05	0.08	0.30	44
11/17/2017	0.08	0.00	0.08	0.15	53
12/15/2017	0.10	0.00	0.10	0.06	179
1/19/2018	0.18	0.00	0.18	0.07	257

Table 11. SS2 contributions of TSS loads

Date	SS2 (kg/day)	RD (kg/day)	Reservoir Storage (Input-Output)	SDS2 (kg/day)	SS2 Contributions (% of SDS2)
4/7/2017	390.66	749.72	-359.06	94.72	412.44
6/9/2017	24.83	44.23	-19.41	0.00	NA
7/13/2017	9.90	0.00	9.90	0.00	NA
10/27/2017	8.62	0.00	8.62	11.90	72.42
12/15/2017	16.33	0.00	16.33	0.00	NA
1/19/2018	123.29	0.00	123.29	0.00	NA

CHAPTER 5 – DISCUSSION

Weather and Climate Implications

The significantly greater amount of precipitation from March to June may have important effects on hydrographs and showed a greater response of baseflow than what is typical (Florea and Vacher 2006). The increased amount of precipitation compared to the past 30-year climatic may have increased flow rates as well as sediment and nutrient yields (Correll et al. 1999). The limited amount of snowfall indicates that snowmelt did not greatly influence the watershed during the study period. Warmer temperatures during the study period, compared to previous years, have likely increased which may have affected nutrient cycling and amplified algal growth (Kaushal et al. 2010).

Flow Characteristics of Sanders Spring

In some cases, springs with diffuse flow many show large hydrograph responses only during multiple storm events and periods of prolonged precipitation (Florea and Vacher 2006). Baseflow at Sanders Spring was particularly high during spring and summer months after several days of relatively high rainfall, suggesting that flow from Sanders Spring may still be characterized as predominately diffuse, specifically during periods of lower flow. Baseflow hydrograph separation techniques outlined by Eckhardt can indicate quick flow which, in karst, can be considered conduit-dominated flow (Eckhardt 2005). High percentages of baseflow contributions to total flow can indicate springs that are characterized by a more diffuse flow system (Raeisi and Karami 1997; Adji and Bahtiar 2016). The high baseflow percentages at Sanders Spring reflect these

findings. Low baseflow contributions at FR-102 and RD indicate that flow at those sites occurs mainly due to rain events.

Water quality parameters may have further implications for characterizing subsurface flows. Specific Conductivity has been shown to reflect hardness which can be used to determine characteristics of karst spring flow as diffuse or conduit driven (Shuster and White 1971). The CV for SC concentrations at Sanders Spring was 7%. Seasonal variation in water temperatures at karst springs suggests that flow moves relatively quickly through the subsurface (Luhmann et al. 2011). Temperatures that vary seasonally reflect air temperatures which are typically seen in surface water. Therefore, spring temperatures showing relatively little variation with changes of less than a few degrees reflect diffuse, rather than conduit, flow through the subsurface (Shuster and White 1971).

Based on these water quality results and the high baseflow contributions at Sanders Spring, flow through the subsurface may be characterized as diffuse during periods of no precipitation. However, the major fault system near the reservoir and spring makes this conclusion uncertain. Faults can make characterization of subsurface flow difficult in that they can either provide pathways for flow, divert flow, or have no effect at all (White 2003). Historically, the fault zone has been known to cause leakage from the reservoir, so it is possible that the faults affect flow to the spring as well (Beveridge 1963). Future work is needed to characterize flow during rain events to understand the karst system in more detail.

Temporal and Spatial Variation of Water Quality

Seasonal variation of Cl at all sites suggests there may be some influence of road salts from runoff, although values were not very high (Panno et al. 2006). Similar variation of SC values across sites may indicate that the subsurface structure is similar across the study site. Values of pH at SS1 were lower in April, which likely reflects that water moves more quickly through the subsurface during periods of higher rainfall (Shuster and White 1971).

Concentrations of nutrients from Sanders Spring are affected largely at the VWMR. Ratios of water quality parameters showed little change between Sanders Spring and the reservoir inlet. Ratios between the inlet and reservoir dam showed significant changes for DO, TN, TSS, and TP concentrations. Additionally, ratios showed little change between the upstream site on the South Dry Sac River and the downstream site except in April when concentrations were high at the reservoir. Therefore, it is important to analyze the changes and potential causes of these changes for TN, TSS, and TP concentrations at the reservoir.

The higher concentration of TSS and TP at the reservoir during the April sample date indicates that TP may be associated with sediment which has been seen in previous studies on shallow lakes (Hargeby et al. 2005). This may reflect the peaks in P concentration often seen during spring turnover, when vertical mixing of lake water occurs due to changes in temperature (Dillon and Rigler 1974; Davis and Bell 1998). Additionally, wind can greatly influence the remobilization of sediments and subsequently the release of TP (Havens and Steinman 2015). Therefore, the reservoir may be a significant source of TP and TSS to the South Dry Sac River during these times.

More sampling in the future may confirm this. Dissolved oxygen levels at the reservoir increase during early blooms and decreased when algal biomass is abundant. Therefore, variations in DO concentrations at the reservoir may reflect biological processes associated with algal blooms in the reservoir. Furthermore, the increase of TSS and TP from upstream on the South Dry Sac River to downstream the confluence near the dam indicates that reservoir may be acting as a source of these nutrients during this time. Ratios of TN:TP at the reservoir during the sample period indicates that P may be the primary nutrient driving the algal blooms in the summer, which is common in many Missouri lakes (MDNR 2001). The lower concentrations of TP at the reservoir, compared to other sites, suggests that the reservoir was acting as sink for TP during the rest of the sample dates.

The lower TN concentrations at RD during the sample date in July may indicate that TN from Sanders Spring gets utilized by algae or microbes in the reservoir, particularly when algal biomass was significant in July. Increased TN concentrations after disappearance of algae may reflect these processes (Ishida et al. 2008). Furthermore, TN concentrations were lower at the reservoir than at both upstream and downstream sites which indicates that the reservoir may be acting as a sink or trap for N.

To understand the controls on water quality, a Pearson's correlation coefficient matrix was done using SPSS for SS1, RD, and SDS2 (Appendix J). At SS1, there was negative relationship between measured discharge and SC. A p-value less than 0.05 indicates that this relationship is significant. This suggests that there may be an effect of dilution with increased discharge. Additionally, there was a significant positive relationship between Cl and TSS which could reflect runoff as a source of chloride due to

road salts or other anthropogenic sources. At RD, there was also a significant negative relationship between discharge and SC which is likely the reflection of little change in SC concentrations between SS3 and RD. Discharge showed a positive relationship with both TSS and TP. This may reflect the influence of reservoir dam overflow on the transport of these nutrients. There was also a significant positive relationship between TSS and TP, which was expected. Lastly, there was a significant negative relationship between SC and TP, which was expected due to the negative relationship between discharge and SC.

Relationships between water quality variables at SDS2 were identical to RD except for an additional significant, negative relationship between DO and temperature. The inverse relationship between DO and temperature is well documented and may reflect the primary production of phytoplankton (Loperfido et al. 2009). This relationship is expected in lakes but may not have occurred due to sample location and relatively few numbers of samples taken. Levels of DO have been known to vary both seasonally and with depth in shallow lakes (Hunter and Hearn 1987). The lack of significant relationships between water quality variables at Sanders Spring and the apparent increase in the number of significant relationships at the VWMR and South Dry Sac River suggests that the reservoir may play a large role in the source and downstream transport of nutrients.

Overall Contributions of Sanders Spring

Nutrient concentrations at Sanders Spring are typically higher than the EPA recommended limits for Missouri streams and reservoirs that lack TMDLs, but these limits may be low for many Missouri waters. The average TN concentration at SS1

during the study period was 1.67 mg/L compared the recommended limit of 0.29 mg/L. The average TP concentration was 27.74 mg/L. However, in many Missouri Ozark streams, these values are typical and have even been seen to be up to 20 times higher (Table 1). Furthermore, TMDLs listed for some Missouri watersheds in counties surrounding the study area have listed that concentrations of TP be no higher than 60 to 75 ug/L and concentrations of TN be no higher than 1.0 to 1.5 mg/L. Thus, concentrations of TN from Sanders Spring may be significant in the VWMW, but concentrations of TP are likely insignificant.

Basic nutrient budgets showed that Sanders Spring may contribute a significant portion of TN load to the South Dry Sac River although much of it likely ends up stored in the reservoir or taken up by algae or microbes. Total phosphorus loads to the South Dry Sac River may be low during most of the year. However, during winter months the percent of load was over 100% greater at Sanders Spring which suggests that P was likely stored in the reservoir during these times. More research during stormflow is needed to confirm these findings. Additionally, significant TSS loads during the April sample date may have been contributed by the spring although much of it was stored in the reservoir. Based on these results, it is important to understand whether there were significant losses due to seepage at the reservoir. These losses would imply that some of nutrient load may end up outside the watershed.

There was a slight positive relationship between average monthly inflow at Sanders Spring during baseflow and monthly precipitation (Figure 48). A p-value of 0.01 suggests that this relationship is statistically significant. It is important to note that the outlier in Figure 48 was removed to potentially illustrate the natural conditions more

accurately, but this has little effect on the overall curve. This outlier showed that SS2 had a baseflow of 0.8 m^3/s for a monthly precipitation of 188 mm, which is unexpected and could signify error from the rating curve. The potential occurrence of net loss during months with higher precipitation suggests that there may be deeper, unmeasured leakages

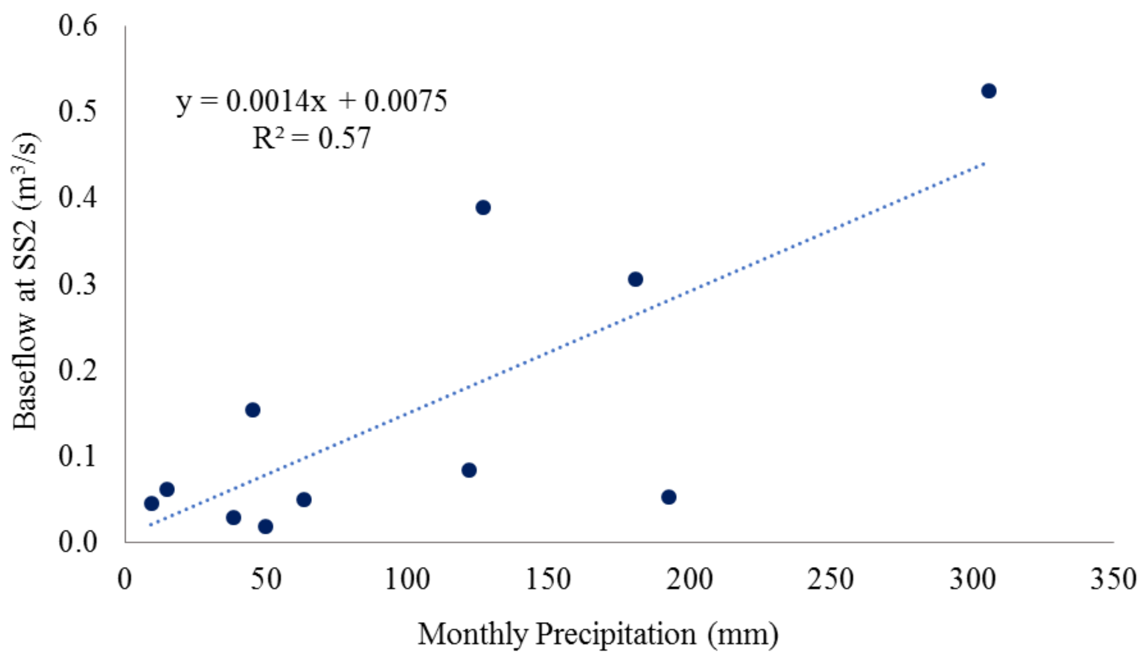


Figure 48. Relationship between precipitation and Sanders Spring baseflow

occurring in the spring. On average, 33% of flow from Sanders Spring is potentially lost by seepage from the reservoir. Licher (2003) also suggested reservoir seepage and evaporation may reflect short estimated residence times despite the lack of flow over the dam during baseflow. Reservoirs over karst-dominated landscapes may have greater water loss, specifically where there are widened fractures in the subsurface (Romanov et al. 2003). The major fault that lies under the reservoir could facilitate leakage that

potentially ends up at Grandview Tributary (Figure 4). With evaporation accounted for, it is assumed that the remaining flow may be due to deeper seepage. The relationship of seepage loss as a percent of inflow and the amount of inflow from Sanders Spring may explain the occurrence of net loss at the reservoir during months with higher precipitation (Figure 49). However, a p-value of 0.06 suggests that this relationship is not statistically significant. This relationship would likely be stronger if there were more measurements during periods of higher baseflow.

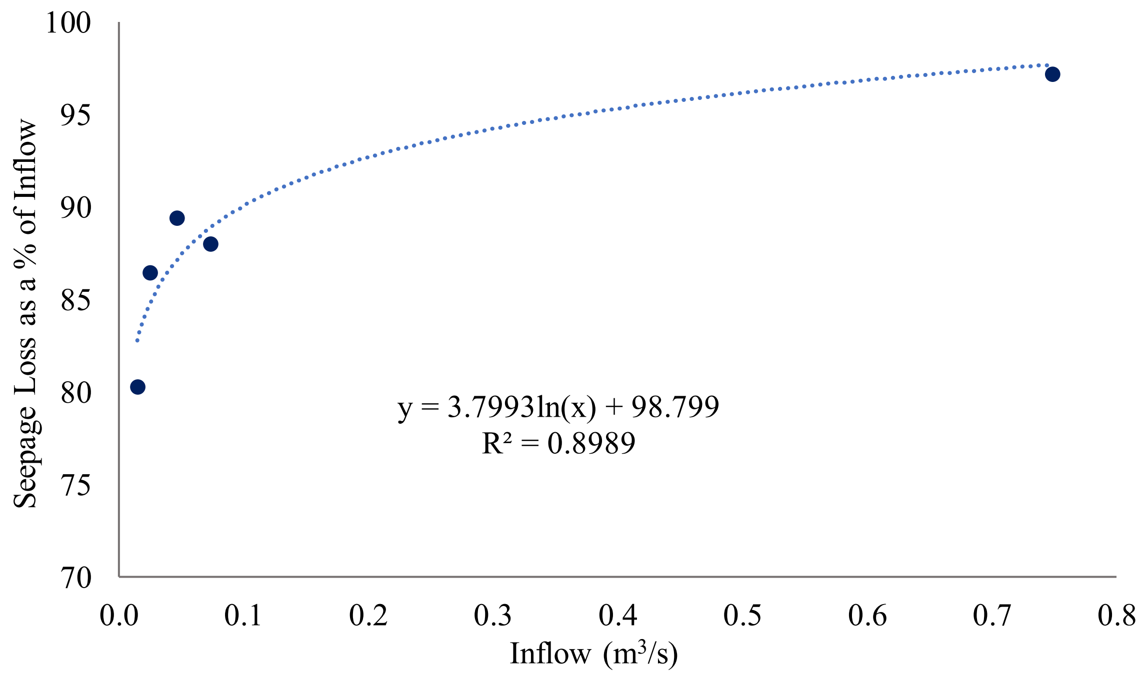


Figure 49. Percent seepage loss vs. inflow

CHAPTER 6 – CONCLUSIONS

This study quantified nutrient and sediment contributions during baseflow to understand transport and short-term storage mechanisms within a karst spring-reservoir system. Water quality parameters including temperature and SC were measured to understand flow paths and groundwater and surface water interactions in a karst watershed. Measurements of total nitrogen, total phosphorus, and total suspended solids concentrations were measured to understand the role of Sanders Spring and the VWMR to the South Dry Sac River. Water and nutrient budgets were calculated to understand how N, P, and sediment are transported and stored within the HW-SDSW and VWMW. From the results of this study, we can draw five conclusions:

1. Subsurface flow from Sanders Spring may be characterized as diffuse during baseflow due to little variation in SC, pH, and water temperature as well as high baseflow contributions to total flow. Most water quality parameters had a CV of less than 10% at SS1 while most CVs were above 10% at SDS2. However, the presence of a major fault system makes this conclusion uncertain. More research during stormflow is needed to better characterize this karst system.

2. Water did not flow over the Valley Water Mill Reservoir dam for 244 days out of the year (65% of the study period). Estimated discharge was 0 m^3/s from September 2017 to January 2018. During this time, water is either lost to evaporation, lost to seepage, or is stored in the reservoir.

3. The Valley Water Mill Reservoir acted as a sink of N during the sample dates. The reservoir had consistently lower concentrations and loads compared to all other sites in the study area. Average TN concentrations were 1.67 mg/L at Sanders Spring, 0.92 mg/L at the reservoir, and 1.16 mg/L at the South Dry Sac River USGS gage. Total nitrogen was lowest in July, when algae growth peaked in the reservoir which may reflect denitrification or uptake by algae. Lower TN concentrations at the reservoir could also be due to sedimentation or seepage.

4. The Valley Water Mill Reservoir showed a significant increase of TP during the sample date in April. This could potentially be due to effects of spring turnover This P may be transported to the South Dry Sac River when high discharge

transports it over the dam, but more research during stormflow is needed. Conversely, the reservoir appeared to be a sink of P during most of the days sampled.

5. On average, baseflow from Sanders Spring was up to 46% of the total flow at the South Dry Sac River. Average baseflow at SS2 was 0.21 m^3/s and average total flow at SDS2 was 0.63 m^3/s. There were potential net losses to the reservoir during spring and winter months which could indicate seepage loss. Close to 33% of flow from Sanders Spring may be lost to seepage in the reservoir. However, some of this calculated loss could be due to error. Relationships between total seepage loss during baseflow and inflow from SS2 indicate that precipitation may influence seepage loss from the reservoir.

Future Work

These results are important to managing the surface water within the VWMW. The results of this study are limited to baseflow and only show a snapshot of transport and temporary storage behavior, but they suggest that management efforts may be focused on sediment and P control within the VWMR. However, future work should include stormflow analysis on nutrient transport to understand the temporary and long-term storage effects of the reservoir on nutrient loads to the South Dry Sac River. Much of the N load was likely either stored or taken up by algae or microbes within the reservoir, but monitoring efforts of N is still important due to high concentrations during the year. Additionally, measuring leakages is difficult in karst landscapes. Lastly, results of this study indicate that future work should include dye tracing within the VWMW and more robust reservoir seepage calculations to understand where nutrients and flow from the spring ultimately end up.

REFERENCES

Adji TN, Bahtiar IY (2016) Rainfall–discharge relationship and karst flow components analysis for karst aquifer characterization in Petoyan Spring, Java, Indonesia. Environ Earth Sci 75:735

Alexander RB, Smith RA, Schwarz GE (2004) Estimates of diffuse phosphorus sources in surface waters of the United States using a spatially referenced watershed model. Water Sci Technol 19:1-10

Anderson DM, Glibert PM, Burkholder JM (2002) Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. Estuaries 25:704–726

Arguez A, Durre I, Applequist S et al (2010) NOAA's U.S. climate normals (1981-2010) NOAA National Centers for Environmental Information

Austin BJ (2015) Effects of landscape disturbances on autotrophic processes within Arkansas Ozark streams. University of Arkansas, Fayetteville

Bailey BW, Haggard BE, Massey LB (2012) Water quality trends across select 319 monitoring sites in northwest Arkansas. University of Arkansas, Fayetteville

Barlow PM, Cunningham WL, Zhai T et al (2014) U.S. Geological Survey Groundwater Toolbox, a graphical and mapping interface for analysis of hydrologic data (version 1.0)-User guide for estimation of base flow, runoff, and groundwater recharge from streamflow data. U.S. Geological Survey techniques and methods book 3, chapter B10

Barlow PM, Cunningham WL, Zhai T et al (2017) U.S. Geological Survey Groundwater Toolbox version 1.3.1, a graphical and mapping interface for analysis of hydrologic data: U.S. Geological Survey Software Release 26 May 2017

Beveridge, TR (1963) The Valley Mills Fault Zone. In: The geology in the vicinity of Joplin, Missouri including Westside-Webber Mine, Okla. Association of Missouri Geologists

Bolgrien DW, Scharold JV, Angradi TR et al (2009) Trophic status of three large Missouri River reservoirs. Lake Reserv Manage 25:176–190

Bonacci O (1993) Karst springs hydrographs as indicators of karst aquifers. Hydrolog Sci J 38:51–62

Borchelt GG (2007) Nutrient concentrations at baseflow conditions in the Upper White River Basin, Southwest Missouri and Northwest Arkansas. Missouri State University

Bosch NS, Allan JD (2008) The influence of impoundments on nutrient budgets in two catchments of Southeastern Michigan. Biogeochemistry 87:325–338

Bowen MW (2004) Consequences of reservoir drainage on downstream water chemistry, suspended sediment, and nutrients, Southwest Missouri. Missouri State University

Brown JB, Sprague LA, Dupree JA (2011) Nutrient sources and transport in the Missouri River Basin, with emphasis on the effects of irrigation and reservoirs. JAWRA 47:1034–1060

Bullard L, Thomson KC, Vandike JE (2001) The springs of Greene County, Missouri. Missouri Department of Natural Resources Geological Survey and Resource Assessment Division. Rolla, MO.

Burford MA, Johnson SA, Cook AJ et al (2007) Correlations between watershed and reservoir characteristics, and algal blooms in subtropical reservoirs. Water Res 41:4105–4114

Burford MA, Green SA, Cook AJ et al (2012) Sources and fate of nutrients in a subtropical reservoir. Aquat Sci 74:179–190

Carpenter, SR, Caraco NF, Correll DL et al (1998) Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Application 8:559–568

Chambers DK, Arruda JA, Jaywardhana AA (2005) A synoptic water quality survey of the spring river and its tributaries. Transactions of the Kansas Academy of Science 108:47–56

Christophoridis C, Fytianos K (2006) Conditions affecting the release of phosphorus from surface lake sediments. J Environ Qual 35:1181

Correll D (1999) Phosphorus: a rate limiting nutrient in surface waters. Poultry Sci 78:674–682

Correll DL, Jordan TE, Weller DE (1992) Nutrient flux in a landscape: effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. Estuaries 15:431–442

Dahm CN, Grimm NB, Marmonier P et al (1998) Nutrient dynamics at the interface between surface waters and groundwaters. Freshwater Biol 40:427–451

Davis JV, Bell RW (1998) Water-quality assessment of the Ozark plateaus study unit, Arkansas, Kansas, Missouri, and Oklahoma: Nutrients, bacteria, organic carbon, and suspended sediment in surface water, 1993–1995. Water Resources Investigations Report 56

Dendy FE (1974) Sediment trap efficiency of small reservoirs. Trans of ASAE 17:898-988

Dillon PJ, Rigler FH (1974) The phosphorus-chlorophyll relationship in lakes. Limnol Oceanogr 19:767–773

Downing JA, Prairie YT, Cole JJ et al (2006) The global abundance and size distribution of lakes, ponds, and impoundments. Limnol Oceanogr 51:2388–2397

Dreiss SJ (1989) Regional scale transport in a Karst Aquifer: 2. Linear systems and time moment analysis. Water Resour Res 25:126–134

Eckhardt K (2005) How to construct recursive digital filters for baseflow separation. Hydrol Process 19:507–515

EPA (1983) Methods for chemical analysis of water and wastes. United States Environmental Protection Agency Office of Research and Development. Washington, DC

EPA (1987) Handbook of methods for acid deposition studies: Laboratory analysis for surface water chemistry. United States Environmental Protection Agency Office of Research and Development. Washington, DC

EPA (1999) Protocol for Developing Nutrient TMDLs. United States Environmental Protection Agency Office of Water. Washington, DC

Fairchild GW, Velinsky DJ (2006) Effects of Small Ponds on Stream Water Chemistry. Lake Reserv Manage 22:321–330

Florea LJ, Vacher HL (2006) Springflow hydrographs: eogenetic vs. telogenetic karst. Ground Water 44:352–361

Friedl G, Wüest A (2002) Disrupting biogeochemical cycles: consequences of damming. Aquat Sci 64:55–65

Frink CR (1967) Nutrient budget: rational analysis of eutrophication in a Connecticut lake. Environ Sci Technol 1:425–428

Ghobadi MH, Khanlari GR, Djalaly H (2005) Seepage problems in the right abutment of the Shahid Abbaspour dam, southern Iran. Eng Geol 82:119–126

Hamon WR (1961) Estimating Potential Evapotranspiration. Massachusetts Institute of Technology

Hanberry BB, Jones-Farrand DT, Kabrick JM (2014) Historical Open Forest Ecosystems in the Missouri Ozarks: Reconstruction and Restoration Targets. Ecological Restoration 32:407–416

Hargeby A, Blindow I, Hansson LA (2004) Shifts between clear and turbid states in a shallow lake: multi-causal stress from climate, nutrients and biotic interactions. Archiv für Hydrobiologie 161:433–454

Harrison JA, Maranger RJ, Alexander RB et al (2009) The regional and global significance of nitrogen removal in lakes and reservoirs. Biogeochemistry 93:143–157

Hatch CE, Fisher AT, Revenaugh JS et al (2006) Quantifying surface water-groundwater interactions using time series analysis of streambed thermal records: method development. Water Resour Res 42

Havens KE (2003) Phosphorus–Algal bloom relationships in large lakes of South Florida: implications for establishing nutrient criteria. Lake Reserv Manage 19:222–228

Havens KE, Steinman AD (2015) Ecological responses of a large shallow lake (Okeechobee, Florida) to climate change and potential future hydrologic regimes. Environ Manage 55:763–775

Hippe DJ, Win EC, Giovannitti RM (1994) Hydrogeology, herbicides and nutrients in ground water and springs, and relation of water quality to land use and agricultural practices near Carlisle, Pennsylvania. USGS Water-Resources Investigations Report 66

Homer CG, Dewitz JA, Yang L et al (2015) Completion of the 2011 National Land Cover Database for the conterminous United States-Representing a decade of land cover change information. Photogrammetric Engineering and Remote Sensing 81:345–354

Howarth RW, Billen G, Swaney D et al (1996) Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences. Bieogeochemistry 35:75-139

Huebsch M, Fenton O, Horan B et al (2014) Mobilisation or dilution? Nitrate response of karst springs to high rainfall events. Hydrol Earth Syst Sc 18:4423–4435

Hughes HE (1982) Soil survey of Greene and Lawrence Counties, Missouri. U.S. Department of Agriculture Soil Conservation Service. Washington, DC

Hunter JR, Hearn CJ (1987) Lateral and vertical variations in the wind-driven circulation in long, shallow lakes. J Geophys Res 92:13106-13114

Ignatius AR, Rasmussen TC (2016) Small reservoir effects on headwater water quality in the rural-urban fringe, Georgia Piedmont, USA. J Hydrol: Regional Studies 8:145–161

Ishida CK, Arnon S, Peterson CG et al (2008) Influence of Algal Community Structure on Denitrification Rates in Periphyton Cultivated on Artificial Substrata. Microb Ecol 56:140–152

Janke BD, Finlay JC, Hobbie SE et al (2014) Contrasting influences of stormflow and baseflow pathways on nitrogen and phosphorus export from an urban watershed. Biogeochemistry 121:209–228

Kaushal SS, Likens GE, Jaworski NA et al (2010) Rising stream and river temperatures in the United States. Front Ecol Environ 8:461–466

Kennedy RH, Walker WW (1990) Reservoir nutrient dynamics. Reservoir limnology: ecological perspectives. John Wiley and Sons, New York 109–132

Kenny JA, Hayward BW (2009) Karst in stone: karst landscapes in New Zealand: a case for protection. Geological Society of New Zealand, Lower Hutt, NZ

Khan FA, Ansari AA (2005) Eutrophication: An Ecological Vision. Bot Rev 71:449–482

King JE (1973) Late Pleistocene Palynology and Biogeography of the Western Missouri Ozarks. Ecol Monogr 43:539–565

Kingsbury JA (2008) Relation between flow and temporal variations of nitrate and pesticides in two karst springs in Northern Alabama. J Am Water Resour As 44:478–488

Koirala AK (2009) An evaluation of pre- and post-timber harvest water quality in low-order streams in the Missouri Ozarks. University of Missouri

Kumar US, Sharma S, Navada SV (2008) Recent studies on surface water-groundwater relationships at hydro-projects in India using environmental isotopes. Hydrol Process 22:4543–4553

Lamb JA, Fernandez FG, Kaiser DE (2014) Understanding Nitrogen in Soils. University of Minnesota Extension

Leonard J, Mietton M, Najib H, Gourbesville P (2000) Rating curve modelling with Manning's equation to manage instability and improve extrapolation. Hydrolog Sci J 45:739–750

Lerch RN, Wicks CM, Moss PL (2005) Hydrologic characterization of two karst recharge areas in Boone County, Missouri. Journal of Cave and Karst Studies 67:158–173

Licher SS (2003) History of sedimentation and contamination in Valley Mill Reservoir, Springfield, Missouri. Missouri State University

Loperfido JV, Just CL, Schnoor JL (2009) High-frequency diel dissolved oxygen stream data modeled for variable temperature and scale. J Environ Eng 135:1250–1256

Luhmann AJ, Covington MD, Peters AJ et al (2011) Classification of thermal patterns at karst springs and cave streams. Ground Water 49:324–335

Luu TNM, Garnier J, Billen G et al (2012) N, P, Si budgets for the Red River Delta (northern Vietnam): how the delta affects river nutrient delivery to the sea. Biogeochemistry 107:241–259

Matzinger A, Pieters R, Ashley KI et al (2007) Effects of impoundment on nutrient availability and productivity in lakes. Limnol Oceanogr 52:2629–2640

MDEQ (2008) Total maximum daily load: Total nitrogen and total phosphorus for Harris Bayou. Jackson, MS: Office of Pollution Control. Jackson, MS

MDNR (2001) Total maximum daily load (TMDL) for James River, Webster, Greene, Christian and Stone Counties, Missouri. Missouri Department of Natural Resources

MDNR (2010) Total maximum daily load (TMDL) for Cave Springs Branch McDonald County, Missouri. Missouri Department of Natural Resources Water Protection Program

Miller DE, Vandike JE (1997) Groundwater resources of Missouri. Missouri Department of Natural Resources Division of Geology and Land Survey Water Resources Report 46

Miller RB (2006) Nutrient Loads in an urban Ozark watershed: Jordan, Fassnight and upper Wilson's Creeks, Springfield, Missouri. Missouri State University

Niyogi DK, Bandeff JM, Selman C, Menke DE (2010) Nutrient flux, uptake, and transformation in a spring-fed stream in the Missouri Ozarks, USA. Aquat Sci 72:203–212

Nolan BT, Stoner JD (2000) Nutrients in groundwaters of the conterminous United States, 1992−1995. Environ Sci Technol 34:1156–1165

Nowlin WH, Evarts JL, Vanni MJ (2005) Release rates and potential fates of nitrogen and phosphorus from sediments in a eutrophic reservoir: Nutrient release from reservoir sediments. Freshwater Biol 50:301–322

O'Driscoll MA, DeWalle DR (2006) Stream–air temperature relations to classify stream–ground water interactions in a karst setting, central Pennsylvania, USA. J Hydrol 329:140–153

Owen MR, Pavlowsky RT (2011) Base flow hydrology and water quality of an Ozarks spring and associated recharge area, southern Missouri, USA. Environ Earth Sci 64:169–183

Paerl HW, Fulton RS, Moisander PH, Dyble J (2001) Harmful freshwater algal blooms, with an emphasis on cyanobacteria. The Scientific World Journal 1:76–113

Panno SV, Hackley KC, Hwang HH et al (2006) Characterization and identification of Na-Cl sources in ground water. Ground Water 44:176–187

Partington D, Brunner P, Simmons CT et al (2012) Evaluation of outputs from automated baseflow separation methods against simulated baseflow from a physically based, surface water-groundwater flow model. J Hydrol 458–459:28–39

Penn MR, Auer MT, Doerr SM et al (2000) Seasonality in phosphorus release rates from the sediments of a hypereutrophic lake under a matrix of pH and redox conditions. Can J Fish Aquati Sci 57: 1033-1041

Peterson EW, Davis RK, Brahana JV, Orndorff HA (2002) Movement of nitrate through regolith covered karst terrane, northwest Arkansas. J Hydrol 256:35–47

Pittman JR, Hatzell HH, Oaksford ET (1997) Spring contributions to water quantity and nitrate loads in the Suwannee River during base flow in July 1995. US Geological Survey Water Resources Investigative Report 12

Powers SM, Tank JL, Robertson DM (2015) Control of nitrogen and phosphorus transport by reservoirs in agricultural landscapes. Biogeochemistry 124:417–439

Raeisi E, Karami G (1997) Hydrochemographs of Berghan Karst Spring as indicators of aquifer characteristics. J Cave Karst Stud 59:112–118

Richards JM, Johnson BT (2002) Water quality, selected chemical characteristics, and toxicity of base flow and urban stormwater in Pearson Creek and Wilsons Creek Basins, Greene County, Missouri, August 1999 to August 2000. United States Geological Survey Water-Resources Investigations Report

Romanov D, Gabrovšek F, Dreybrodt W (2003) Dam sites in soluble rocks: a model of increasing leakage by dissolutional widening of fractures beneath a dam. Eng Geol 70:17–35

Sanchez E, Colmenarejo MF, Vicente J et al (2007) Use of the water quality index and dissolved oxygen deficit as simple indicators of watersheds pollution. Ecol Indic 7:315–328

Sauer TJ, Alexander RB, Brahana JV, Smith RA (2008), The importance and role of watersheds in the transport of nitrogen. Nitrogen in the Environment 203–240

Shuster ET, White WB (1971) Seasonal fluctuations in the chemistry of lime-stone springs: A possible means for characterizing carbonate aquifers. J Hydrol 14:93–128

Shuster WD, Bonta J, Thurston H et al (2005) Impacts of impervious surface on watershed hydrology: a review. Urban Water J 2:263–275

Skrobialowski SC, Focazio MJ (1997) Hydrologic characteristics and water budget for Swift Creek Reservoir, Virginia, 1996. United States Geological Survey Open-File Report 97-229

Smart MM, Jones JR, Sebaugh JL (1985) Stream-watershed relations in the Missouri Ozark Plateau Province. J Environ Qual 14:77-82

Smith S, Renwick W, Bartley J, Buddemeier R (2002) Distribution and significance of small, artificial water bodies across the United States landscape. Sci Total Environ 299:21–36

Soil Survey Staff (2018) Soil Survey Geographic (SSURGO) database for Springfield, MO. Natural Resources Conservation Service United States Department of Agriculture.

Swank WT, Waide JB (1988) Characterization of baseline precipitation and stream chemistry and nutrient budgets for control watersheds. In: Forest Hydrology and Ecology at Coweeta. Springer, New York, NY, pp 57–79

Taylor CJ, Greene EA (2008) Hydrogeologic characterization and methods used in the investigation of karst hydrology. In: Field techniques for estimating water fluxes between surface water and ground water.

U.S. Census Bureau (2016) ACS demographic and housing estimates. Springfield, MO. Available online at https://factfinder.census.gov/faces/tableservices/jsf/pages/productview.xhtml?src=CF

USGS (2018) USGS 06918493 South Fork Dry Sac River near Springfield, MO. Available online at https://waterdata.usgs.gov/mo/nwis/inventory/?site_no=06918493&agency_cd=USGS

USNO (2018) Duration of daylight/darkness table for one year. Available online at http://aa.usno.navy.mil/data/docs/Dur_OneYear.php

Valiela I, Costa JE (1988) Eutrophication of Buttermilk Bay, a cape cod coastal embayment: Concentrations of nutrients and watershed nutrient budgets. Environ Manage 12:539–553

Ward AD, Trimble SW, Burckhard SR et al (2016) Environmental Hydrology, 3rd edn. CRC Press, Boca Raton, FL

Watson VJ, Loucks OL, Mitchell J, Clesceri NL (1979) Impact of development on watershed hydrologic and nutrient budgets. J Water Pollut Contr Fed 51:2876–2885

WCO (2009) Watershed Center at Valley Water Mill federal grant final report. Watershed Committee of the Ozarks

Wetzel RG (2001) Limnology, lake and river ecosystems. Elsevier, Amsterdam

White WB (2003) Conceptual models for carbonate aquifers: revisited. in: hydrologic problems in karst terrain. Western Kentucky University, Bowling Green, Kentucky, pp 176–187

Wicks CM, Engeln JF (1997) Geochemical evolution of a karst stream in Devils Icebox Cave, Missouri, USA. J Hydrol 198:30–41

Winter TC (1981) Uncertainties in estimating the water balance of lakes. Water Res Bull 17:82–115

Winter TC, Rosenberry DO, Sturrock AM (1995) Evaluation of 11 equations for determining evaporation for a small lake in the North Central United States. Water Resour Res 31:983–993

Wollheim WM, Vörösmarty CJ, Bouwman AF et al (2008) Global N removal by freshwater aquatic systems using a spatially distributed, within-basin approach. Global Biogeochem Cy 22:GB2026

Wright Water Engineers (1995) Phase 1 Fulbright Spring protection study. Denver, CO

Yurista PM, White DS, Kipphut GW et al (2004) Nutrient patterns in a mainstem reservoir, Kentucky Lake, USA, over a 10-year period. Lake Reserv Manage 20:148–163

APPENDICES

Appendix A. Rating Curve Data

Appendix A-1. FR-102 Cross-Section Data

Distance (m)	Rod (m)	Elevation (m)	Notes
0.3	1.16	2.3	Top of head wall
0.5	1.29	2.17	top of wing wall
0.5	2.95	0.51	base of wing wall
1.5	3.01	0.45	bottom of culvert
2.4	3.01	0.45	bottom of culvert
3.4	2.96	0.5	bottom of culvert
4.2	2.81	0.65	bottom of culvert
5	2.76	0.7	bottom of culvert
5.8	2.76	0.7	base of wing wall
5.8	1.35	2.11	top of wing wall
6.2	1.34	2.12	top of wing wall
6.2	2.65	0.81	base of wing wall
6.6	2.59	0.87	bottom of culvert
6.9	2.37	1.09	bottom of culvert
7.4	2.38	1.08	bottom of culvert
8	2.31	1.15	bottom of culvert
8.5	2.49	0.97	bottom of culvert
9.3	2.54	0.92	bottom of culvert
10.3	2.66	0.8	bottom of culvert
11.4	2.72	0.74	base of wing wall
11.4	1.36	2.1	top of wing wall
11.7	1.35	2.11	top of wing wall
11.7	3.12	0.34	base of wing wall
12.9	3.25	0.21	base of culvert
14	3.35	0.11	base of culvert
15.1	3.43	0.03	base of culvert
16.1	3.46	0	base of culvert
16.9	3.43	0.03	base of wing wall
16.9	1.39	2.07	top of wing wall
17.3	1.24	2.22	top of head wall

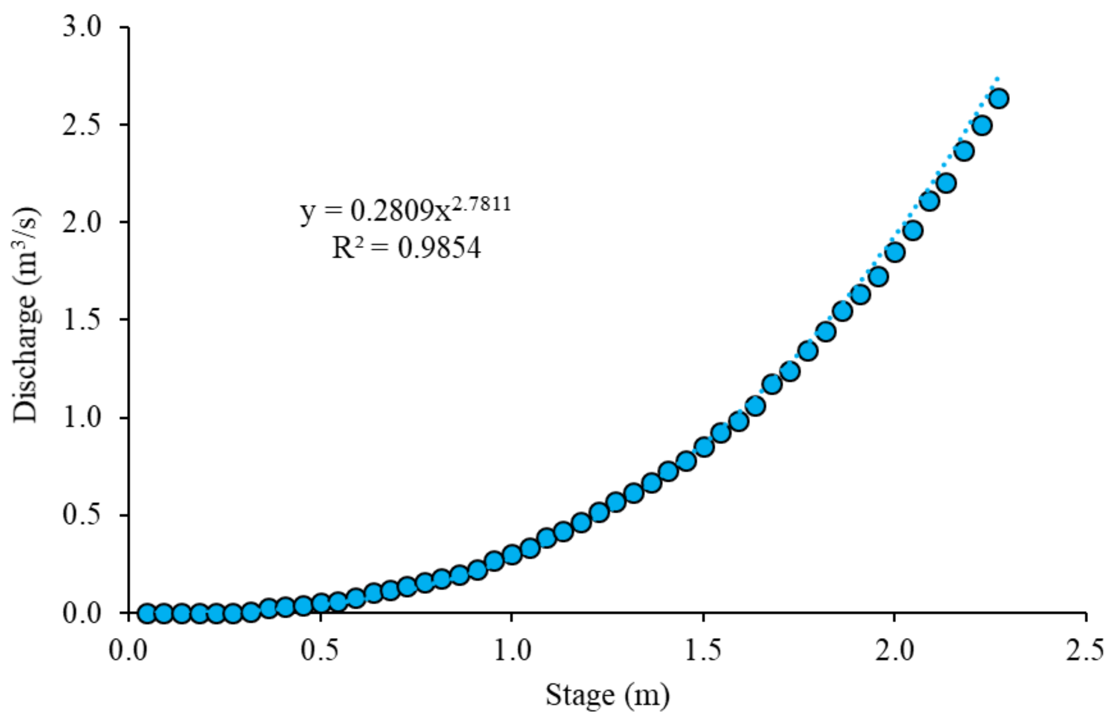
Appendix A-2. SS2 Cross-Section Data

Distance (m)	Rod (m)	Elevation (m)	Notes
0	0.09	2.35	left bank
1.8	0.79	1.65	
3.5	1.36	1.08	top of bank
4.3	2	0.44	mid bank
5	2.23	0.21	toe
5.4	2.26	0.18	water edge
6.6	2.27	0.17	
7.6	2.35	0.09	
8.5	2.39	0.05	
9	2.4	0.04	
9.8	2.42	0.02	thalweg
10.6	2.44	0	
11.3	2.35	0.09	
11.9	2.26	0.18	bar head
12.6	2.37	0.07	
13.1	2.26	0.18	water edge
13.5	1.44	1	top of bank
15.5	1.41	1.03	floodplain
16.45	1.45	0.99	hiking trail edge
17.05	1.46	0.98	middle of trail
17.9	1.46	0.98	edge of trail
20.2	1.53	0.91	floodplain
22.7	1.48	0.96	
24.6	1.6	0.84	top bank of chute
25.3	1.81	0.63	top of chute
26.1	1.78	0.66	top of chute
27	1.74	0.7	
28.15	1.53	0.91	top bank of chute
30.8	1.52	0.92	floodplain
34	1.61	0.83	
37.8	1.72	0.72	
40.8	1.91	0.53	
43	1.91	0.53	
44.2	1.76	0.68	base of terrace
45.4	1.47	0.97	
50	0.4	2.04	
52	0.24	2.2	top of terrace

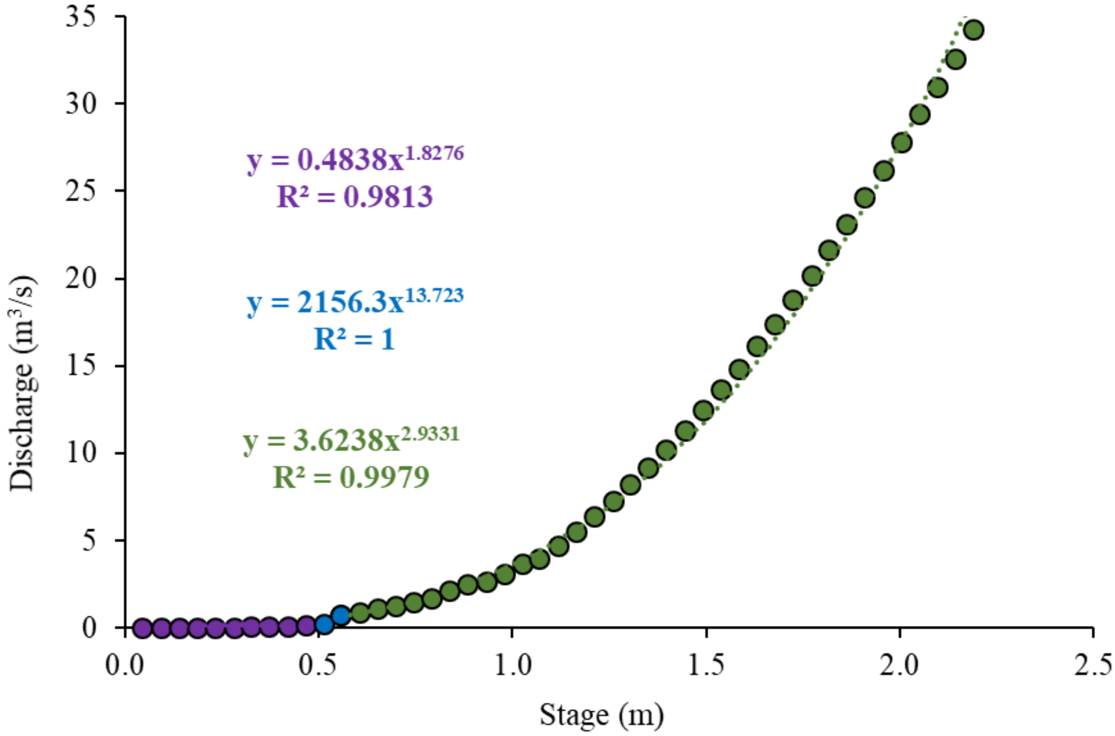
Appendix A-3. RD Weir Data

Water Surface Elevation (m)	Levelogger Stage (m)	Discharge (m^3/s)
367.31	0.75	0.00
367.44	0.88	2.00
367.59	1.03	6.33
367.74	1.19	12.84
367.89	1.34	20.91
368.05	1.49	29.20
368.20	1.64	41.60
368.81	1.80	90.42

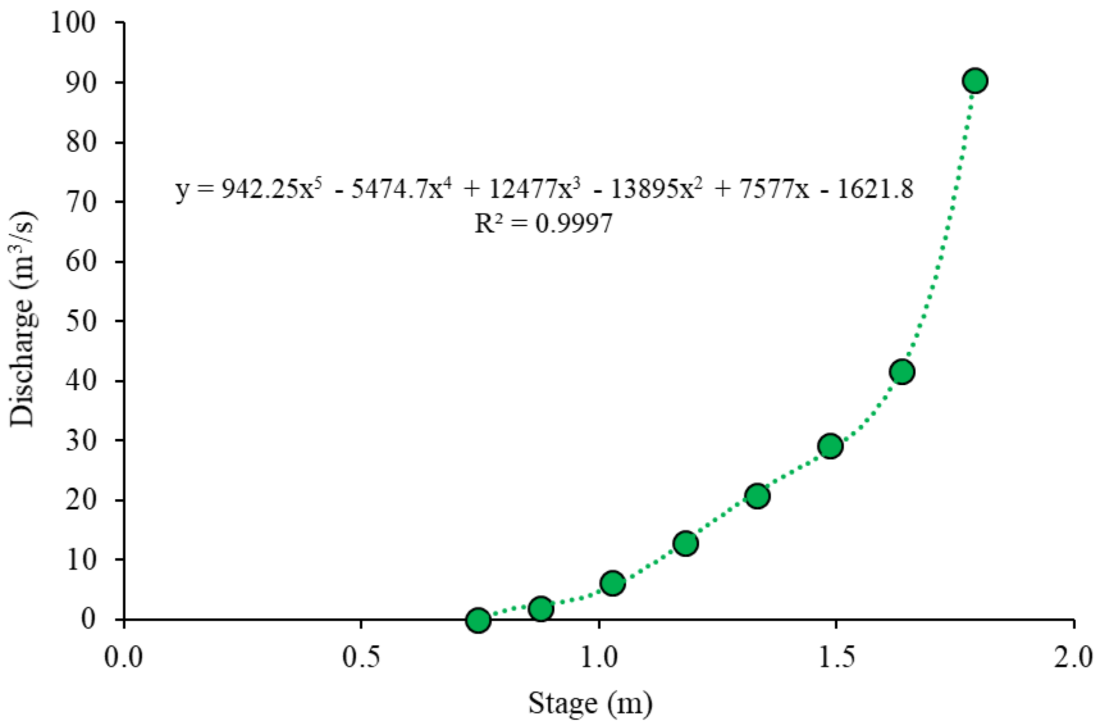
Appendix A-4. Rating Curve for FR-102



Appendix A-5. Rating Curve for SS2



Appendix A-6. Rating curve for RD



Appendix B. Percent Differences

Site	Date	Stage	Measured Q (m^3/s)	Estimated Q (m^3/s)	% Difference
FR-102	4/7/2017	0.29	0.008	0.009	-11.47
SS2	2/21/2017	0.20	0.073	0.026	64.86
	4/7/2017	0.54	0.573	0.459	20.02
	6/9/2017	0.52	0.236	0.273	-15.75
	7/13/2017	0.34	0.071	0.067	5.34
	10/27/2017	0.36	0.077	0.075	2.56
	11/17/2017	0.28	0.046	0.047	-2.34
	12/15/2017	0.26	0.027	0.041	-52.79
	1/19/2018	0.15	0.044	0.015	65.84
RD	4/7/2017	0.77	0.578	0.830	-43.47
	6/9/2017	0.75	0.127	0.118	7.34

Appendix C. Average Estimated Total Flow and Baseflow

	FR-102 (m^3/s)		SS2 (m^3/s)		RD (m^3/s)		SDS2 (m^3/s)	
Month	Total Flow	Baseflow	Total Flow	Baseflow	Total Flow	Baseflow	Total Flow	Baseflow
Mar-17	0.006	0.002	0.216	0.084	0.213	0.063	0.678	0.311
Apr-17	0.031	0.007	0.906	0.525	0.958	0.185	2.608	1.035
May-17	0.021	0.013	0.881	0.770	1.446	0.777	1.737	1.355
Jun-17	0.000	0.000	0.531	0.390	0.240	0.172	0.326	0.289
Jul-17	0.000	0.000	0.224	0.155	0.001	0.001	0.146	0.122
Aug-17	0.004	0.001	0.515	0.306	0.388	0.130	0.453	0.277
Sep-17	0.000	0.000	0.065	0.061	0.000	0.000	0.131	0.119
Oct-17	0.000	0.000	0.071	0.049	0.000	0.000	0.148	0.111
Nov-17	0.000	0.000	0.053	0.045	0.000	0.000	0.090	0.086
Dec-17	0.000	0.000	0.036	0.029	0.000	0.000	0.082	0.057
Jan-18	0.001	0.000	0.034	0.018	0.002	0.000	0.142	0.094
Feb-18	0.015	0.007	0.152	0.052	0.444	0.147	1.005	0.360
Mean	0.006	0.003	0.307	0.207	0.308	0.123	0.629	0.351
SD	0.010	0.004	0.323	0.242	0.459	0.219	0.795	0.413
CV (%)	160.759	167.083	105.224	116.766	149.401	178.300	126.356	117.428

Appendix D. Flow Conditions for the Valley Water Mill Reservoir

Date	Stage	Flow Condition
4/7/2017	0.77	Overflow
6/9/2017	0.75	Overflow
7/13/2017	0.55	No Overflow
10/27/2017	0.56	No Overflow
11/17/2017	0.00	No Overflow
12/15/2017	0.00	No Overflow
1/19/2018	0.00	No Overflow

Appendix E. Hydrograph Storm Event Data for 2/24/2018

	FR-102	SS2	RD	SDS2
Peak of Rain Event	2/24/2018 1:47 AM	2/24/2018 1:47 AM	2/24/2018 1:47 AM	2/24/2018 1:47 AM
Rising limb	2/24/2018 1:00 PM	2/24/2018 1:00 PM	2/24/2018 2:15 PM	2/24/2018 1:00 PM
Peak flow	2/24/2018 2:15 PM	2/24/2018 2:30 PM	2/24/2018 3:15 PM	2/24/2018 3:15 PM
falling limb	2/24/2018 5:30 PM	2/24/2018 6:00 PM	2/24/2018 5:00 PM	2/24/2018 6:30 PM
Approximate Duration	5 hours	5 hours	3 hours	6 hours
Approximate Lag time	13 hours	13 hours	14 hours	14 hours

Appendix F. Supplemental Discharge Measurements

Date	Site Name	Site Description	Dicharge (m^3/s)
7/13/2017	L1	Shotgun	0.01
10/27/2017	L2	Grandview	0.06
11/17/2017	L2	Grandview	0.00
11/17/2017	L1	Shotgun	0.00
12/15/2017	SDS0	SDS-above dam	0.05
12/15/2017	SDS3	SDS-below dam	0.05
12/15/2017	L2	Grandview	0.00

Appendix G. Coefficients of Variation for Triplicate Sample Dates

Appendix G-1. Coefficient of Variation for 3 successive sampling runs on 6/9/17.

Site	Cl CV (%)	Temp. CV (%)	DO CV (%)	SC CV (%)	pH CV (%)	TN CV (%)	TP CV (%)	TSS CV (%)
SS1	2.04	0.65	12.52	0.09	4.24	1.71	8.96	155.90
SS2	1.96	1.61	11.39	0.03	6.38	1.11	0.77	173.21
SS3	2.82	2.28	16.83	0.10	8.94	7.85	2.78	138.56
RD	1.71	0.50	3.59	0.16	1.55	0.47	8.79	32.83
SDS2	17.06	3.75	1.23	0.18	0.73	6.21	5.56	264.58
SDS1	0.86	3.39	2.81	0.39	0.63	2.37	5.49	229.13

Appendix G-2. Coefficient of Variations for 3 successive sampling runs on 7/13/17.

Site	Cl CV (%)	Temp. CV (%)	DO CV (%)	SC CV (%)	pH CV (%)	TN CV (%)	TP CV (%)	TSS CV (%)
SS1	0.88	1.25	6.96	0.18	4.31	1.15	26.27	88.19
SS2	1.56	1.85	12.69	0.36	5.95	2.96	9.43	110.22
SS3	0.55	3.33	12.40	0.22	7.62	2.94	8.39	98.97
RD	5.11	2.28	28.14	1.16	0.92	10.10	13.94	18.23
SDS2	1.08	3.23	1.16	0.36	0.95	7.43	8.08	173.21
SDS1	1.11	3.04	4.05	0.23	0.46	5.51	3.98	173.21

Appendix H. General Water Quality Data

Appendix H-1. SS1 General Water Quality Data

Date	Cl (mg/L)	pH	DO (mg/L)	SC (uS/cm)	Temp (°C)
4/7/2017	48.20	6.46	6.93	483.80	14.50
6/9/2017	45.66	7.11	7.37	552.50	15.55
7/13/2017	46.54	6.85	7.17	583.10	16.00
10/27/2017	44.17	6.78	7.10	590.10	16.20
11/17/2017	56.26	6.60	6.50	559.20	15.80
12/15/2017	47.42	6.72	7.97	582.20	14.90
1/19/2018	64.57	6.55	8.25	609.30	14.20
Min	44.17	6.46	6.50	483.80	14.20
Max	64.57	7.11	8.25	609.30	16.20
Mean	50.40	6.72	7.33	565.74	15.31
Median	47.42	6.72	7.17	582.20	15.55
SD	7.36	0.22	0.60	40.82	0.78
CV (%)	14.60	3.23	8.23	7.21	5.08

Appendix H-2. SS2 General Water Quality Data

Date	Cl (mg/L)	pH	DO (mg/L)	SC (uS/cm)	Temp (°C)
4/7/2017	42.89	6.31	7.17	486.60	14.40
6/9/2017	45.52	6.87	7.33	552.13	15.67
7/13/2017	46.75	7.04	7.66	585.57	16.20
10/27/2017	47.02	6.79	7.29	590.70	16.00
11/17/2017	54.36	6.66	6.32	558.80	15.60
12/15/2017	47.63	6.69	7.90	583.00	14.40
1/19/2018	63.83	6.46	8.70	610.90	14.20
Min	42.89	6.31	6.32	486.60	14.20
Max	63.83	7.04	8.70	610.90	16.20
Mean	49.71	6.69	7.48	566.81	15.21
Median	47.02	6.69	7.33	583.00	15.60
SD	7.14	0.25	0.73	40.50	0.85
CV (%)	14.35	3.70	9.76	7.15	5.56

Appendix H-3. SS3 General Water Quality Data

Date	Cl (mg/L)	pH	DO (mg/L)	SC (uS/cm)	Temp (°C)
4/7/2017	36.83	6.10	6.65	484.60	14.10
6/9/2017	45.76	6.87	7.41	553.27	15.80
7/13/2017	48.28	7.05	7.36	583.53	16.53
10/27/2017	48.01	7.15	6.81	589.10	15.40
11/17/2017	51.78	6.80	5.61	559.10	15.20
12/15/2017	49.28	6.79	7.89	588.10	13.30
1/19/2018	65.45	6.60	8.65	611.90	13.40
Min	36.83	6.10	5.61	484.60	13.30
Max	65.45	7.15	8.65	611.90	16.53
Mean	49.34	6.76	7.20	567.09	14.82
Median	48.28	6.80	7.36	583.53	15.20
SD	8.54	0.34	0.97	41.36	1.24
CV (%)	17.31	5.08	13.46	7.29	8.37

Appendix H-4. RD General Water Quality Data

Date	Cl (mg/L)	pH	DO (mg/L)	SC (uS/cm)	Temp (°C)
4/7/2017	63.73	7.27	7.27	416.50	13.60
6/9/2017	37.63	7.24	13.91	504.30	20.20
7/13/2017	38.72	7.40	6.00	477.17	27.40
10/27/2017	38.46	7.15	9.50	508.30	14.00
11/17/2017	56.92	7.21	10.74	530.40	10.80
12/15/2017	50.04	7.27	14.34	523.60	5.50
1/19/2018	Ice	Ice	Ice	Ice	Ice
Min	37.63	7.15	6.00	416.50	5.50
Max	63.73	7.40	14.34	530.40	27.40
Mean	47.58	7.26	10.29	493.38	15.25
Median	44.38	7.25	10.12	506.30	13.80
SD	11.09	0.08	3.40	41.95	7.63
CV (%)	23.30	1.17	33.05	8.50	50.05

Appendix H-5. SDS1 General Water Quality Data

Date	Cl (mg/L)	pH	DO (mg/L)	SC (uS/cm)	Temp (°C)
4/7/2017	31.59	7.42	10.12	328.60	13.20
6/9/2017	27.23	7.51	8.59	435.95	18.45
7/13/2017	33.39	7.60	7.53	476.40	21.43
10/27/2017	29.56	7.47	8.48	486.60	14.60
11/17/2017	24.25	7.40	9.22	471.50	13.40
12/15/2017	25.67	7.56	11.43	449.60	9.00
1/19/2018	36.07	7.19	11.92	486.20	6.00
Min	24.25	7.19	7.53	328.60	6.00
Max	36.07	7.60	11.92	486.60	21.43
Mean	29.68	7.45	9.61	447.84	13.73
Median	29.56	7.47	9.22	471.50	13.40
SD	4.28	0.14	1.62	55.84	5.24
CV (%)	14.42	1.81	16.84	12.47	38.19

Appendix H-6. SDS2 General Water Quality Data

Date	Cl (mg/L)	pH	DO (mg/L)	SC (uS/cm)	Temp (°C)
4/7/2017	46.81	7.27	7.27	416.50	13.60
6/9/2017	24.93	7.50	8.81	450.10	18.93
7/13/2017	31.34	7.62	7.67	477.47	21.77
10/27/2017	30.57	7.47	8.39	491.90	14.50
11/17/2017	34.23	7.36	9.44	472.70	13.20
12/15/2017	26.60	7.50	11.68	450.60	8.80
1/19/2018	37.48	7.07	12.11	487.60	5.80
Min	24.93	7.07	7.27	416.50	5.80
Max	46.81	7.62	12.11	491.90	21.77
Mean	33.13	7.40	9.34	463.84	13.80
Median	31.34	7.47	8.81	472.70	13.60
SD	7.38	0.18	1.89	26.52	5.47
CV (%)	22.28	2.48	20.23	5.72	39.66

Appendix I. Measured Discharge, Nutrient, and Sediment Data

Appendix I-1. SS1 Discharge, Nutrient, and Sediment Data

Date	Dicharge (m^3/s)	TN (mg/L)	TP (ug/L)	TSS (mg/L)	TN Load (kg/day)	TP Load (kg/day)	TSS Load (kg/day)
4/7/2017	0.57	1.75	26.00	8.00	85.46	1.27	390.66
6/9/2017	0.23	1.88	24.30	1.25	37.34	0.48	24.83
7/13/2017	0.08	1.66	23.80	1.50	10.93	0.16	9.90
10/27/2017	0.08	1.45	20.10	1.30	9.64	0.13	8.62
11/17/2017	0.05	1.58	20.00	ND	6.30	0.08	ND
12/15/2017	0.03	1.80	43.70	7.00	4.19	0.10	16.33
1/19/2018	0.06	1.59	36.30	25.30	7.77	0.18	123.29
Min	0.03	1.45	20.00	1.25	4.19	0.08	8.62
Max	0.57	1.88	43.70	25.30	85.46	1.27	390.66
Mean	0.15	1.67	27.74	7.39	23.09	0.34	95.60
Median	0.08	1.66	24.30	4.25	9.64	0.16	20.58
SD	0.19	0.15	8.91	9.28	29.71	0.43	151.02
CV (%)	125.50	8.72	32.13	125.57	128.65	125.47	157.96

Appendix I-2. SS2 Discharge, Nutrient, and Sediment Data

Date	Dicharge (m^3/s)	TN (mg/L)	TP (ug/L)	TSS (mg/L)	TN Load (kg/day)	TP Load (kg/day)	TSS Load (kg/day)
2/21/2017	0.07	ND	ND	ND	ND	ND	ND
4/7/2017	20.24	1.71	29.00	7.70	84.69	1.44	381.37
6/9/2017	8.12	1.89	24.00	<0.5	37.48	0.48	<9.95
7/13/2017	2.70	1.68	19.60	1.22	11.06	0.13	8.07
10/27/2017	2.71	1.40	20.40	2.70	9.25	0.14	17.90
11/17/2017	1.63	1.51	20.00	ND	6.02	0.08	ND
12/15/2017	0.95	1.45	30.30	7.50	3.39	0.07	17.50
1/19/2018	1.99	1.57	69.20	<0.5	7.67	0.34	<2.44
Min	0.03	1.39	19.60	<0.5	3.39	0.07	<2.44
Max	0.57	1.89	69.20	7.70	84.69	1.44	381.37
Mean	4.80	1.60	30.36	3.19	22.80	0.38	72.87
Median	2.35	1.57	24.00	1.96	9.25	0.14	13.72
SD	6.69	0.17	17.67	3.56	29.59	0.49	151.25
CV (%)	139.35	10.59	58.20	111.71	129.83	128.42	207.56

Appendix I-3. SS3 Discharge, Nutrient, and Sediment Data

Date	Dicharge (m^3/s)	TN (mg/L)	TP (ug/L)	TSS (mg/L)	TN Load (kg/day)	TP Load (kg/day)	TSS Load (kg/day)
4/7/2017	0.57	1.77	35.00	8.30	87.67	1.73	411.09
6/9/2017	0.23	1.95	24.70	1.67	38.74	0.49	33.10
7/13/2017	0.08	1.63	18.80	1.17	10.77	0.12	7.70
10/27/2017	0.08	1.40	22.80	2.00	9.25	0.15	13.26
11/17/2017	0.05	1.51	23.00	ND	6.02	0.09	ND
12/15/2017	0.03	1.45	23.50	2.00	3.39	0.05	4.67
1/19/2018	0.06	1.59	30.00	6.70	7.77	0.15	32.65
Min	0.03	1.40	18.80	1.17	3.39	0.05	4.67
Max	0.57	1.95	35.00	8.30	87.67	1.73	411.09
Mean	0.16	1.62	25.40	3.64	23.37	0.40	83.74
Median	0.08	1.59	23.50	2.00	9.25	0.15	22.95
SD	0.20	0.19	5.38	3.05	30.75	0.61	160.83
CV (%)	126.44	11.93	21.17	83.78	131.55	151.90	192.05

Appendix I-4. RD Discharge, Nutrient, and Sediment Data

Date	Dicharge (m^3/s)	TN (mg/L)	TP (ug/L)	TSS (mg/L)	TN Load (kg/day)	TP Load (kg/day)	TSS Load (kg/day)
4/7/2017	0.58	1.49	105.00	15.00	74.47	5.25	749.72
6/9/2017	0.13	1.18	14.70	3.83	13.59	0.17	44.23
7/13/2017	No flow	0.47	17.00	3.17	No flow	No flow	No flow
10/27/2017	0.04	0.89	14.00	<0.5	3.17	0.05	<1.78
11/17/2017	No flow	0.97	14.00	ND	No flow	No flow	No flow
12/15/2017	No flow	0.95	13.00	5.00	No flow	No flow	No flow
1/19/2018	Ice	Ice	28.00	Ice	Ice	Ice	Ice
Min	0.00	0	13.00	<0.5	0.00	0.00	0.00
Max	0.58	1.49	105.00	15.00	74.47	5.25	749.72
Mean	0.11	0.99	29.39	5.40	13.03	0.78	113.68
Median	0.00	0.96	14.70	3.83	0.00	0.00	0.00
SD	0.21	0.34	33.74	5.68	27.54	1.97	280.95
CV (%)	199.65	34.00	114.82	105.13	211.33	252.29	247.15

Appendix J. Pearson's Correlation Coefficient Matrices

Appendix J-1. Pearson's Correlation Coefficient Matrix for SS1

		Discharge	Temperature	DO	pH	SC	Cl	TN	TSS	TP
Discharge	Coefficient	1	-0.367	-0.306	-0.254	-0.921**	-0.246	0.394	-0.108	-0.203
	P-value		0.418	0.504	0.582	0.003	0.595	0.382	0.838	0.662
Temperature	Coefficient	-0.367	1	-0.594	0.570	0.203	-0.560	-0.337	-0.826*	-0.693
	P-value	0.418		0.160	0.182	0.663	0.192	0.460	0.043	0.084
DO	Coefficient	-0.306	-0.594	1	0.034	0.542	0.338	0.217	0.751	0.852*
	P-value	0.504	0.160		0.942	0.209	0.458	0.640	0.085	0.015
pH	Coefficient	-0.254	0.570	0.034	1	0.249	-0.549	0.368	-0.631	-0.204
	P-value	0.582	0.182	0.942		0.591	0.202	0.417	0.179	0.661
SC	Coefficient	-0.921**	0.203	0.542	0.249	1	0.307	-0.432	0.272	0.284
	P-value	0.003	0.663	0.209	0.591		0.503	0.333	0.603	0.538
Cl	Coefficient	-0.246	-0.560	0.338	-0.549	0.307	1	-0.271	0.977**	0.283
	P-value	0.595	0.192	0.458	0.202	0.503		0.556	0.001	0.539
TN	Coefficient	0.394	-0.337	0.217	0.368	-0.432	-0.271	1	-0.167	0.378
	P-value	0.382	0.460	0.640	0.417	0.333	0.556		0.752	0.403
TSS	Coefficient	-0.108	-0.826*	0.751	-0.631	0.272	0.977**	-0.167	1	0.584
	P-value	0.838	0.043	0.085	0.179	0.603	0.001	0.752		0.224
TP	Coefficient	-0.203	-0.693	0.852*	-0.204	0.284	0.283	0.378	0.584	1
	P-value	0.662	0.084	0.015	0.661	0.538	0.539	0.403	0.224	

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Appendix J-2. Pearson's Correlation Coefficient Matrix for RD

		Discharge	Temperature	DO	pH	SC	Cl	TN	TSS	TP
Discharge	Coefficient	1	-0.040	-0.335	0.007	-0.887*	0.604	0.805	0.919*	0.973**
	P-value		0.941	0.516	0.990	0.018	0.204	0.053	0.027	0.001
Temperature	Coefficient	-0.040	1	-0.538	0.580	-0.309	-0.562	-0.439	-0.216	-0.072
	P-value	0.941		0.271	0.228	0.552	0.246	0.384	0.727	0.893
DO	Coefficient	-0.335	-0.538	1	-0.434	0.657	-0.134	0.229	-0.260	-0.460
	P-value	0.516	0.271		0.390	0.157	0.800	0.662	0.673	0.359
pH	Coefficient	0.007	0.580	-0.434	1	-0.368	-0.067	-0.440	0.194	0.104
	P-value	0.990	0.228	0.390		0.473	0.899	0.383	0.754	0.845
SC	Coefficient	-0.887*	-0.309	0.657	-0.368	1	-0.397	-0.443	-0.845	-0.912*
	P-value	0.018	0.552	0.157	0.473		0.436	0.378	0.071	0.011
Cl	Coefficient	0.604	-0.562	-0.134	-0.067	-0.397	1	0.611	0.931*	0.700
	P-value	0.204	0.246	0.800	0.899	0.436		0.197	0.022	0.122
TN	Coefficient	0.805	-0.439	0.229	-0.440	-0.443	0.611	1	0.726	0.706
	P-value	0.053	0.384	0.662	0.383	0.378	0.197		0.165	0.117
TSS	Coefficient	0.919*	-0.216	-0.260	0.194	-0.845	0.931*	0.726	1	0.944*
	P-value	0.027	0.727	0.673	0.754	0.071	0.022	0.165		0.016
TP	Coefficient	0.973**	-0.072	-0.460	0.104	-0.912*	0.700	0.706	0.944*	1
	P-value	0.001	0.893	0.359	0.845	0.011	0.122	0.117	0.016	

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

Appendix J-3. Pearson's Correlation Coefficient Matrix for SDS2

		Discharge	Temperature	DO	pH	SC	Cl	TN	TSS	TP
	Coefficient	1	0.108	-0.577	-0.240	-0.796*	0.737	0.524	0.980**	0.982**
Discharge	P-value		0.817	0.175	0.604	0.032	0.059	0.227	0.001	0.000
	Coefficient	0.108	1	-0.809*	0.752	-0.071	-0.263	0.040	-0.021	0.261
Temperature	P-value	0.817		0.028	0.051	0.879	0.569	0.933	0.969	0.572
	Coefficient	-0.577	-0.809*	1	-0.435	0.305	-0.259	-0.041	-0.510	-0.682
DO	P-value	0.175	0.028		0.329	0.507	0.575	0.931	0.301	0.092
	Coefficient	-0.240	0.752	-0.435	1	0.006	-0.657	-0.260	-0.324	-0.087
pH	P-value	0.604	0.051	0.329		0.990	0.109	0.573	0.531	0.852
	Coefficient	-0.796*	-0.071	0.305	0.006	1	-0.367	-0.628	-0.751	-0.810*
SC	P-value	0.032	0.879	0.507	0.990		0.417	0.131	0.085	0.027
	Coefficient	0.737	-0.263	-0.259	-0.657	-0.367	1	0.280	0.840*	0.685
Cl	P-value	0.059	0.569	0.575	0.109	0.417		0.543	0.036	0.089
	Coefficient	0.524	0.040	-0.041	-0.260	-0.628	0.280	1	0.412	0.499
TN	P-value	0.227	0.933	0.931	0.573	0.131	0.543		0.417	0.254
	Coefficient	0.980**	-0.021	-0.510	-0.324	-0.751	0.840*	0.412	1	0.954**
TSS	P-value	0.001	0.969	0.301	0.531	0.085	0.036	0.417		0.003
	Coefficient	0.982**	0.261	-0.682	-0.087	-0.810*	0.685	0.499	0.954**	1
TP	P-value	0.000	0.572	0.092	0.852	0.027	0.089	0.254	0.003	

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)