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# Water Quality Trends and Nutrient Loads for the Watershed Research and Education Center in Northwest Arkansas, 2009-2012

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WATER QUALITY TRENDS AND NUTRIENT LOADS  
FOR THE WATERSHED RESEARCH AND EDUCATION CENTER  
IN NORTHWEST ARKANSAS, 2009-2012

WATER QUALITY TRENDS AND NUTRIENT LOADS  
FOR THE WATERSHED RESEARCH AND EDUCATION CENTER  
IN NORTHWEST ARKANSAS, 2009-2012

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

By

John Thomas Metrailler  
University of The South  
Bachelor of Science in Natural Resources, 2004

August 2012  
University of Arkansas

## ABSTRACT

Nitrogen, phosphorus, and sediment transport is a concern for Northwest Arkansas due to high exports through riverine discharge. Urban, agricultural, and pastured watersheds have been associated with increased N, P, and sediment concentrations when compared to forested catchments. The objective of this study was to evaluate discharge and nutrient loads associated with a small urban, agricultural (row crop), wetland influenced, and pasture/farmland sub-catchment within four ephemeral drainages and located at the Watershed Research and Education Center in Fayetteville, AR. Samples were collected during base flow conditions and periodic storm flow conditions from 2009-2012. Flow adjusted concentration trends were used to develop seasonal and annual constituent loads for each catchment. A strong correlation between discharge and N, P, and sediment ( $r > 0.896$ ,  $p < 0.001$ ) occurred throughout all ephemeral drainages. The largest yields for N, P, and sediment were associated with the pastured/farmland sub-catchment, while high yields were generated from the agricultural sub-catchment. The lowest N and P yields were generated from the urban sub-catchment, and the lowest sediment yield generated from the wetland influenced sub-catchment. Results of this study reveal the relationship between small watershed scale (<140 ha) landuse and its effect on N, P, and sediment transport and storage.

This thesis is approved for recommendation  
to the Graduate Council.

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## TABLE OF CONTENTS

**Abstract**

**Table of Contents**

|   |    |
|---|----|
| <b>Introduction</b>                       | 1  |
| <b>Methodology</b>                        | 3  |
| Study Site Description                    | 3  |
| Monitoring Stations                       | 5  |
| Water-Quality Data                        | 7  |
| Staff Gage Heights                        | 8  |
| Daily Discharge Estimations               | 9  |
| Trend Analysis                            | 11 |
| Load Estimations                          | 12 |
| Storage Calculation                       | 13 |
| Livestock Records                         | 14 |
| Hay Production and Atmospheric Deposition | 16 |
| <b>Results</b>                            | 17 |
| Discharge                                 | 17 |
| Water Balance                             | 21 |
| Flow Adjusted Concentraions Trends        | 24 |



|                             |    |
|-----------------------------|----|
| Chloride                    | 24 |
| Ammonia                     | 24 |
| Nitrate                     | 28 |
| Total Nitrogen              | 28 |
| Soluble Reactive Phosphorus | 29 |
| Total Phosphorus            | 30 |
| Total Suspended Solids      | 31 |
| Estimated Loads             | 31 |
| Chloride                    | 32 |
| Ammonia                     | 33 |
| Nitrate                     | 36 |
| Total Nitrogen              | 37 |
| Soluble Reactive Phosphorus | 39 |
| Total Phosphorus            | 40 |
| Total Suspended Solids      | 41 |
| Riverine Constituent Export | 43 |
| Watershed Mass Balance      | 47 |
| <b>Discussion</b>           | 49 |
| Chloride                    | 49 |
| Nitrogen                    | 50 |
| Phosphorus                  | 53 |
| Total Suspended Solids      | 55 |

|                     |    |
|---------------------|----|
| <b>References</b>   | 58 |
| <b>Appendix I</b>   | 61 |
| <b>Appendix II</b>  | 68 |
| <b>Appendix III</b> | 75 |

## INTRODUCTION

Nutrients and sediments within fluvial channels generally increase as human influence increases within the watershed. For example, nitrogen (N) and phosphorus (P) concentrations in stream water increase with the percentage of land use associated with row crops (Jordan et al., 1986), pasture (Haggard et al., 2003; Migliaccio et al., 2007; Giovannetti et al., 2012), and urban development (Paul and Meyer, 2001; Toland et al., 2012). The nutrient contents within bed material of the fluvial channel are often related to concentrations in the water column, and it has also been shown to be influenced by watershed land uses (Giovannetti et al., 2012). Nutrients in fluvial channels result from the watershed sources, transport potential, and landscape management which influences the transport of water, whereas sediments are typically delivered from landscape erosion and within fluvial channel processes.

The sources of nutrients at a watershed scale would include the import of feed, fiber, and fertilizers, and the transport pathways would be surface runoff during episodic rainfall events and subsurface flow return (i.e., interflow and groundwater). The transport pathways for individual constituents will vary based on chemical and physical nature, where runoff is the primary pathway for sediment and sediment-associated constituents and subsurface flow for nitrate ( $\text{NO}_3$ ). For example, increased N fertilization can result in increases in groundwater  $\text{NO}_3$  delivery within small pastured watersheds (Owens et al., 2008), because of the mobility of  $\text{NO}_3$ . Nitrate also has the opportunity to be lost through denitrification, unlike P which would be stored in deposited sediment and microbial organisms within the fluvial channel. These nutrients need to be managed at the watershed scale to reduce transport to streams, and employing best management practices (BMPs) within the landscape and the riparian corridor might reduce the source and transport potential. However, Meals (1996) suggested that watershed scale response to BMP implementation was not simply the sum of the implementation of individual edge-of-field changes.

Best management practices generally target either the source and or potential pathways for nutrients and sediment to be delivered to streams. The best examples might be riparian restoration, buffers and filter strips which reduce delivery by promoting infiltration of runoff waters through physical screening and associated sedimentation (Lee et al., 2003). Nitrate removal within riparian zones results from vegetation uptake and microbial denitrification, but can also relate to mixing with  $\text{NO}_3$  depleted groundwater (Hill, 1996; Peter et al., 2012). The removal rates through riparian areas at individual fields may range from 5% to 30%/m (Sabater et al., 2003). There are many other BMPs that may reduce the source and transport pathways, especially farm ponds within agricultural settings.

Riparian buffers apply to both agricultural and urban landscapes, but urban BMPs often focus more on a runoff reduction theory. The typical urban BMPs might include rain barrels, rain gardens, green roofs, green spaces, and storm water retention basins, where these BMPs reduce delivery through the capture, infiltration, and evaporation of storm water. Best management applications to residential and urban development may decrease nutrient fluxes associated with urban and suburban watersheds (Groffman et al., 2004). The difficulty with existing urban development would be the space needs to construct BMPs, which requires urban planning to include BMPs in future development.

The source of the nutrients at the landscape scale would be generally tied to the import of feed, fertilizer and legume fixation, and the management of nutrients has shifted over the last decade from strict agronomics N needs to a balance between agronomic N needs and environmental P concerns. This concern arises with the use of animal manure as fertilizer, because it has a low N:P ratio resulting in the over application of P from a strict plant requirements perspective when meeting agronomic N needs (Shreve et al., 1995). There are practices which address the potential for nutrient loss from the source, such chemical amendments to animal manure to reduce soluble nutrients and improve the N:P ratio

(Shreve et al., 1995). The balance of agronomic N needs could be supplied through inorganic fertilizers (Harmel et al., 2009) or N fixation by legumes.

Understanding the nutrient sources and effects of BMPs is an integral part of watershed management and education. The Watershed Research and Education Center (WREC) was founded in 2006 with the comprehensive goal of providing opportunity for research, demonstration and education on agricultural conservation practices and urban development BMPs. This study presents an investigation into the nutrient mass balance and changes over time at WREC from January 2009 through April 2012. The specific objectives of this study were to (1) evaluate discharge in and out, (2) determine water quality (i.e., chemical concentrations) changes over time, (3) quantify nutrient and sediment loads in and out, and (4) discuss the retention and export of nutrients considering landscape inputs, riverine inputs and riverine outputs.

## **METHODOLOGY**

### **Study Site Descriptions**

The Watershed Research and Education Center (WREC) is located approximately 2.4 km northwest of the University of Arkansas at the Arkansas Agriculture Research and Extension Center (AAREC), and its physical borders are Deane Street to the south, Garland Avenue (Highway 112) to the east, Knapp Street to the north, and Interstate 540 to the west. The Division's WREC is 121 ha, but the actual drainage area of the watershed outlet is 191 ha. The WREC watershed is a part of the Hamstring Creek Hydrologic Unit Code (HUC) 12 and the Illinois River Watershed HUC8. Land use and land cover within the entire drainage area is comprised of pasture (70 percent), commercial agricultural facilities (16 percent), agricultural crop land (4 percent), urban development (7 percent), and roads and

waterways (3 percent). Many agricultural facilities and field sites dedicated to ongoing research projects are included within boundaries of WREC (Figure 1).

An Agroforestry Experimental Field (AEF) occupies approximately 5 ha in the northwest section of the watershed. The AEF was planted in fall 1999 through fall 2000 with rows of Northern red oak, Eastern black walnut, and pecan trees with orchardgrass seeded in the alleys. Soil water samplers and groundwater monitoring wells were installed between 2000 and 2002. The agroforestry research was a joint venture between the USDA Agricultural Research Service, the University of Arkansas, and the Division of Agriculture. The research focus was on tree growth, survival, and production across different fertilization schemes.

The Department of Poultry Science maintains facilities on approximately 14 ha in the north central portion of the watershed. These facilities include a hatchery, genetics unit, pullet rearing facility, battery brooder, caged layer house, broiler breeder houses, and turkey houses. The department also maintains a pilot poultry processing plant for teaching processing techniques and food safety research, which has a 0.1 ha footprint within WREC. A poultry feed mill conducting specific dietary research is also located in this area.

The Pauline Whitaker Animal Science Center and Arena, located in the northeast corner of WREC off Knapp Street, is maintained by the Department of Animal Sciences. This 16 ha facility consists of livestock barns and fenced grazing areas for horses, sheep, cattle, and pigs. The number of animal units per area or field varies annually. The majority of the lands are currently used for horse grazing at relatively low densities.

WREC was remodeled in 2008 to establish a more research oriented farm management strategy. Fence lines were removed, fields were plowed under, and a riparian buffer zone was established along

portions of the drainages. The fence lines were then reestablished to follow topographic boundaries and delineate the watershed into sub-catchments. The intent was to allow edge-of-field monitoring at WREC to be tied to one unique land management and farming practice, so nutrient and sediment loads could be estimated in the future.

### **Monitoring Stations**

Three ephemeral to intermittent first order streams are inflows into WREC, including the North Research Branch (site 1), South Research Branch (site 2), and Wetland Branch (site 3). North Research Branch, site 1, is surrounded by pasture within WREC. The areas outside WREC draining to this site include row crops, impervious surfaces, and a recreational facility (Agricultural Park). South Research Branch, site 2, is surrounded by pasture and drains primarily urban development; the majority of the site 2 watershed outside WREC boundaries contains single family homes and apartment complexes. The Wetland Branch, site 3, is fed by springs and the upstream area remains wet year round. This inflow also drains research facilities at AAREC including rooftops, paved surfaces, and gravel areas (Figure 1).

The convergence of the North and South Branch produces the main stem of Research Branch which flows west through WREC. The main stem is initially monitored at Research Branch at Gifford Avenue (site 4). Site 4 is located approximately 45 m downstream of the confluence between the north and south branches. A riparian zone downstream of site 4 was installed in spring 2009 (north portion) and 2010 (south portion). The north portion restoration effort mimicked three different techniques, including (1) an urban buffer zone with 2-5 cm diameter trees, (2) an urban buffer zone with <2.5 cm diameter trees, and (3) a naturalized area. The south portion restoration effort represented a typical agricultural three zone buffer, with <2 cm diameter trees planted mechanically. The north buffer is approximately 30 m wide and 280 m along Research Branch, and the south buffer is approximately 40 m wide and 190 m along Research Branch (Figure 1).

Approximately 365 m downstream of site 4 and the riparian restoration project, the Wetland Branch enters the main channel. The Upper Outlet Culvert of Research Branch (site 5) is located approximately 520 m downstream of the confluence between the Wetland Branch and Research Branch. The Research Branch Outlet (site 6) is the most downstream station located approximately 240 m west of site 5. Research Branch Outlet is a second order intermittent stream that drains WREC. Research Branch continues flowing west where it joins Hamstring Creek which drains to Clear Creek and eventually the Illinois River. The Illinois River flows into Lake Tenkiller and eventually drains to the Arkansas River (Figure 1).



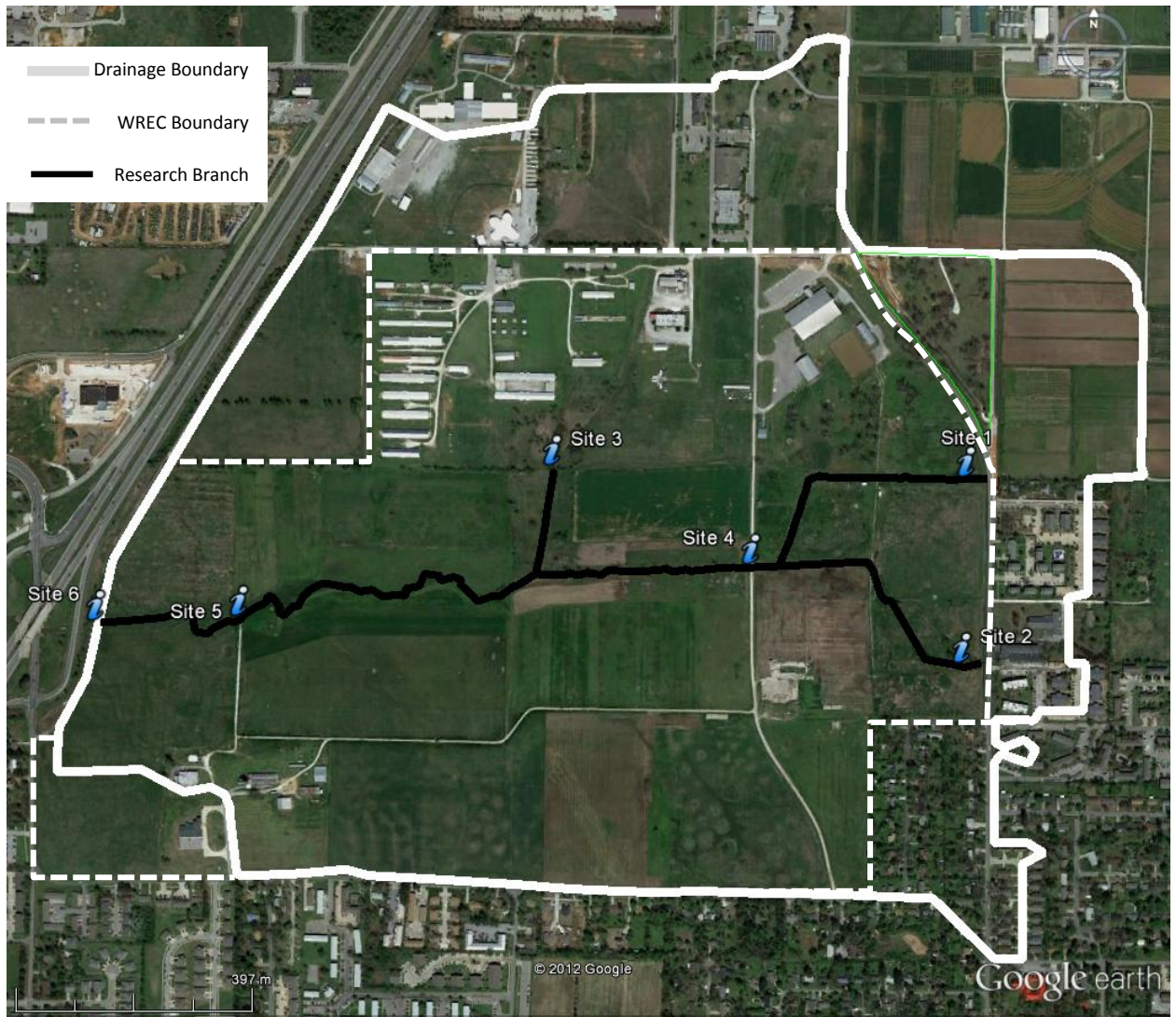


Figure 1. Aerial image of the Watershed Research Education Center catchment area and property boundary with monitoring site locations stream locations.

### Water-Quality Data

Water samples and field measurements were collected by the Arkansas Water Resources Center (AWRC) on a weekly basis and during storm events from March 6, 2009 to April 30, 2012. Field measurements including pH, dissolved oxygen (mg/L), conductivity ( $\mu\text{S}/\text{cm}$ ), and temperature ( $^{\circ}\text{C}$ ) were

taken using a YSI 85 (Columbus, Ohio), and Oakton pH Testr 30 (Vernon Hills, Illinois). The water samples were collected in acid-washed HDPE bottles, which were field rinsed three times with stream water at each sampling location before the environmental sample was collected. These samples were processed by the AWRC Water Quality Lab and then analyzed for total dissolved ammonia ( $\text{NH}_4\text{-N}$ ), nitrate ( $\text{NO}_3\text{-N}$ ), total nitrogen (TN), total phosphorus (TP), soluble reactive phosphorus (SRP), total suspended solids (TSS), turbidity (NTU), and chloride (Cl). The lab is accredited for the analysis of these constituents in water samples by the Arkansas Department of Environmental Quality (ADEQ), and information on methods can be found at <http://www.uark.edu/depts/awrc/waterqualitylab.htm>. These measurements along with the date, time, and staff gage height were organized into a Microsoft excel spreadsheet for data processing.

### **Staff Gage Heights**

Staff gage heights were recorded by the United States Geological Survey (USGS) in fifteen minute increments for site 1 from April 30, 2008 to September 2, 2010. The USGS recorded site 1 as the “North Research Branch at the WREC at Fayetteville, AR” with the station identification number 071948135. Staff gage heights were recorded by the USGS in fifteen minute increments for site 2 from May 19, 2008 to September 2, 2010. The USGS recorded site 2 as the “South Research Branch at the WREC at Fayetteville, AR” with the station identification number 071948140. Staff gage heights were recorded by the USGS in fifteen minute increments for site 3 from April 30, 2008 to September 2, 2010. The USGS recorded site 3 as the “Wetland Branch at the WREC at Fayetteville, AR” with the station identification number 071948150. Sites 1, 2, and 3 contain v-notch weirs that pool water upstream where the staff gage is located requiring offsets, which were provided by the USGS. Staff gage heights were recorded by the USGS in fifteen minute increments for site 6 from April 1, 2008 to September 2, 2010. The USGS recorded site 6 as the “Research Branch Outlet at the WREC at Fayetteville, AR” with

the station identification number 07194816. Site 6 contains four 1.22 m corrugated culverts and has a staff gages upstream and downstream of the culverts. Files containing this information were obtained from the USGS on May 16, 2012.

The AWRC began managing the monitoring stations after the USGS contract ended in September 2009. Two additional monitoring stations were installed as sites 4 and 5. Site 4 is located at a 1.05 m diameter concrete culvert known as Research Branch at Gifford Avenue. Site 5 is located at a 0.91 m concrete culvert known as the Upper Outlet Culvert of Research Branch. Sites 4 and 5 have monitoring stations on the upstream entrance and downstream exit of the culverts. The monitoring stations continued recording staff gage heights in fifteen minute increments on September 7, 2010 for sites 1 and 2. Offsets of 0.18 and 0.25 m were applied to sites 1 and 2, respectively, to account for the pooling effect of the v-notch weirs. Staff gage heights for sites 4 and 5 were recorded starting September 3, 2010 and September 8, 2010, respectively. A break in monitoring did not occur for the staff gage heights of sites 3 and 6 as recordings continued on September 3, 2010. An offset of 0.13 m was applied to site 3 to account for the pooling effect of the v-notch weir. The AWRC continues to manage the WREC monitoring stations and downloads the staff gage height recordings on a weekly basis.

### **Daily Discharge Estimations**

Discharge measurements for sites 1, 2, 3, and 6 were recorded by the USGS between June 9, 2008 and April 15, 2010. Twenty-eight discharge measurements were recorded for site one ranging from staff gage height 0.03 to 0.48 m with corresponding discharges from 0.005 to 2.89 cfs, respectively. Flows below 0.03 m were considered negligible for site one. Twenty-two discharge measurements were recorded for site two ranging from staff gage height 0.02 to 0.26 m with corresponding discharges from 0.001 to 1.09 cfs, respectively. Flows below 0.04 m were considered negligible for site two. Twenty-six

discharge measurements were recorded for site three ranging from staff gage height 0.06 to 0.42 m with corresponding discharges from 0.006 to 0.9 cfs, respectively. Flows below 0.05 m were considered negligible for site three. Twenty discharge measurements were recorded for site six ranging from staff gage height 0.21 to 0.80 m with corresponding discharges from 0.11 to 40.4 cfs, respectively. Flows below 0.05 m were considered negligible for site six.

Based on these discharge measurements, a rating curve was created by the USGS for sites 1, 2, 3, and 6. Estimations for each site were calculated for every hundredth of a foot starting at 0.00 m. The discharge estimations ranged up to 0.62 m corresponding with 3.30 cfs for site 1, 0.40 m corresponding with 1.10 cfs for site 2, 0.48 m corresponding with 1.60 cfs for site 3, and 1.02 m corresponding with 85.3 cfs for site 6. After plotting the USGS discharge estimation (cfs) against the corresponding staff gage height (m), a second order polynomial equation trendline was created in excel for sites 1, 2, 3, and 6. The trendline equation was used with the Microsoft excel function (=if) to exclude the negligible flows below 0.03 m, 0.04 m, and 0.05 m, for sites 1, 2, and 3, respectively. The trendline equation was not as accurate for the culverted site 6. For site 6, the Microsoft excel function (=round) was used to round the recorded staff gage heights to the hundredth decimal place. Then, the Microsoft excel function (=lookup) was used to couple the rounded stage heights to the corresponding USGS discharge estimation. This method was used for site 6 staff gage height recordings less than or equal to 1.02 m, the maximum staff gage height used by the USGS for discharge estimation. For site 6 staff gage heights exceeding 1.02 m, the site 6 trendline equation was used to estimate discharge.

Using these methods for sites 1, 2,3, and 6, a discharge estimation was created for each 15 minute increment staff gage height recording. The 15 minute increment discharge estimations were averaged on a daily basis using the excel function (=averageif) to create an average daily flow for each

study day containing staff gage height recordings. The average daily discharges were coupled to the corresponding days constituent data using the Microsoft excel function (=lookup).

### **Trend Analysis**

The trends in constituent concentrations were evaluated following the procedures by White et al. (2004). The average daily discharges (cfs) and corresponding days constituent data (mg/L) were  $\text{Log}_{10}$  transformed using the Microsoft excel function (=Log10) in order to account for the log normal distribution of water quality data and to minimize the effect of outliers within the data (Hirsch et al., 1991; Lettenmaier et al., 1991). These values were inserted into SigmaPlot 12.0 and plotted with  $\text{Log}_{10}$  discharge on the x-axis and  $\text{Log}_{10}$  constituent on the y-axis. The LOESS Smoother 2D application with a sampling proportion of 0.5 was used to create flow adjusted concentration, which were represented by the residuals. The LOESS Smoother 2D application uses algorithms that are locally weighted based on the sampling proportion in order to avoid problems associated with formulating and selecting a parametric model. The fraction of observations used for the local smoothed estimates is represented by the sampling proportion (Lettenmaier et al., 1991; White et al., 2004). A sampling proportion of 0.5 was employed because previous studies concerning trend analysis of water quality data indicate this sampling proportion is adequate in limiting discharge effects, when discharge is the only independent variable considered (Bekele and McFarland, 2004). In order to determine if a study period time trend or seasonal variation trend was applicable, time (study day) was plotted on the x-axis and the residuals on the y-axis for each constituent at each site. A linear regression application was used to determine the significance of the trend in flow adjusted concentrations (FAC). P-values less than 0.1 were considered significant, and visual evaluations of these graphs determined the applicability of a seasonal variation trend. An annual percent change (% $\Delta$ ) was calculated for significant trends using the following equation:

$$\% \Delta = (10^{\text{slope}} - 1) * 100 * 365 \quad \text{Equation 1.}$$

where the slope was from the regression of FACs over time.

### Load Estimations

Four log-log linear regression equations were evaluated when estimating constituent loads, and the equations were:

$$\text{Log}_{10}L = B_0 + B_1\text{Log}_{10}Q \quad \text{Equation 2.}$$

$$\text{Log}_{10}L = B_0 + B_1\text{Log}_{10}Q + B_2T \quad \text{Equation 3.}$$

$$\text{Log}_{10}L = B_0 + B_1\text{Log}_{10}Q + B_2 \sin(2\pi t) + B_3 \cos(2\pi t) \quad \text{Equation 4.}$$

$$\text{Log}_{10}L = B_0 + B_1\text{Log}_{10}Q + B_2 \sin(2\pi t) + B_3 \cos(2\pi t) + B_4T \quad \text{Equation 5.}$$

These are common equations used in load estimation and are defined in Migliaccio et al. (2011). For these equations, L is the estimated daily load (kg/d), Q is the average daily discharge (cfs), T is the study day (d), and t is the decimal time computed by T/365 (yr). Equation 2 is the most basic model that calculates daily constituent loads as a function of discharge. Equation 3 calculates daily constituent loads as a function of discharge and changes over time, assuming a monotonic increase or decrease in constituent loads. Equation 4 calculates daily constituent loads as a function of discharge and seasonal variation using Fourier's equation. Equation 5 is the most complicated model that calculates daily constituent loads as a function of discharge, seasonal variation, and changes over time.

Log transformed average daily discharges and corresponding constituent concentrations were inserted into Statistix9. Using Statistix9 linear regression, the constituent of concern was applied as the dependent variable and Log Q,  $\sin(2\pi t)$ ,  $\cos(2\pi t)$ , and or T were applied as the independent variable depending on the equation being evaluated. Each of the four equations was applied for all constituents at sites 1, 2, 3, and 6. The applied load equation was determined by evaluating the statistics from the

trend analysis (p-value and  $R^2$ ), and visual seasonal variations and overall trends from the trend analysis. The selected equation was applied to the calculated average daily discharges resulting in estimated daily constituent concentrations. A bias correction factor was applied to account for the potential under-estimation of the constituent concentrations when retransformed. The bias correction factor (BCF; Helsel and Hirsh, 2002), Equation 5, was calculated by dividing the difference between measured and estimated daily loads by the number of samples.

$$BCF = \frac{\sum 10^e}{n} \quad \text{Equation 5.}$$

Daily constituent loads were calculated for each site on days containing estimated discharges using the selected regression model. Estimated daily loads were multiplied by the bias correction factor and summed for monthly loads. Monthly loads were used to determine seasonal and annual loads.

### **Storage Calculation**

Riverine storage (S) of each constituent was estimated for daily loads by subtracting the inputs from the outputs.

$$\Delta S = (\text{sites } 1 + 2 + 3) - \text{site } 6 \quad \text{Equation 6.}$$

The inputs consist of sites 1, 2, and 3 and the output consists of site 6. The storage here represents the contributions or retention of constituents at the watershed scale. Monthly, seasonal, and annual storage were estimated through this application. The inputs neglect constituents imported into the watershed from the land application of poultry litter and fertilizer, as well as the import of animal feed. These land application factors can be included in the inputs as  $X_n$ , and this variable was included to evaluate storage and export at the watershed scale based on all inputs, not just riverine.

Nutrient imports into WREC also included the application of poultry litter, fertilizer, and animal waste generated from selective foods brought into the watershed over the study period. Interviews were conducted with AAREC employees familiar with historical land use and land applications concerning WREC on June 28, 2012. WREC fertilizer application information was obtained on a per field basis and then summed into annual inputs; fertilizer data was provided as N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O applications per unit area and converted into annual N and P loads (kg) applied (personal communication, V. Skinner Jr.) Poultry litter was also applied to the fields, and N and P inputs from this source were based on application rates, field area, and assuming 4% total N and 1.5% total P litter composition (Singh et al., 2010).

### **Livestock Records**

Cattle records (personal communication, R. Rhein) indicate that approximately 315 cattle (138,000 kg of beef) occupied WREC when the center was initiated in 2006. Multiple shipments occurred throughout 2006, decreasing the cattle herd to 101 (43,000 kg) in January of 2007. Shipments of cattle offsite continued until June 2007 when all of the cattle were removed; no cattle were present within WREC in 2008. A small herd of cattle (12; 4,500 kg) were brought in on March 6, 2009 and then shipped on July 1, 2009. Then again, 11 cattle (5,900 kg) were brought in on December 12, 2011, with one being shipped on March 1, 2012 to bring the current cattle total to 10 (5,200 kg).

Grain was the only feed imported into the watershed for cattle, whose primary diet consisted of hay produced within WREC, and foraged fields within WREC. All cattle were fed approximately 1 to 2 kg of grain daily, equating to 10-15% of their daily intake. ASAE (2005) estimated typical manure (urine and feces combined) characteristics excreted by beef indicate 0.19 kg/day-animal of N, and 0.044 kg/day-animal of P. Annual N and P loads were calculated for the imported grain (12.5% of diet) fed to the cattle



occupying WREC between 2006 and 2012, using the ASAE (2005) standards for animal feed and excretion multiplied by the imported grain percentage.

Horses foraged the east fields of WREC surrounding the equine barn, which is located just southeast of the Pauline Whitaker Animal Science Center (personal communication, K. Jogan). A breeding herd consisting of 0 to 21 adult horses (545 kg), 0 to 7 young horses (317 kg), and up to 5 foals (113 kg) occupied WREC from 2006 to 2012. The horse diets consisted of hay produced within the watershed, Purina Equine Junior (1,134 kg/year) for the young horses and foals, and Purina Strategy (4989 kg/year) for the adult horses. Annual N and P loads were calculated for the imported horse feeds from 2006 to 2012 using nutritional values of the feed and the following ASAE (2005) equations for sedentary horses:

$$N_E = (55.4 * BW * 10^{-3}) + (0.586 * DMI * C_{CP})/6.25 \quad \text{Equation 7.}$$

$$P_E = (4.56 * BW * 10^{-3}) + (0.793 * DMI * C_P) \quad \text{Equation 8.}$$

$N_E$  refers to the total nitrogen excretion per animal per day (g/animal-day),  $P_E$  refers to the total P excretion per animal per day (g/animal-day),  $BW$  refers to the average live body weight (kg),  $DMI$  refers to feed dry matter intake (g dry feed/day),  $C_{CP}$  refers to the concentration of crude protein of total ration (g protein/g dry feed), and  $C_P$  refers to the concentration of P of total ration (g P/g dry feed).

Sheep forage fields adjacent to the Pauline Whitaker Animal Science Arena sheep barn located in the northeast portion of WREC (personal communication, D. Belcher). On average, 22 ewes, 40 market lambs (October-November), 36 lambs (March-April), and 10 lambs (September-December) were housed in the sheep barn from 2006 to 2012. The sheep diets consisted of hay produced within the watershed, and sheep creep and sheep feed brought into the watershed. Approximately 35% of the sheep diet was imported from 2006 to 2007 and 42% imported through 2012. Adult ewes produce 4.1

kg of excreta daily consisting of 0.65% N and 0.26% P<sub>2</sub>O<sub>5</sub> (0.11% Phosphorus) while lambs produce 1.1 kg of excreta daily consisting of 0.59% N and 0.18% P<sub>2</sub>O<sub>5</sub> (0.08% Phosphorus) (Smith and Frost, 2000).

Annual N and P loads were calculated by multiplying the imported feed (35-42% of diet) amount by the values from Smith and Frost.

Pigs are housed in the pig barn located adjacent to Gifford Avenue, approximately 220 m southwest of the Pauline Whitaker Animal Science Building (personal communication, D. Belcher). Between 12 and 15 pigs occupy the barn sporadically throughout the years of 2006 to 2012, and are restricted to the barn and attached 20 m x 6 m pen. Approximately 4,000-5,000 pounds of pig feed is imported into the watershed annually. ASAE (2005) estimated typical manure (urine and feces combined) characteristics excreted by swine indicate 0.032 kg/day-animal of nitrogen, and 0.009 kg/day-animal of phosphorus. Annual N and P loads were calculated for the imported feed of the pigs occupying WREC using the ASAE (2005) estimated characteristics.

### **Hay Production and Atmospheric Deposition**

Hay varieties including alfalfa (10%), bermuda grass (40%), fescue (30%), orchard grass (10%) and other annuals (10%) were produced in the central, west, and south fields of WREC from 2006 to 2011 (personal communication, R. Rhein). Approximately 5% (14,400 kg) of the hay harvested within the WREC boundary was exported in 2006, and approximately 80% of the hay harvested, ranging from 130,000 to 308,000 kg, was exported from the watershed between 2007 and 2011. The compositional percentages of all hays produced in Arkansas are 12% crude protein and 0.3% P (Davis et al., 2002). Annual N and P loads were calculated for the hay exported from WREC between 2006 and 2012 by multiplying the annual exported hay weights by the typical values reported by Davis et al. Nitrogen fixation from the alfalfa plots was also taken into consideration, and was calculated using the annual

areas of the alfalfa plots multiplied by the typical N fixation rate for alfalfa of 148 kg/ha (Heichel et al., 1981).

Atmospheric deposition of N and P was another source importing nutrients into the watershed. Annual reports were obtained from the National Atmospheric Deposition Program (NADP) site AR27 from <http://nadp.sws.uiuc.edu/data/>. Site AR 27 is located approximately 600 m north of WREC. Annual  $\text{NH}_4$  and  $\text{NO}_3$  deposition rates (kg/ha) from the reports were used to determine the atmospheric deposition of N for WREC since 2006. The average  $\text{PO}_4\text{-P}$  concentration of 0.005 mg/L was multiplied by annual precipitation amounts to estimate the atmospheric deposition of P for WREC since 2006.

## RESULTS

### Discharge

A simple quadratic function was fit to the rating curves provided by the USGS (Figure 5), and these equations are provided below:

|         |                                    |               |
|---------|------------------------------------|---------------|
| Site 1. | $y = 0.9825x^2 - 0.4473x + 0.0655$ | $R^2 = 0.999$ |
| Site 2. | $y = 0.7523x^2 - 0.1951x + 0.0162$ | $R^2 = 0.999$ |
| Site 3. | $y = 0.8921x^2 - 0.4857x + 0.0724$ | $R^2 = 0.998$ |
| Site 6. | $y = 11.899x^2 - 16.952x + 4.7783$ | $R^2 = 0.996$ |

From visual observation, these equations provided a good representation of the rating curves at sites 1-3 explaining more than 99% of the variation in the rating curves. The measured discharge was available up to stage heights of 0.48 m, 0.26 m, and 0.42 m at sites 1, 2, and 3, respectively. During the study period, recorded staff gage heights exceeded the USGS stage-discharge relation for 0.02% of the

recordings for site 1, 0.07% for site 2, and 0.43% for site 3. These quadratic equations were extended outside the rating curves and measured data boundaries only for these small percentages of the instantaneous flows (Figure 2).

The quadratic equation at site 6 had a similar  $R^2$  (0.996), but it did not visually fit the minor changes in the rating curve provided by the USGS (Figure 2). So, the actual rating curve was used to estimate instantaneous discharge and the quadratic equation was only applied when staff gage heights exceeded the maximum stage available in the curve, which was 0.1% of the staff gage heights. The slight inconsistencies between the rating curve and the quadratic equation probably had to do with differences in the sites structure. Site six has four corrugated metal culverts, whereas sites 1-3 are v-notch weirs used as flow control structures. Flow through the culverts may be a bit more variable with stage because the area is restricted to the culvert openings.

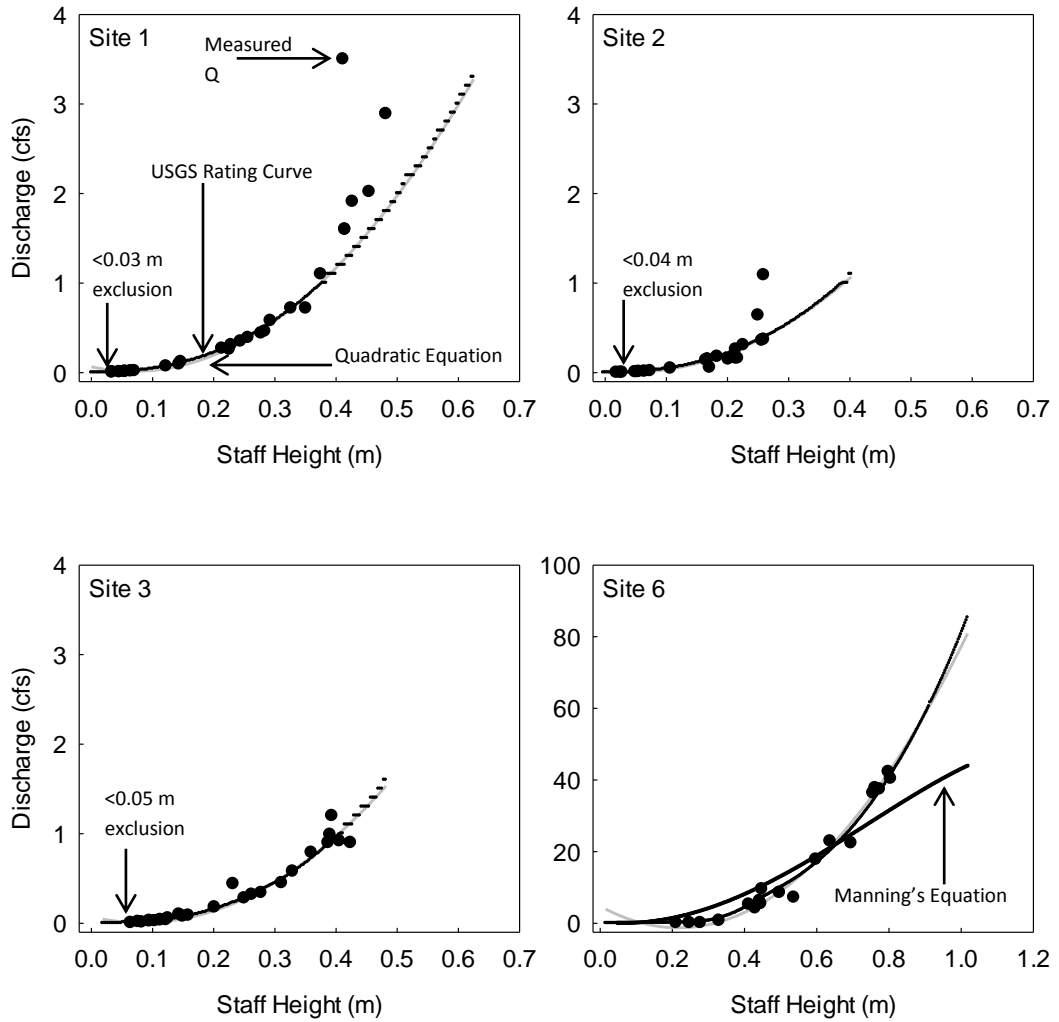
Manning's equation was also fitted to the observed data and compared to the provided rating curve at site 6.

$$Q = \frac{1.49}{n} * R^{\frac{2}{3}} * S^{\frac{1}{2}} * A \quad \text{Manning's Equation.}$$

Discharge (Q) is calculated in cfs using Manning's dimensionless number (n) of 0.021 for a corrugated metal pipe, the hydraulic radius (R) defined as the flow area divided by the wetted perimeter which was calculated from the pipe diameter and staff gauge height, slope (S) as a percent, and flow area (A) calculated from the pipe diameter and staff gauge height (Haan et al., 1994). The slope was adjusted in order to fit a stage-discharge relation resembling the USGS discharge measurements. Manning's Equation proves to be heavily relying on slope, whereas an almost negligible slope of 0.00015 m/m was used to produce a similar curve (Figure 2). Manning's equation was applied to the culverts and stage records at sites 4 and 5, attempting to estimate flow at these sites. Unfortunately, the sensitivity of

Manning's equation to slope did not allow flow estimation at sites 4 and 5. Due to the lack of field discharge measurements, a justifiable rating curve was unable to be generated for sites 4 and 5. Therefore, these sites were excluded from the study. Future flow measurements at sites 4 and 5 would allow the development of a rating curve and corresponding application of trend analysis and load calculations or these sites.

Figure 2. Discharge as a function of staff height for sites 1, 2, 3, and 6 from the provided USGS rating curve calculations and measured values.



## Water Balance

Water storage within the WREC was variable over the study period, and water inputs and outputs were closely related to patterns in rainfall and seasonal fluctuations. The discharge from the inputs was seasonal, and largely driven by rainfall runoff. However, site 3 drains a perched aquifer and wetland area, and it generally sustains a small amount of baseflow discharge year round. The discharge at site six is solely from rainfall runoff, and flow generally ceases after a rainfall event.

The greatest amount of flow at all sites occurred in April 2011, when 428 mm of precipitation resulted in an average discharge of 7.1 cfs. More than  $\frac{3}{4}$  of the months precipitation occurred over three days, totaling 90 mm, 96 mm, and 110 mm on April 23, 24, and 25, respectively. These consecutive days of precipitation and flooding produced peak stage heights for the study period of 0.70 m for site 1, 0.48 m for site 2, 0.92 m for site 3, 1.66 m for site 4, 1.65 m for site 5, and 2.27 m for site 6. There were other precipitation events similar to these resulting in high flows in and out of WREC, e.g. July 2010 and October 2009. The discharge at WREC is strongly driven by precipitation, especially when multiple days occur with significant rainfall over a short period (Figure 3).

The low flows at WREC were associated with dry periods, especially typical summer and early fall. These dry conditions were often sustained for long periods of time, and then precipitation events would not produce as much runoff as expected, e.g. September 2010. August 2010 was a month with almost negligible rainfall (only 0.4 mm) and an average temperature of 35°C. The following month had almost 200 mm of precipitation, but this only produced an average 0.18 cfs of discharge exported (Figure 3).

It is important to understand that flow at the outlet is driven by antecedent moisture conditions across WREC. For example, May 2011 required only 211 mm of rainfall to produce an average discharge

of 3.0 cfs whereas July 2010 required 319 mm of rainfall to produce 2.9 cfs following a dry June (only 36 mm of rain). The amount and temporal distribution of rainfall also plays a role as large individual events or sequential smaller events may result in outflows from WREC. Overall, the patterns of discharge are tied to rainfall plus seasonal factors (i.e. temperature) that influence evapotranspiration.



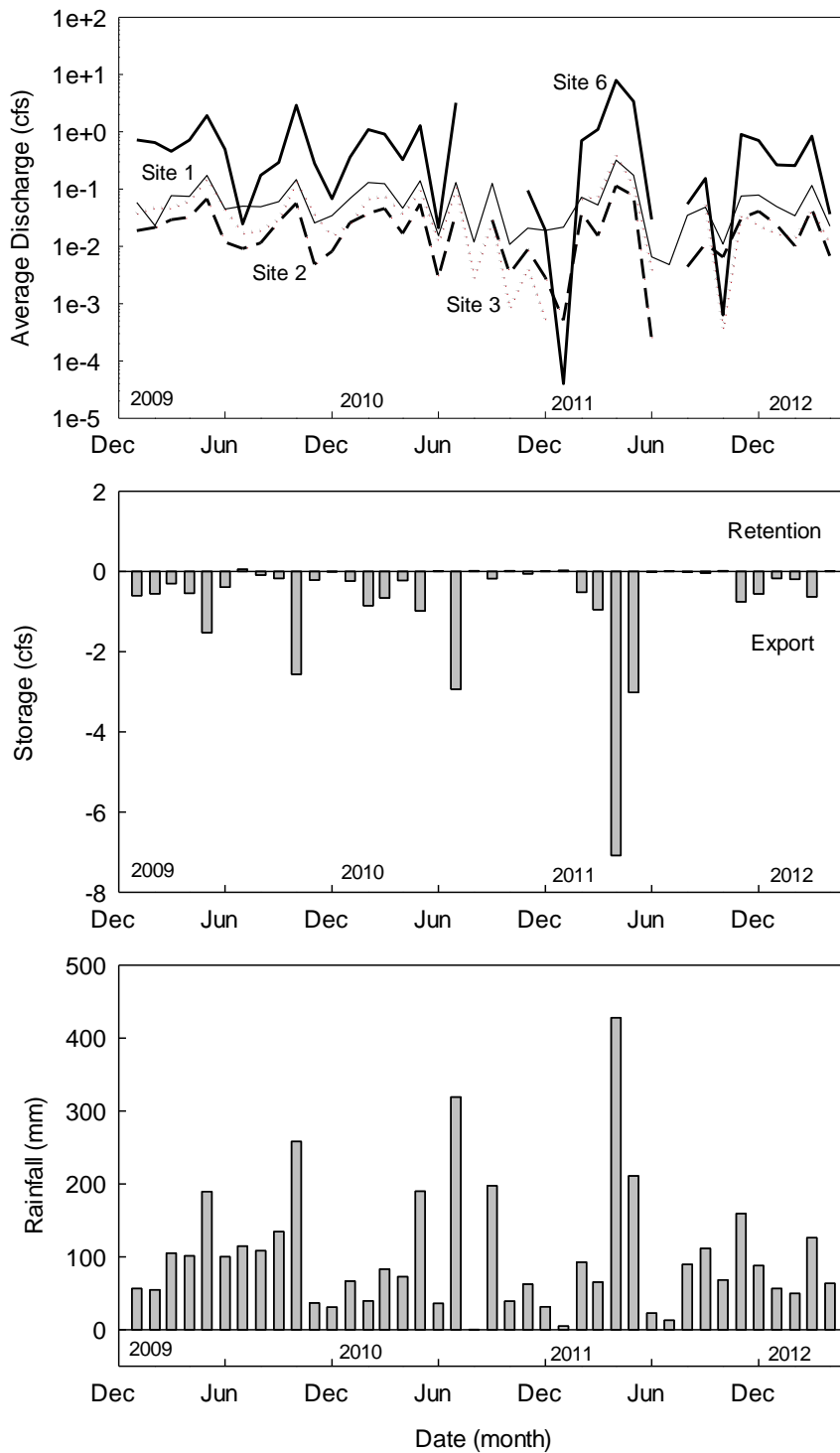


Figure 3. Log transformed average monthly discharge during the study period with discontinuities resembling flows of 0.0 cfs(upper), monthly water storage at the Watershed Research and Education Center based on inflows and the single outflow (middle), and monthly rainfall total from a weather station within the watershed boundary (data provided by K. R. Brye) (lower).

## **Flow Adjusted Concentration Trends**

### **Chloride**

Chloride was highly variable, but had a relatively similar range in concentration across the inflows and outflow, ranging from 0.41 to 160 mg/L (excluding two data points, Table 1). Extremely high Cl concentrations were observed at site 2 on October 1, 2009 (1,325 mg/L) and February 25, 2010 (1,000 mg/L). The lesser concentrations (< 2 mg/L) occurred throughout the years at these sites, whereas the greater concentrations (> 20 mg/L) for sites 1, 2, and 6 were generally observed during the winter months. Cl concentrations at site 3 were generally greatest during the fall and early winter months (September through December). Cl concentrations followed relatively similar patterns with discharge across these sites, where the LOESS regression line showed concentrations generally decreased with increasing discharge (Appendix I).

The LOESS residuals varied from -1.01 to 2.06 across all four sites, and these were used to represent the FACs for Cl. There were no individual data points treated as outliers, including the two concentrations over 1,000 mg/L. Cl FACs did not significantly change over time at sites 1 (agricultural and urban inflow), 2 (urban inflow), 3 (wetland inflow), or site 6 (outflow) (Table 2). The cyclical patterns observed in FACs suggested that seasonal variations in Cl were evident at sites 1 and 2, but were not visible at the other sites (Appendix II).

### **Ammonia**

Ammonia had a relatively similar range in concentration across the inflows and outflow, ranging from <0.1 to 0.40 mg/L (excluding two data points, Table 1). The incident of high ammonia concentrations occurred on June 8, 2011 at site 1 (1.08 mg/L) and on March 25, 2010 at site 3 (2.30

mg/L). There were no patterns in  $\text{NH}_4\text{-N}$  concentrations evident seasonally or across the study period, and concentrations did not change across the range of discharge for these four sites (Appendix I).

The LOESS residuals varied from -1.18 to 1.42 across all four sites, and these were used to represent the FAC for  $\text{NH}_4\text{-N}$ . There were no individual data points treated as outliers, including the two incidents of  $\text{NH}_4\text{-N}$  exceeding 1 mg/L. (Table 2).  $\text{NH}_4\text{-N}$  FACs showed two different relationships over time, (1) FACs did not significantly change over time at sites 2 (urban inflow), 3 (wetland inflow), and 6 (outflow), and (2) FACs significantly increased ( $p=0.009$ ) over time at site 1 (agricultural and urban inflow). The increasing trend while significant only explained 7% of variation in FACs, but trends overtime generally explain only small portions of the variation (low  $R^2$ ).  $\text{NH}_4\text{-N}$  FACs increased at a rate of 17% per year at site 1 (Table 1), and seasonal variations in  $\text{NH}_4\text{-N}$  were not evident at any of the sites, since there was no cyclical pattern in FACs over time (Appendix II).

Table 1. Descriptive statistics of constituent concentrations in water quality samples collected at the Watershed Research and Education Center, 2009-2012.

| <b>Constituent</b> | <b>n</b> | <b>Min</b> | <b>Median</b> | <b>Max</b> | <b>Average</b> | <b>STD</b> |
|--------------------|----------|------------|---------------|------------|----------------|------------|
| ----- (mg/L) ----- |          |            |               |            |                |            |
| Site 1             |          |            |               |            |                |            |
| Cl                 | 110      | 1.01       | 11.9          | 119        | 13.9           | 14.9       |
| NH <sub>4</sub> -N | 107      | 0.00       | 0.08          | 1.08       | 0.12           | 0.13       |
| NO <sub>3</sub> -N | 116      | 0.00       | 0.25          | 2.32       | 0.39           | 0.44       |
| SRP                | 111      | 0.01       | 0.08          | 0.61       | 0.12           | 0.12       |
| TN                 | 109      | 0.23       | 0.95          | 6.91       | 1.11           | 0.74       |
| TP                 | 109      | 0.02       | 0.17          | 1.06       | 0.26           | 0.25       |
| TSS                | 73       | 0.90       | 8.60          | 490        | 46.1           | 98.9       |
| Site 2             |          |            |               |            |                |            |
| Cl                 | 81       | 0.77       | 7.32          | 1325       | 40.5           | 183        |
| NH <sub>4</sub> -N | 78       | 0.00       | 0.07          | 0.29       | 0.09           | 0.07       |
| NO <sub>3</sub> -N | 73       | 0.00       | 0.09          | 1.07       | 0.16           | 0.20       |
| SRP                | 82       | 0.01       | 0.10          | 0.33       | 0.10           | 0.06       |
| TN                 | 80       | 0.31       | 0.80          | 1.76       | 0.85           | 0.29       |
| TP                 | 80       | 0.04       | 0.18          | 0.47       | 0.19           | 0.09       |
| TSS                | 53       | 1.40       | 10.7          | 55.0       | 15.6           | 12.9       |
| Site 3             |          |            |               |            |                |            |
| Cl                 | 132      | 0.52       | 15.1          | 28.0       | 13.9           | 5.64       |
| NH <sub>4</sub> -N | 129      | 0.00       | 0.07          | 2.30       | 0.10           | 0.21       |
| NO <sub>3</sub> -N | 137      | 0.00       | 0.35          | 1.38       | 0.41           | 0.34       |
| SRP                | 133      | 0.00       | 0.01          | 0.89       | 0.08           | 0.15       |
| TN                 | 132      | 0.19       | 0.81          | 6.12       | 0.96           | 0.74       |
| TP                 | 131      | 0.01       | 0.09          | 1.29       | 0.16           | 0.20       |
| TSS                | 92       | 0.80       | 7.85          | 89.2       | 12.2           | 15.3       |
| Site 6             |          |            |               |            |                |            |
| Cl                 | 57       | 0.41       | 8.83          | 73.4       | 10.1           | 9.93       |
| NH <sub>4</sub> -N | 56       | 0.00       | 0.06          | 0.35       | 0.08           | 0.07       |
| NO <sub>3</sub> -N | 57       | 0.10       | 0.41          | 3.04       | 1.02           | 0.79       |
| SRP                | 58       | 0.02       | 0.22          | 1.11       | 0.33           | 0.31       |
| TN                 | 57       | 0.37       | 1.75          | 3.63       | 1.87           | 0.75       |
| TP                 | 57       | 0.05       | 0.42          | 1.67       | 0.48           | 0.39       |
| TSS                | 38       | 0.50       | 8.85          | 2308       | 92.8           | 372        |

Table 2. General statistics for trend analysis of Flow Adjusted Concentrations (LOESS Residuals) and Time (days) at WREC.

| Constituent        | n   | Slope<br>(FAC/days) | R <sup>2</sup> | p-value | Δ % <sup>[a]</sup> |
|--------------------|-----|---------------------|----------------|---------|--------------------|
| Site 1             |     |                     |                |         |                    |
| Cl                 | 107 | 0.00002             | 0.000          | 0.842   |                    |
| NH <sub>4</sub> -N | 101 | 0.00020             | 0.067          | 0.009   | 17                 |
| NO <sub>3</sub> -N | 103 | 0.00030             | 0.051          | 0.021   | 25                 |
| SRP                | 108 | -0.00009            | 0.007          | 0.400   |                    |
| TN                 | 106 | 0.00010             | 0.039          | 0.044   | 8                  |
| TP                 | 106 | 0.00020             | 0.025          | 0.106   |                    |
| TSS                | 71  | 0.00020             | 0.027          | 0.175   |                    |
| Site 2             |     |                     |                |         |                    |
| Cl                 | 65  | -0.00020            | 0.013          | 0.375   |                    |
| NH <sub>4</sub> -N | 63  | 0.00010             | 0.024          | 0.231   |                    |
| NO <sub>3</sub> -N | 60  | 0.00040             | 0.112          | 0.009   | 34                 |
| SRP                | 66  | -0.00002            | 0.001          | 0.835   |                    |
| TN                 | 65  | -0.00001            | 0.000          | 0.899   |                    |
| TP                 | 65  | 0.00001             | 0.001          | 0.818   |                    |
| TSS                | 43  | 0.00010             | 0.017          | 0.401   |                    |
| Site 3             |     |                     |                |         |                    |
| Cl                 | 114 | -0.00005            | 0.012          | 0.248   |                    |
| NH <sub>4</sub> -N | 106 | -0.00010            | 0.022          | 0.130   |                    |
| NO <sub>3</sub> -N | 114 | -0.00001            | 0.000          | 0.944   |                    |
| SRP                | 114 | -0.00006            | 0.003          | 0.576   |                    |
| TN                 | 114 | -0.00020            | 0.091          | 0.001   | -17                |
| TP                 | 113 | -0.00010            | 0.021          | 0.125   |                    |
| TSS                | 74  | -0.00006            | 0.004          | 0.584   |                    |
| Site 6             |     |                     |                |         |                    |
| Cl                 | 57  | -0.00003            | 0.001          | 0.799   |                    |
| NH <sub>4</sub> -N | 55  | 0.00008             | 0.006          | 0.572   |                    |
| NO <sub>3</sub> -N | 57  | -0.00007            | 0.006          | 0.565   |                    |
| SRP                | 58  | 0.00010             | 0.017          | 0.327   |                    |
| TN                 | 58  | 0.00002             | 0.002          | 0.775   |                    |
| TP                 | 57  | 0.00010             | 0.019          | 0.304   |                    |
| TSS                | 38  | 0.00010             | 0.006          | 0.655   |                    |

<sup>[a]</sup>when p-value < 0.1, Δ% = (10<sup>slope</sup> -1) \* 100 \* 365

## Nitrate

Nitrate had a relatively similar range in concentration across the inflows and outflow, ranging from <0.1 mg/L to 3.04 mg/L (Table 1). The lesser concentrations (< 0.1 mg/L) occurred throughout the study period whereas the greater concentrations (> 1 mg/L) for sites 1, 2, and 3 were observed during the winter and spring months. Greater concentrations for site 6 occurred throughout the study period, likely because flow at this site is dependent on runoff. The LOESS regression line showed that NO<sub>3</sub>-N concentrations did not change across the range of discharge at sites 1 and 2. However, NO<sub>3</sub>-N concentrations did change with discharge at sites 3 and 6, where the LOESS regression line showed that concentrations generally decreased with increasing discharge during runoff events at these sites (Appendix I).

The LOESS residuals varied from -1.49 to 0.98 across all four sites, and these were used to represent the NO<sub>3</sub>-N FACs. There were no individual data points treated as outliers. NO<sub>3</sub>-N FACs showed two different relationships over time (Table 2): (1) FACs did not significantly change over time at sites 3 (wetland inflow) and 6 (outflow) and (2) FACs significantly increased ( $p \leq 0.021$ ) at sites 1 (agricultural and urban inflow) and 2 (urban inflow). NO<sub>3</sub>-N FACs increased at a rate of 25% per year or more at these two inflows (sites 1 and 2), and time explained 5% or more of the variation in FACs at these sites. The cyclical patterns in FACs suggested that seasonal variations in NO<sub>3</sub>-N were evident at site 3, but were not visible at the other sites (Appendix II).

## Total Nitrogen

Total Nitrogen had a relatively similar range in concentration across the inflows and outflow, ranging from 0.19 to 3.67 mg/L (excluding three data points, Table 1). The incidents of high TN concentrations occurred on June 8, 2011 at site 1 (6.91 mg/L), and on January 14, 2010 (6.12 mg/L) and

March 25, 2010 (4.05 mg/L) at site 3. The high TN samples of 6.91 and 4.05 mg/L are from the same samples associated with the abnormally high  $\text{NH}_4\text{-N}$  concentrations. There were no patterns in TN concentrations evident seasonally or across the study period for all four sites. The LOESS regression line showed that TN concentrations did not change across the range of discharge at sites 1 and 2. However, TN concentrations did change with discharge at sites 3 and 6, where the LOESS regression line showed that concentrations increased with increasing base flow and then decrease with increasing discharge during runoff events (Appendix I).

The LOESS residuals varied from -0.56 to 0.95 across all four sites, and these were used to represent the TN FACs. There were no individual data points treated as outliers, including the three incidents of high concentrations. TN FACs showed three different relationships over time (Table 2): (1) FACs did not significantly change over time at sites 2 (urban inflow) and 6 (outflow), (2) FACs significantly increased ( $P=0.044$ ) over time at site 1 (agricultural and urban inflow), and (3) FACs significantly decreased ( $P=0.001$ ) over time at site 3 (wetland inflow). TN FACs increased at a rate of 8% per year at site 1 and decreased at a rate of 17% per year at site 3. The cyclical patterns in FACs suggested that seasonal variations in TN were evident at site 3, but were not visible at the other sites (Appendix II).

### **Soluble Reactive Phosphorus**

Soluble Reactive Phosphorus had a relatively similar range in concentration across the inflows and outflow, ranging from  $<0.1$  to  $0.89$  mg/L (excluding one data point, Table 1). The one incident of high SRP concentrations occurred at site 6 on August 5, 2009 ( $1.11$  mg/L). The lesser concentrations ( $<0.1$  mg/L) were generally observed during low flow in the spring months, whereas the greater concentrations ( $>0.5$  mg/L) occurred throughout the years during high flows at these sites. SRP concentrations did change with discharge across all four sites, where the LOESS regression line showed

that concentrations generally increased with increasing discharge. The individual data point driving the decrease (via LOESS regression) at site 6 was associated with the flood event on April 25, 2011 (Appendix I).

The LOESS residuals varied from -1.38 to 1.23 across all four sites, and these were used to represent the SRP FACs. There were no individual data points treated as outliers, including the one sample over 1 mg/L. SRP FACs did not significantly change over time at sites 1 (agricultural and urban inflow), 2 (urban inflow), 3 (wetland inflow), or site 6 (outflow) (Table 2). The cyclical patterns in FACs suggested that seasonal variations in SRP were evident at sites 1 and 3, but were not visible at the other sites (Appendix II).

### **Total Phosphorus**

Total Phosphorus had a relatively similar range in concentration across the inflows and outflow, ranging from 0.01 to 1.67 mg/L. The lesser concentrations (< 0.05 mg/L) were generally observed in the winter and spring months whereas the greater concentrations (> 1.0 mg/L) occurred throughout the study period during runoff events. The LOESS regression line showed that TP concentrations did not change across the range of discharge at site 2. However, TP concentrations did change with discharge at sites 1, 3 and 6, where the LOESS regression line showed that concentrations decreased with increasing base flow and then increased with increasing discharge during runoff events. The LOESS regression line for site 6 decreases at the high flow extremity due to one data point associated with the flood event on April 25, 2011 (Appendix I).

The LOESS residuals varied from -0.80 to 0.91 across all four sites, and these were used to represent the flow adjusted TP FACs. TP FACs did not significantly change over time across these sites



( $p > 0.1$ , Table 2). The cyclical patterns in FACs suggested that seasonal variations in SRP were evident at sites 1 and 3, but were not visible at the sites 2 and 4 (Appendix II).

### **Total Suspended Solids**

Total Suspended Solids was highly variable but had a relatively similar range in concentration across the inflows and outflow, ranging from 0.50 mg/L to 490 mg/L (excluding one data point, Table 1). An extremely high TSS concentration was observed at Site 6 on March 24, 2009 (2,308 mg/L). There were no patterns in TSS concentrations evident seasonally or across the study period for all four sites. The LOESS regression line showed that TSS concentrations did not change across the range of discharge at sites 2 or 3. However, TN concentrations did change with discharge at sites 1 and 6, where the LOESS regression line showed that concentrations generally increased with increasing discharge at these two sites (Appendix I).

The LOESS residuals varied from -1.58 to 1.89 across all four sites, and these were used to represent the TSS FACs. There were no individual data points treated as outliers, and TSS FACs did not significantly change over time across these sites ( $p > 0.1$ , Table 2). Seasonal variations in TSS were not evident at any of the sites, since there were no cyclical patterns in FACs (Appendix II).

### **Estimated Loads**

Daily loads were generally estimated using the most basic model to calculate daily constituent loads as a function of discharge, but each of the four equations was used during the study period by at least one of the constituents. Statistical analysis ( $R^2$ , BCF, and p-value), influences of seasonal variation, and significance of time trends determined the applicable equation for load estimations (Tables 2 and 3). The year of 2012 (January to April) was not a complete calendar year (CY) during the study period, so the total, annual average, and 2009, 2010 and 2011 CYs were time periods used to analyze constituent

loads and average annual discharges (Table 4). Large increases in all of the estimated constituent loads and annual average discharge rates occur between the inflows and outflow due to a significant amount of the catchment area occurring between the inflow monitoring stations and the outflow monitoring station. Discharge measurements for sites 4 and 5 would aid in determining the source of load accumulations throughout the watershed, and should be a focus of future research at WREC.

### **Chloride**

Equation four was used to estimate Cl loads for site 1 (agricultural and urban inflow) due to seasonal variations observed during the study period (Table 3 and 4). The average annual estimated Cl load for site 1 of 519 kg was generated by an average annual discharge rate of 0.070 cfs. The Cl loads for site 1 ranged from 491 (2010) to 527 kg/yr (2011) and were generated from average annual flows of 0.070 and 0.081 cfs, respectively. The four estimated Cl loads (average, CY 2009, 2010, and 2011) from site 1 were greater than the corresponding estimated Cl loads from the other inflows (sites 2 and 3).

Equation four was used to estimate Cl loads for site 2 (urban inflow) due to seasonal variations observed during the study period (Table 3 and 4). Site 2 contained the lowest estimated Cl loads and associated discharges of the inflows. An average annual estimated Cl load for site 2 of 128 kg/yr was generated by an average annual discharge of 0.025 cfs. The Cl loads for site 2 ranged from 99 (2010) to 155 kg/yr (2011) and were generated from average annual flows of 0.022 and 0.028 cfs, respectively. The pattern of increasing estimated Cl loads for complete years associated with increasing discharge rates is apparent between sites 1 and 2, and is generally sustained by site 3.

Equation two was used to estimate Cl loads for site 3 (wetland inflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). Site 3 contained estimated Cl loads and discharge rates between the other two inflows. An average annual estimated Cl

load for site 3 of 324 kg/yr was generated by an average annual discharge of 0.049 cfs. The Cl loads for site 3 ranged from 281 (2010) to 406 kg/yr (2009) and were generated from average annual flows of 0.038 and 0.054 cfs, respectively. The estimated Cl load of 325 kg/yr (0.064 cfs) for CY 2011 does not follow the pattern of an increasing load associated with an increasing discharge when compared to CY 2009 for site 3.

Equation four was used to estimate Cl loads for site 6 (outflow) due to seasonal variations observed during the study period (Table 3 and 4). The average annual estimated Cl load at the outflow of 4,053 kg was generated by a discharge rate of 0.818 cfs. The Cl loads for site 6 ranged from 3,107 (2010) to 5,219 kg/yr (2009) and were generated from average annual flows of 0.640 and 0.726 cfs, respectively.

### **Ammonia**

Equation three was used to estimate  $\text{NH}_4\text{-N}$  loads for site 1 (agricultural and urban inflow) due to the observation of cyclical changes over time during the study period (Table 3 and 4). An average annual estimated  $\text{NH}_4\text{-N}$  load for site 1 (agricultural and urban inflow) of 8.4 kg/yr was generated by an average annual discharge of 0.070 cfs. The  $\text{NH}_4\text{-N}$  loads for site 1 ranged from 6.5 (2009) to 11 kg/yr (2011) and were generated from average annual flows of 0.068 and 0.075 cfs, respectively. The four estimated  $\text{NH}_4\text{-N}$  loads (average, CY 2009, 2010, and 2011) from site 1 were greater than the corresponding estimated  $\text{NH}_4\text{-N}$  loads from the other inflows (sites 2 and 3).

Equation two was used to estimate  $\text{NH}_4\text{-N}$  loads for site 2 (urban inflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). The urban inflow (site 2) contained the least estimated  $\text{NH}_4\text{-N}$  loads and associated discharges of the inflows. An average annual estimated  $\text{NH}_4\text{-N}$  load for site 2 of 2.0 kg/yr was generated by an average annual

discharge of 0.025 cfs. The  $\text{NH}_4\text{-N}$  loads for site 2 ranged from 1.8 (2010) to 2.3 kg/yr (2011) and were generated from average annual flows of 0.022 and 0.028 cfs, respectively. The pattern of increasing estimated  $\text{NH}_4\text{-N}$  loads for the complete years associated with increasing discharge rates is apparent between sites 1 and 2, and is sustained by site 3.

Equation three was used to estimate  $\text{NH}_4\text{-N}$  loads for site 3 (wetland inflow) due to the observation of cyclical changes over time during the study period (Table 3 and 4). The wetland inflow (site 3) had estimated  $\text{NH}_4\text{-N}$  loads and discharge rates between the other two inflows. An average annual estimated  $\text{NH}_4\text{-N}$  load for site 3 of 5.3 kg/yr was generated by an average annual discharge of 0.049 cfs. The  $\text{NH}_4\text{-N}$  loads for site 3 ranged from 4.0 (2010) to 7.3 kg/yr (2011) and were generated from average annual flows of 0.038 and 0.064 cfs, respectively.

Equation four was used to estimate  $\text{NH}_4\text{-N}$  loads for site 6 (outflow) due to seasonal variations observed during the study period (Table 3 and 4). The average annual estimated  $\text{NH}_4\text{-N}$  load at the outflow of 107 kg/yr was generated by an average annual discharge rate of 0.818 cfs. The  $\text{NH}_4\text{-N}$  loads for site 6 ranged from 70 (2009) to 195 kg/yr (2011) and were generated from average annual flows of 0.726 and 1.245 cfs, respectively.

Table 3. Statistical results of constituent equations used to calculate daily flow adjusted concentration loads from discharge measurements at the Watershed Research and Education Center, 2009-2012. All p-values <0.001

| constituent        | equation | R <sup>2</sup> | BCF  | seasonal variation |
|--------------------|----------|----------------|------|--------------------|
| Cl                 | 4        | 0.760          | 1.28 | Y                  |
| NH <sub>4</sub> -N | 3        | 0.815          | 1.33 | N                  |
| NO <sub>3</sub> -N | 3        | 0.712          | 1.64 | N                  |
| SRP                | 4        | 0.904          | 1.36 | Y                  |
| TN                 | 3        | 0.927          | 1.13 | N                  |
| TP                 | 5        | 0.924          | 1.22 | Y                  |
| TSS                | 2        | 0.779          | 2.58 | N                  |
| Cl*                | 4        | 0.717          | 1.43 | Y                  |
| NH <sub>4</sub> -N | 2        | 0.804          | 1.27 | N                  |
| NO <sub>3</sub> -N | 3        | 0.778          | 1.37 | N                  |
| SRP                | 2        | 0.921          | 1.14 | N                  |
| TN                 | 2        | 0.950          | 1.05 | N                  |
| TP                 | 2        | 0.936          | 1.09 | N                  |
| TSS                | 2        | 0.838          | 1.32 | N                  |
| Cl                 | 2        | 0.835          | 1.10 | N                  |
| NH <sub>4</sub> -N | 3        | 0.822          | 1.49 | N                  |
| NO <sub>3</sub> -N | 4        | 0.818          | 1.31 | Y                  |
| SRP                | 4        | 0.863          | 1.73 | Y                  |
| TN                 | 5        | 0.954          | 1.09 | Y                  |
| TP                 | 5        | 0.918          | 1.27 | Y                  |
| TSS                | 2        | 0.841          | 1.58 | N                  |
| Cl                 | 4        | 0.783          | 1.25 | N                  |
| NH <sub>4</sub> -N | 4        | 0.832          | 1.32 | N                  |
| NO <sub>3</sub> -N | 2        | 0.720          | 1.29 | N                  |
| SRP                | 2        | 0.881          | 1.37 | N                  |
| TN                 | 2        | 0.919          | 1.08 | N                  |
| TP                 | 2        | 0.876          | 1.33 | N                  |
| TSS                | 2        | 0.710          | 5.57 | N                  |

Table 4. Estimated constituent loads (kg) from water quality samples and estimated average annual discharge (cfs) from staff gage heights for the Watershed Research and Education Center, 2009-2012

| Constituent |          | NH <sub>4</sub> -N | Cl    | NO <sub>3</sub> -N | SRP   | TN    | TP    | TSS     | Discharge |
|-------------|----------|--------------------|-------|--------------------|-------|-------|-------|---------|-----------|
|             |          | ----- kg/yr -----  |       |                    |       |       |       |         | cfs       |
| Site One    | CY 2009  | 6.5                | 526   | 23                 | 18    | 71    | 26    | 4,325   | 0.068     |
|             | CY 2010  | 7.7                | 491   | 31                 | 20    | 78    | 38    | 5,126   | 0.070     |
|             | CY 2011  | 11                 | 527   | 48                 | 29    | 96    | 70    | 6,646   | 0.075     |
|             | Average* | 8.4                | 519   | 35                 | 21    | 80    | 44    | 5,228   | 0.070     |
| Site Two    | CY 2009  | 2.1                | 125   | 3.3                | 2.8   | 19    | 4.6   | 365     | 0.025     |
|             | CY 2010  | 1.8                | 99    | 2.9                | 2.6   | 17    | 4.1   | 313     | 0.022     |
|             | CY 2011  | 2.3                | 155   | 3.9                | 3.5   | 22    | 5.5   | 411     | 0.028     |
|             | Average  | 2.0                | 128   | 3.3                | 2.9   | 19    | 4.7   | 359     | 0.025     |
| Site Three  | CY 2009  | 5.6                | 406   | 24                 | 9.7   | 68    | 15    | 768     | 0.054     |
|             | CY 2010  | 4.0                | 281   | 14                 | 8.1   | 35    | 15    | 547     | 0.038     |
|             | CY 2011  | 7.3                | 325   | 28                 | 31    | 53    | 50    | 1,203   | 0.064     |
|             | Average  | 5.3                | 324   | 21                 | 15    | 48    | 24    | 784     | 0.049     |
| Site Six    | CY 2009  | 70                 | 5,219 | 543                | 320   | 1,123 | 429   | 75,538  | 0.726     |
|             | CY 2010  | 82                 | 3,107 | 446                | 359   | 955   | 452   | 87,092  | 0.640     |
|             | CY 2011  | 195                | 4,450 | 710                | 1,013 | 1,694 | 1,184 | 253,000 | 1.245     |
|             | Average  | 107                | 4,053 | 538                | 521   | 1,188 | 637   | 127,695 | 0.818     |

\*Average annual load calculated from the sum of all monthly loads (Jan. 2009-Apr. 2012) divided by the total number of months (40) in the study period, then multiplied by 12 months/year.

## Nitrate

Equation three was used to estimate NO<sub>3</sub>-N loads for site 1 (agricultural and urban inflow) due to the observation of cyclical changes over time during the study period (Table 3 and 4). The average annual estimated NO<sub>3</sub>-N load for site 1 of 35 kg was generated by an average annual discharge rate of 0.070 cfs. The NO<sub>3</sub>-N loads for site 1 ranged from 23 (2009) to 48 kg/yr (2011) and were generated from average annual flows of 0.068 and 0.075 cfs, respectively. Three of the estimated NO<sub>3</sub>-N loads (average, CY 2010, and 2011) from site 1 were greater than the corresponding estimated NO<sub>3</sub>-N loads from the other inflows (sites 2 and 3).

Equation three was used to estimate NO<sub>3</sub>-N loads for site 2 (urban inflow) due to the observation of cyclical changes over time during the study period (Table 3 and 4). Site 2 contained the lowest estimated NO<sub>3</sub>-N loads and associated discharges of the inflows. An average annual estimated NO<sub>3</sub>-N load for site 2 of 3.3 kg/yr was generated by an average annual discharge of 0.025 cfs. The NO<sub>3</sub>-N loads for site 2 ranged from 2.9 (2010) to 3.9 kg/yr (2011) and were generated from average annual flows of 0.022 and 0.028 cfs, respectively. The pattern of increasing estimated NO<sub>3</sub>-N loads for the complete years associated with increasing discharge rates is apparent between sites 1 and 2, and is generally sustained by site 3.

Equation four was used to estimate NO<sub>3</sub>-N loads for site 3 (wetland inflow) due to seasonal variations observed during the study period (Table 3 and 4). Site 3 contained estimated NO<sub>3</sub>-N loads and discharge rates between the other two inflows for average annual, CY 2010, and 2011, but contained the greatest estimated NO<sub>3</sub>-N load (24 kg/yr) of the inflows in CY 2009. An average annual estimated NO<sub>3</sub>-N load for site 3 of 21 kg/yr was generated by an average annual discharge of 0.049 cfs. The least estimated NO<sub>3</sub>-N load for site 3 was 14 kg/yr (2010) generated from average annual flow of 0.038 cfs.

Equation two was used to estimate NO<sub>3</sub>-N loads for site 6 (outflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). An average annual estimated NO<sub>3</sub>-N load at the outflow of 538 kg was generated by a discharge rate of 0.818 cfs. The NO<sub>3</sub>-N loads for site 6 ranged from 446 (2010) to 710 kg/yr (2011) and were generated from average annual flows of 0.640 and 1.245 cfs, respectively.

### **Total Nitrogen**

Equation three was used to estimate TN loads for site 1 (agricultural and urban inflow) due to the observation of cyclical changes over time during the study period (Table 3 and 4). The average

annual estimated TN load for site 1 of 80 kg was generated by an average annual discharge rate of 0.070 cfs. The TN loads for site 1 ranged from 71 (2009) to 96 kg/yr (2011) and were generated from average annual flows of 0.068 and 0.075 cfs, respectively. The four estimated TN loads (average, CY 2009, 2010, and 2011) from site 1 were greater than the corresponding estimated TN loads from the other inflows (sites 2 and 3).

Equation two was used to estimate TN loads for site 2 (urban inflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). Site 2 contained the lowest estimated TN loads and associated discharges of the inflows. An average annual estimated TN load for site 2 of 19 kg/yr was generated by an average annual discharge of 0.025 cfs. The TN loads for site 2 ranged from 17 (2010) to 22 kg/yr (2011) and were generated from average annual flows of 0.022 and 0.028 cfs, respectively. The pattern of increasing estimated TN loads for complete years associated with increasing discharge rates is apparent between sites 1 and 2, and is generally sustained by site 3.

Equation five was used to estimate TN loads for site 3 (wetland inflow) due to seasonal variations and changes over time being observed during the study period (Table 3 and 4). Site 3 contained estimated TN loads and discharge rates between the other two inflows. An average annual estimated TN load for site 3 of 48 kg/yr was generated by an average annual discharge of 0.049 cfs. The TN loads for site 3 ranged from 35 (2010) to 68 kg/yr (2009) and were generated from average annual flows of 0.038 and 0.054 cfs, respectively. The estimated TN load of 53 kg/yr (0.064 cfs) for CY 2011 does not follow the pattern of an increasing load associated with an increasing discharge when compared to CY 2009 for site 3.

Equation two was used to estimate TN loads for site 6 (outflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). The average annual estimated TN load at the outflow of 1,188 kg was generated by a discharge rate of 0.818 cfs. The TN



loads for site 6 ranged from 955 (2010) to 1,694 kg/yr (2011) and were generated from average annual flows of 0.640 and 1.245 cfs, respectively.

### **Soluble Reactive Phosphorus**

Equation four was used to estimate SRP loads for site 1 (agricultural and urban inflow) due to seasonal variations observed during the study period (Table 3 and 4). The average annual estimated SRP load for site 1 of 21 kg was generated by an average annual discharge rate of 0.070 cfs. The SRP loads for site 1 ranged from 18 (2009) to 29 kg/yr (2011) and were generated from average annual flows of 0.068 and 0.075 cfs, respectively. Three of the estimated SRP loads (average, CY 2009, and 2010) from site 1 were greater than the corresponding estimated SRP loads from the other inflows (sites 2 and 3).

Equation two was used to estimate SRP loads for site 2 (urban inflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). Site 2 contained the lowest estimated SRP loads and associated discharges of the inflows. An average annual estimated SRP load for site 2 of 2.9 kg/yr was generated by an average annual discharge of 0.025 cfs. The SRP loads for site 2 ranged from 2.6 (2010) to 3.5 kg/yr (2011) and were generated from average annual flows of 0.022 and 0.028 cfs, respectively. The pattern of increasing estimated SRP loads for complete years associated with increasing discharge rates is apparent between sites 1 and 2, and is generally sustained by site 3.

Equation four was used to estimate SRP loads for site 3 (wetland inflow) due to seasonal variations observed during the study period (Table 3 and 4). Site 3 contained estimated SRP loads and discharge rates between the other two inflows for average annual, CY 2009, and 2010, but contained the greatest estimated SRP load (31 kg/yr) of the inflows in CY 2011. An average annual estimated SRP

load for site 3 of 15 kg/yr was generated by an average annual discharge of 0.049 cfs. The least estimated SRP load for site 3 was 8.1 kg/yr (2010) generated from average annual flow of 0.038 cfs.

Equation two was used to estimate SRP loads for site 6 (outflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). The average annual estimated SRP load at the outflow of 521 kg was generated by a discharge rate of 0.818 cfs. The SRP loads for site 6 ranged from 320 (2009) to 1,013 kg/yr (2011) and were generated from average annual flows of 0.726 and 1.245 cfs, respectively.

### **Total Phosphorus**

Equation five was used to estimate TP loads for site 1 (agricultural and urban inflow) due to seasonal variations and changes over time being observed during the study period (Table 3 and 4). The average annual estimated TP load for site 1 of 44 kg was generated by an average annual discharge rate of 0.070 cfs. The TP loads for site 1 ranged from 26 (2009) to 70 kg/yr (2011) and were generated from average annual flows of 0.068 and 0.075 cfs, respectively. The four estimated TP loads (average, CY 2009, 2010, and 2011) from site 1 were greater than the corresponding estimated TP loads from the other inflows (sites 2 and 3).

Equation two was used to estimate TP loads for site 2 (urban inflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). Site 2 contained the lowest estimated TP loads and associated discharges of the inflows. An average annual estimated TP load for site 2 of 4.7 kg/yr was generated by an average annual discharge of 0.025 cfs. The TP loads for site 2 ranged from 4.1 (2010) to 5.5 kg/yr (2011) and were generated from average annual flows of 0.022 and 0.028 cfs, respectively. The pattern of increasing estimated TP loads associated with

increasing discharge rates for the complete years is apparent between sites 1 and 2, and is generally sustained by site 3.

Equation five was used to estimate TP loads for site 3 (wetland inflow) due to seasonal variations and changes over time being observed during the study period (Table 3 and 4). Site 3 contained estimated TP loads and discharge rates between the other two inflows. An average annual estimated TP load for site 3 of 24 kg/yr was generated by an average annual discharge of 0.049 cfs. The TP loads for site 3 ranged from 15 (2009) to 50 kg/yr (2011) and were generated from average annual flows of 0.054 and 0.053 cfs, respectively. The estimated TP load of 15 kg/yr (0.038 cfs) for CY 2010 does not follow the pattern of an increasing load associated with an increasing discharge when compared to CY 2009 for site 3.

Equation two was used to estimate TP loads for site 6 (outflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). The average annual estimated TP load at the outflow of 637 kg was generated by a discharge rate of 0.818 cfs. The TP loads for site 6 ranged from 429 (2009) to 1,184 kg/yr (2011) and were generated from average annual flows of 0.726 and 1.245 cfs, respectively.

### **Total Suspended Solids**

Equation two was used to estimate TSS loads for site 1 (agricultural and urban inflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). The average annual estimated TSS load for site 1 of 5,228 kg was generated by an average annual discharge rate of 0.070 cfs. The TSS loads for site 1 ranged from 4,325 (2009) to 6,646 kg/yr (2011) and were generated from average annual flows of 0.068 and 0.075 cfs, respectively. The four estimated TSS

loads (average, CY 2009, 2010, and 2011) from site 1 were greater than the corresponding estimated TSS loads from the other inflows (sites 2 and 3).

Equation two was used to estimate TSS loads for site 2 (urban inflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). Site 2 contained the lowest estimated TSS loads and associated discharges of the inflows. An average annual estimated TSS load for site 2 of 359 kg/yr was generated by an average annual discharge of 0.025 cfs. The TSS loads for site 2 ranged from 313 (2010) to 411 kg/yr (2011) and were generated from average annual flows of 0.022 and 0.028 cfs, respectively. The pattern of increasing estimated TSS loads associated with increasing discharge rates for the complete years is apparent between sites 1 and 2, and is sustained by site 3.

Equation two was used to estimate TSS loads for site 3 (wetland inflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). Site 3 contained estimated TSS loads and discharge rates between the other two inflows. An average annual estimated TSS load for site 3 of 784 kg/yr was generated by an average annual discharge of 0.049 cfs. The TSS loads for site 3 ranged from 547 (2010) to 1,203 kg/yr (2011) and were generated from average annual flows of 0.038 and 0.064 cfs, respectively.

Equation two was used to estimate TSS loads for site 6 (outflow) due to seasonal variations and changes over time not being observed during the study period (Table 3 and 4). The average annual estimated TSS load at the outflow of 127,695 kg was generated by a discharge rate of 0.818 cfs. The TSS loads for site 6 ranged from 75,538 (2009) to 253,000 kg/yr (2011) and were generated from average annual flows of 0.726 and 1.245 cfs, respectively.

## Riverine Constituent Export

Estimated monthly storage values closely follow the average monthly discharge values associated with rainfall (Figures 3 and 4). Estimated annual storage values reveal all constituents being exported from the site through the water column during the study years. The majority of the constituents (all but Cl) annual export totals are greatest during CY 2011, which is associated with the highest annual discharge rate of 1.08 cfs (Table 5).

The retention or export of Cl on a monthly basis follows similar patterns to discharge and precipitation, where Cl exports increase as discharge rates and precipitation totals increase (data not shown). Cl exports averaged 3,100 kg annually with a total of 10,300 kg being exported from WREC over the study period (Table 5). On an annual basis, Cl exports do not follow the same pattern as average annual discharge. The greatest Cl export of 4,200 kg/yr occurred in CY 2009 when the average annual discharge was 0.068 cfs. Cl export in CY 2010 (2,200 kg) was almost half that in 2009 despite similar annual discharge, and export in CY 2011 was less despite almost twice as much flow.

Monthly TN, and associated  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  species, storage values were strongly correlated ( $r > 0.969$ ,  $p < 0.001$ ) to monthly average discharge storages across all sites, where greater N exports are generated from increased discharges (Figures 3 and 4). Total N exports averaged 1,040 kg per year with a total of 3,467 kg (9%  $\text{NH}_4\text{-N}$  and 46%  $\text{NO}_3\text{-N}$ ) being exported from the watershed over the study period. The least TN export of 826 kg (8%  $\text{NH}_4\text{-N}$  and 48%  $\text{NO}_3\text{-N}$ ) related to the least average discharge (0.51 cfs) in CY 2010, while the greatest TN export of 1,523 kg (11%  $\text{NH}_4\text{-N}$  and 41%  $\text{NO}_3\text{-N}$ ) occurred with the greatest average discharge (1.08 cfs) in CY 2011 (Table 5).

Table 5. Estimated annual export (sites 6 - 1 - 2 - 3) (kg) of constituents within the water column and average annual discharge (cfs) for the Watershed Research and Education Center, 2009-2012.

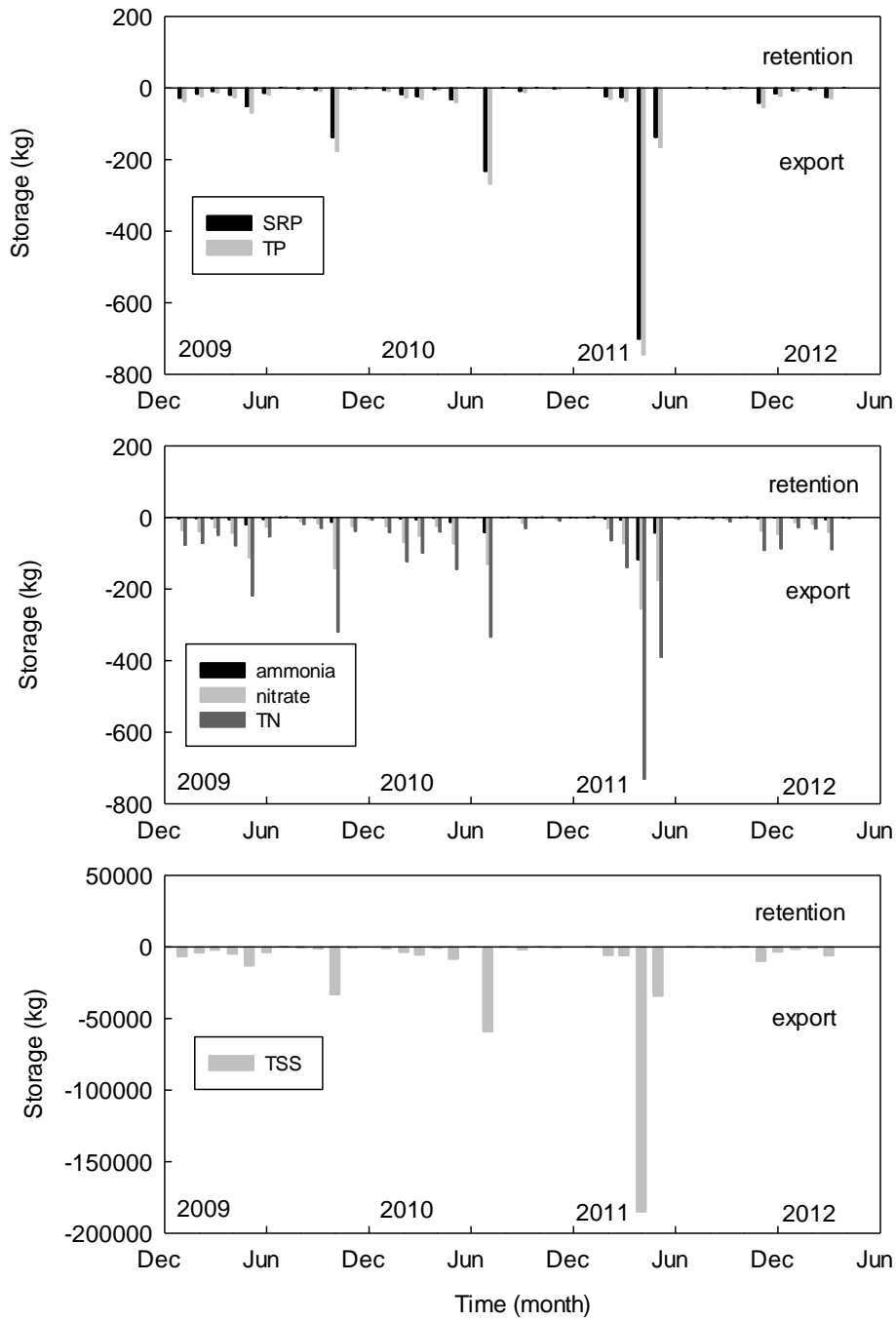
| Time Period | NH <sub>4</sub> -N  | Cl    | NO <sub>3</sub> -N | SRP | TN    | TP    | TSS     | Discharge |
|-------------|---------------------|-------|--------------------|-----|-------|-------|---------|-----------|
|             | ----- (kg/yr) ----- |       |                    |     |       |       |         | (cfs/yr)  |
| CY 2009     | 55.4                | 4,162 | 492                | 290 | 965   | 384   | 70,079  | 0.58      |
| CY 2010     | 68.6                | 2,235 | 398                | 328 | 826   | 396   | 81,106  | 0.51      |
| CY 2011     | 175                 | 3,444 | 631                | 950 | 1,523 | 1,058 | 244,740 | 1.08      |
| Average     | 91.7                | 3,082 | 479                | 482 | 1,040 | 565   | 121,325 | 0.72      |

Monthly TP, and associated SRP, retention and export follow similar patterns to monthly average discharge storages across all sites. There was a significant positive correlation ( $r > 0.952$ ,  $p < 0.001$ ) between monthly P values and monthly average discharge across all sites, where greater P exports are generated from increased discharges (Figures 3 and 4). Total P exports averaged 565 kg per year with a total of 1,882 kg (85% SRP) being exported from the watershed over the study period. The least TP export of 384 kg (75% SRP) occurred with an average discharge 0.58 cfs in CY 2009, and the greatest TP export of 1,058 kg (90% SRP) occurred with the greatest average discharge (1.08 cfs) in CY 2011 (Table 5).

Monthly TSS retention and export follow similar patterns to monthly average discharge storages across all sites. There was a significant positive correlation ( $r = 0.947$ ,  $p < 0.001$ ) between monthly TSS values and monthly average discharge across all sites, where greater TSS exports are generated from increased discharges (Figures 3 and 4). Total TSS exports averaged 121,325 kg per year with a total of 404,415 kg being exported from the watershed over the study period. The least TSS export of 70,079 kg occurred with an average annual discharge 0.58 cfs in CY 2009, and the greatest TSS export of 244,740 kg occurred with the greatest average annual discharge (1.08 cfs) in CY 2011 (Table 5). Notable relationships occur with monthly storages of N and P when compared to average monthly storages of

TSS. TP and SRP indicated the strongest correlation ( $r > 0.997$ ,  $p < 0.001$ ) to TSS. TN and  $\text{NH}_4\text{-N}$  relationships to TSS ( $r > 0.906$ ,  $p < 0.001$ ) were not as strong as TP, and  $\text{NO}_3\text{-N}$  revealed the weakest correlation to TSS ( $r = 0.840$ ,  $p < 0.001$ ).

Figure 4. Estimated monthly storage (inflows – outflow) for constituents within the water column from the Watershed Research and Education Center, 2009-2012.





## **Watershed Mass Balance**

The import of nutrients on the landscape resulted from feed conversion by animals, land application of poultry litter and fertilizer, N fixation by legumes (i.e. alfalfa), and atmospheric deposition (Table 6). The export of nutrients resulted from hay production, when the hay was removed and used offsite. The animals that were present and then removed from WREC also resulted in the export of nutrients. However, this was not able to be quantified based on the available records.

Overall, nutrients were generally exported from the landscape except in CY 2006 when N (9,740 kg) and P (1,380 kg) loads increased from a large cattle presence and limited hay export offsite. The cattle were present in limited numbers the following years, resulting in approximately 80% of the hay produced being used offsite. The increased hay production exported over 5,900 kg of N and 890 kg of P in CY 2007. The import and export of nutrients from the above mentioned sources was almost in balance during this CY. The cattle were completely removed from WREC in CY 2008, resulting in the greatest export of N (1,400 kg) and P (380 kg). The fields at WREC were also revised such that field boundaries more closely followed topographic boundaries starting in 2008.

During the CYs (2009-2011) when riverine exports were available, P was in close balance between the imports and exports from these sources. Phosphorus loads ranged from an export of 230 kg in 2011 to 280 kg in 2009. The export of nutrients during these CYs was likely the result of reduced fertilizer and poultry litter applications, while the fields were being reorganized. Cattle were reintroduced in 2012 and numbers, as well as fertilizer applications, will likely increase.

Table 6. Annual N and P loads imported from feeds of various livestock, fertilizer applications, atmospheric deposition, and legume fixation, and exported from hay harvesting on the Watershed Research and Education Center from 2006 through April, 2012. Negative values represent loads exported from the watershed.

| <b>Nitrogen Load (kg/year)</b>   |        |        |      |       |            |                      |                 |                    |        |
|----------------------------------|--------|--------|------|-------|------------|----------------------|-----------------|--------------------|--------|
| Year                             | Cattle | Horses | Pigs | Sheep | Fertilizer | ADP <sup>[b]</sup>   | Legume fixation | Hay                | Total  |
| 2006                             | 1,790  | 250    | 70   | 100   | 4,660      | 1,660                | 1,490           | -280               | 9,740  |
| 2007                             | 150    | 250    | 70   | 100   | 2,350      | 1,220                | 1,490           | -5,910             | -290   |
| 2008                             | 0      | 250    | 70   | 130   | 380        | 1,560                | 470             | -4,240             | -1,380 |
| 2009                             | 30     | 250    | 70   | 130   | 110        | 1,510                | 620             | -2,550             | 170    |
| 2010                             | 0      | 160    | 70   | 130   | 230        | 1,120                | 620             | -2,490             | -170   |
| 2011                             | 5      | 160    | 70   | 130   | 530        | 1,410 <sup>[c]</sup> | 1,050           | -3,580             | -230   |
| 2012                             | 30     | 50     | 10   | 40    | 30         | NA <sup>[d]</sup>    |                 | TBD <sup>[a]</sup> | 160    |
| <b>Phosphorus Load (kg/year)</b> |        |        |      |       |            |                      |                 |                    |        |
| Year                             | Cattle | Horses | Pigs | Sheep | Fertilizer | ADP <sup>[b]</sup>   | Legume fixation | Hay                | Total  |
| 2006                             | 410    | 50     | 20   | 20    | 970        | 7                    | -               | -40                | 1,430  |
| 2007                             | 30     | 50     | 20   | 20    | 570        | 5                    | -               | -890               | -200   |
| 2008                             | 0      | 50     | 20   | 20    | 170        | 9                    | -               | -640               | -380   |
| 2009                             | 8      | 50     | 20   | 20    | 0          | 7                    | -               | -390               | -280   |
| 2010                             | 0      | 30     | 20   | 20    | 50         | 7                    | -               | -380               | -250   |
| 2011                             | 1      | 30     | 20   | 20    | 230        | 8                    | -               | -540               | -230   |
| 2012                             | 7      | 10     | 4    | 6     | 0          | NA <sup>[d]</sup>    | -               | TBD <sup>[a]</sup> | 30     |

<sup>[a]</sup>TBD, to be determined because the forage was not harvested prior to April 30, 2012.

<sup>[b]</sup>Atmospheric Deposition within Precipitation (ADP) from NH<sub>4</sub>, NO<sub>3</sub>, and PO<sub>4</sub>.

<sup>[c]</sup>N information not available for 2011, so the average N (kg/ha) from 2006-2010 was used.

<sup>[d]</sup>N and P information not available for 2011 and 2012.

## Discussion

### Chloride

Chloride is an indicator of anthropogenic influence, and it is most commonly associated with road salting agents, fertilizer applications, and runoff from impermeable surfaces (Wolf et al., 2007). Chloride concentrations significantly increase in streams after deicers are applied to roadways draining into channels (Allert et al., 2012). The greatest Cl exports from WREC occurred in 2009, which was most likely related to deicer application given that 43 mm of freezing rain occurred on January 26 and 27, 2009. The 2009-2010 winter also had the highest snowfall (655 mm) recorded since 1940 in northwest Arkansas.

Chloride concentrations were generally below drinking water standards (250 mg/L, USEPA, 2012) and aquatic toxicity concerns (230 mg/L, ADEQ 2012), except on two sample dates. The Cl concentrations on these two dates exceeding established criteria, as concentrations were greater than 1,000 mg/L. The first event in 2009 (October 1) was not associated with typical winter conditions, whereas the second event (November 25, 2010) may have been because the month contained many (75%) days with below freezing temperature but relatively little precipitation (40 mm).

Chloride is a conservative ion which often has greater concentrations at low base flow and then dilution occurs with higher discharge. The majority of the Cl transported into WREC occurred during high flow conditions, representing 84% of the load on average across the three inflows. The largest influx was from the urban and (row crop) agricultural sub-catchment (32.2 kg/ha-yr, Table 7), where the other two inflows combined only contributed 44% of the Cl yield. Lowrance et al. (1985) observed that Cl loads and yields were generally greater from agricultural catchments compared to those less agriculturally developed. Row crops are often irrigated which can move chemicals vertically with the recharging of groundwater (Schilling and Libra, 2003), but the agricultural fields at AAREC were only irrigated during

summers to maintain plant variety testing and other experiments. These fields are more intensely managed and have municipal water (with 8 mg/L Cl) used as the irrigation source. In more northern environments, Cl yields are often much greater from urban catchments because of increased deicer use from more sustained winters (Sonzogni et al., 1980). Trends in riverine Cl were no observed at WREC during the study period, which may be due to the limited study time of three years.

Table 7. Estimated yields for constituents from Site 1 (16 ha agricultural), Site 2 (11 ha urban), Site 3 (26 ha pasture/agriculture facilities), and Site 6<sup>[a]</sup> (139 ha pasture) of the Watershed Research and Education Center, 2009-2012.

| Constituent |                               | NH <sub>4</sub> -N     | Cl   | NO <sub>3</sub> -N | SRP  | TN   | TP   | TSS  |
|-------------|-------------------------------|------------------------|------|--------------------|------|------|------|------|
|             |                               | ----- (kg/ha-yr) ----- |      |                    |      |      |      |      |
| Site 1      | Agricultural and Urban Stream | 0.52                   | 32.2 | 2.15               | 1.32 | 5.00 | 2.72 | 325  |
| Site 2      | Urban Stream                  | 0.19                   | 12.2 | 0.32               | 0.28 | 1.82 | 0.44 | 34.2 |
| Site 3      | Wetland Stream                | 0.21                   | 12.7 | 0.82               | 0.58 | 1.89 | 0.96 | 30.7 |
| Site 6      | WREC Contribution             | 0.66                   | 22.2 | 3.45               | 3.47 | 7.49 | 4.06 | 873  |

<sup>[a]</sup> Infows (sites 1-3) were subtracted from site 6 to provide yields associated with the Watershed Research and Education Center.

## Nitrogen

From a watershed perspective, the input of N was much greater to the WREC landscape than that observed in the inflows (sites 1-3). Atmospheric deposition of N with precipitation was a relatively constant input (1120-1660 kg/yr), but the sum of the import of feed, application of fertilizer, and legume N fixation was greater (Table 6). In 2006, there was a net addition of 9,740 kg of N because of the large import of feed and application of fertilizer. However, this changed rapidly to a net export of N in hay when the animals were removed and 80% of the hay produced was used off site. The WREC N balance

also excludes the potential for gaseous losses, where Van Breemen et al. (2002) suggested that half of the N inputs at the watershed scale were lost through this pathway (primarily denitrification).

Annual nitrogen export from the watershed was apparent on the landscape and riverine level. Hay transported out of the watershed was the primary landscape N export, and was annually greater than the riverine N export (site 6 - 1 - 2 - 3) throughout the study period (Figure 5). Hay management strategies can increase total annual N uptake in nutrient rich landscapes, as McLaughlin et al. (2005) revealed a 31-43% increase in total N uptake when employing overseeding techniques and spring hay harvesting to a swine effluent fertilized landscape.

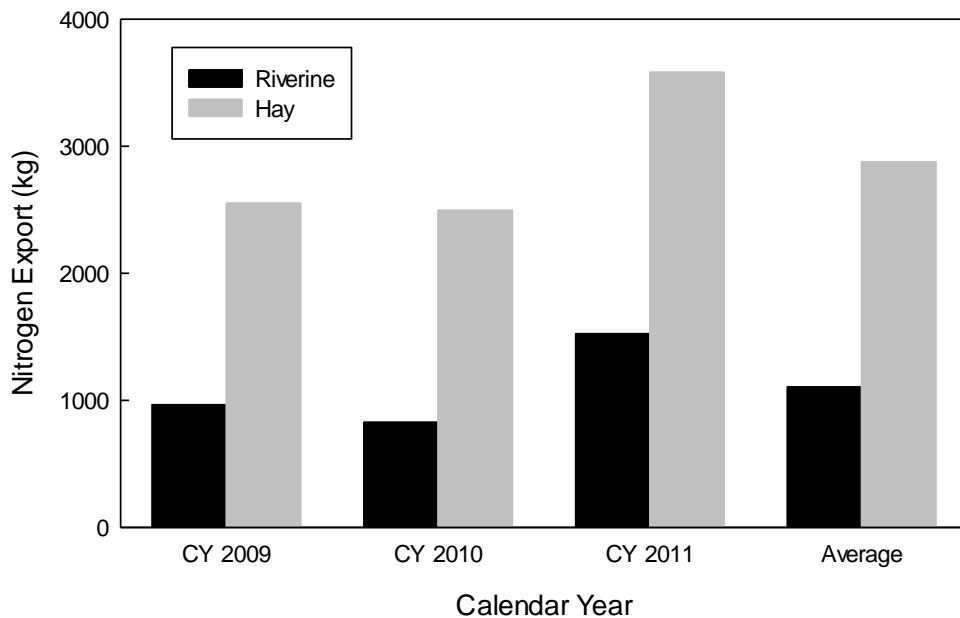


Figure 5. Annual N export through riverine discharge and hay harvest from the Watershed Research and Education Center, 2009-2012.

Despite having a farm-scale (WREC) export of N from the landscape since 2007, the loss of N (7.49 kg/ha-yr) increased at the watershed outlet (site 6) relative to the riverine outputs (sites 1-3). The

latter years (2009-2011) were in close N balance at the landscape level, suggesting that residual N from historical management was likely the source. Atmospheric deposition during rainfall events and saturated soils could be another potential N source, as the atmospheric N within the precipitation would runoff directly to the stream channels. The majority of the TN lost from WREC was in the form of  $\text{NO}_3\text{-N}$  (46% on average), and the transport (e.g. monthly loads) of  $\text{NO}_3\text{-N}$  and TN was significantly related ( $r=0.969$ ,  $p<0.001$ ). The WREC N balance may shift in future years to accumulation (excluding denitrification), because cattle will be reintroduced resulting in import of feed, likely increases in fertilizer application, and reduced hay export from WREC to other sites.

The majority of the TN transported into WREC occurred during high flow conditions, representing 94% of the load on average across the three inflows. The greatest TN inflow (5.0 kg/ha-yr, Table 7) occurred from the urban and agricultural sub-catchment (site 1) and contained 43%  $\text{NO}_3\text{-N}$  and 10%  $\text{NH}_4\text{-N}$  on average. Lowrance et al. (1985) observed that TN loads and yields were generally greater from agricultural catchments compared to those less agriculturally developed. The largest potential source of N is probably the row crop fields, where N inputs are associated with fertilizer applications (Lowrance et al., 1985; Sharpley et al., 1987). Another potential N source includes wastes attributed to Agriculture Park and the urban area, where pet feces, human foods, and grass clippings have been known to contribute inputs of N into the landscape (Fissore et al., 2012). However, it is likely that runoff from the urban areas and agricultural park dilute the N lost from the row crop fields. An increasing TN trend of 8% was observed at site 1, and may be due to fertilization quantities applied to the row crops.

TN inflows from the urban and wetland stream inflows (site 2 and site 3) were 62-64% less than the agricultural dominated sub-catchment. The urban inflow (site 2) contained the least TN yield of 1.82 kg/ha-yr (10%  $\text{NH}_4\text{-N}$  and 17%  $\text{NO}_3\text{-N}$ ), where N sources are most likely from lawn maintenance (fertilization, grass clippings, and compost piles), human foods, and pet waste (Fissore et al., 2012). A TN

yield of 1.89 kg/ha-yr (11% NH<sub>4</sub>-N and 43% NO<sub>3</sub>-N) was calculated for the wetland inflow (site 3). Since 99% of the studied inflow was from high flow conditions (staff gage >0.2 m corresponding to 0.0063 cfs), potential sources of N were associated with storm water runoff from agricultural and research facilities and associated parking lots. The wells in the wetland area have been observed as artesian under select wet conditions, and shallow or deep groundwater return would influence N losses. The dilution associated with this groundwater return may explain the decreasing TN trend of 17%.

### **Phosphorus**

The input of P was much greater to the WREC landscape from a watershed perspective than that observed in the inflows (sites 1-3). The import of feed and application of fertilizer accounted for the majority of P inputs, while atmospheric deposition was relatively low and constant (5-9 kg/ha-yr). In 2006, there was a net addition of 1,430 kg of P because of the large import of feed and application of fertilizer. However, the import of P to WREC substantially decreased in subsequent years with the removal of cattle.

Annual phosphorus export from the watershed was apparent on the landscape and riverine level. Riverine transport (site 6 - 1 - 2 - 3) was the primary export mechanism of annual TP from WREC, whereas hay harvest and offsite relocation was generally lesser (Figure 6). Hay management strategies can increase total annual P uptake in nutrient rich landscapes, as McLaughlin et al. (2005) revealed a 6-22% increase in total P uptake when employing overseeding techniques and spring hay harvesting to a swine effluent fertilized landscape.

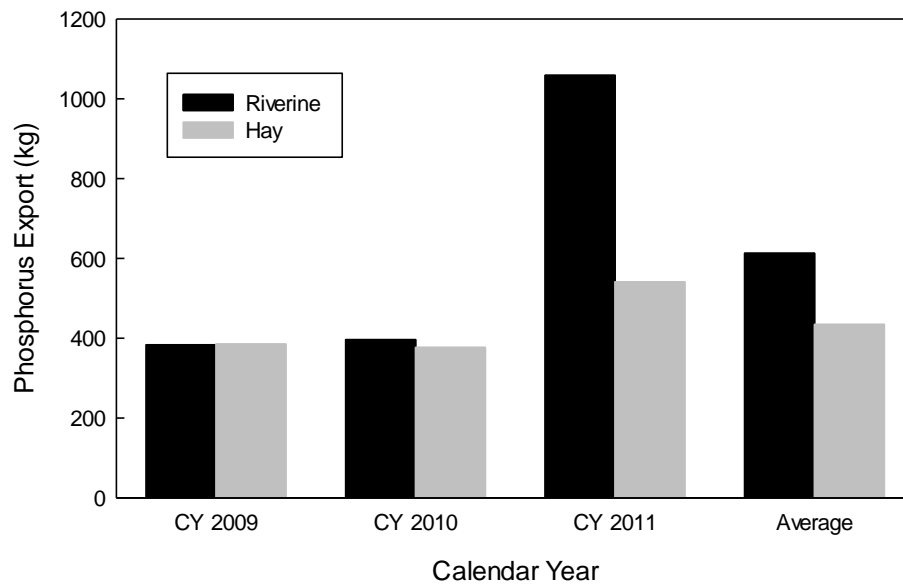


Figure 6. Annual P export through riverine discharge and hay harvest from the Watershed Research and Education Center, 2009-2012.

Despite having a farm-scale (WREC) export of P from the landscape since 2007, the loss of P (4.06 kg/ha-yr) increased at the watershed outlet (site 6) relative to the riverine inputs (sites 1-3). The latter years (2009-2011) revealed P exports at the landscape level ranging from 230 kg to 280 kg, and P was exported through the riverine system at site 6 suggesting that residual P from historical management was likely the source. The majority of the P lost from WREC was in the form of SRP (85% on average) and was significantly related ( $r > 0.997$ ,  $p < 0.001$ ) with TSS. The most likely transport mechanism for P was through SRP attached to TSS, as P has a rapid fixation to surface soil material (Sharpley et al., 1987) and the loss of P in surface water runoff originates primarily from small areas during a few storms (Shapley et al., 2001).

The majority of the TP transported into WREC occurred during high flow conditions, representing 97% of the load on average across the three inflows. The urban and agricultural sub-



catchment (site 1) contained the greatest TP inflow of 2.72 kg/ha-yr (48% SRP on average). Lowrance et al. (1985) observed that TP loads and yields were generally greater from agricultural catchments compared to those less agriculturally developed. The potential source of P and associated high TSS amounts is surface soil runoff of the fertilized row crops, as noted by Beaulac and Reckhow (1982).

The urban sub-catchment (site 2) contained the least TP inflow of 0.44 kg/ha-yr (63% SRP on average). The largest potential sources of P associated with urban areas are from human food, fertilizers (Metson et al., 2012), and pet feces (Fissore et al., 2012). A TP yield of 0.96 kg/ha-yr (11% SRP) was calculated for the wetland inflow (site 3). Since 99% of the studied inflow was from high flow conditions (staff gage >0.2 m corresponding to 0.0063 cfs) , potential sources of P were associated with storm water runoff from agricultural and research facilities and associated parking lots. Trends in riverine TP were no observed at WREC during the study period, which may be due to the limited study time of three years.

### **Total Suspended Solids**

Increased total suspended solids within stormwater are generally accredited to erosional areas containing disturbed soils such as (1) agricultural settings associated with tillage and fallow row crops (Beaulac and Reckhow, 1982), (2) urban settings associated with active construction sites and channel-bank erosion (Nelson and Booth, 2002), and (3) pasture settings associated with compacted soils and higher runoffs (Kurz et al., 2006). The majority of the TSS transported into WREC occurred during high flow conditions, representing 97% of the load on average across the three inflows. The greatest TSS inflow (325 kg/ha-yr, Table 7) occurred from the catchment area containing row crops (site 1), whereas the other two inflows were an order of magnitude less. The largest potential source of sediment is probably the row crop fields, where surface erosion during rainfall-runoff transports sediments into the stream. Russell et al. (2001) used sediment finger printing to show that 90% of sediment transport was

related to field management and only 10% from bank erosion. The sediment yields at this site were 325 kg/ha-yr and much lower than values of 4,000-5,880 kg/ha observed from row crops in Arkansas (Vories et al., 2001). Vories et al. (2001) presented edge of field losses, and the difference here could be sediment contained in the grassed waterways and also dilution by Agriculture Park and the urban areas.

The minimal influx of sediment into the other two streams is not surprising, given that these areas have been developed (urbanized) for several decades. Nelson and Booth (2002) noted that the slow developing urban watersheds (0.3%Δ/year) directly generate relatively little sediment, and that much sediment was produced by bank erosion. The urban inflow (site 2) transports very little sediment from its 10 ha catchment because (1) no major construction activities have occurred since 1994 (aerial imagery) and (2) little channel bank erosion occurs in the urban drainage ditches. The urban drainage ditches are ephemeral with completely grassed waterways, which produce little sediment.

The sediment yield at WREC (873 kg/ha-yr) was three times greater than that from the agricultural and urban inflow (site 1). First, the agricultural catchment is partly urbanized and a semi-forested city park (site 1), which would greatly reduce the sediment yield from this catchment. Second, the fields at WREC began reorganization in 2008 following the removal of cattle. Stream banks were degraded from the previous presence of cattle, and fields were plowed under to reestablish fence lines. Currently, some of these fields undergo occasional surface soil exposure from tilling for rock removal.

The pattern between increased discharge rates associated with increased precipitation was expected, as it has been previously seen on a regional (Haggard et al., 2003; Migliaccio et al., 2007) and small watershed scale (Owens et al., 2008). Understanding discharge from the interior sites of Research Branch (sites 4 and 5) would allow the application of FAC trends and load estimation, which would aid in researching (1) the effectiveness of the riparian buffer and (2) runoff associated with the agricultural practices applied to the catchments of these monitoring stations. A future recommendation is to collect

field measurements of discharge at varying staff gage heights manually or through the implementation of an in stream recording device for sites 4 and 5 to enhance research at WREC. Trends in riverine TSS were no observed at WREC during the study period, which may be due to the limited study time of three years.

## REFERENCES

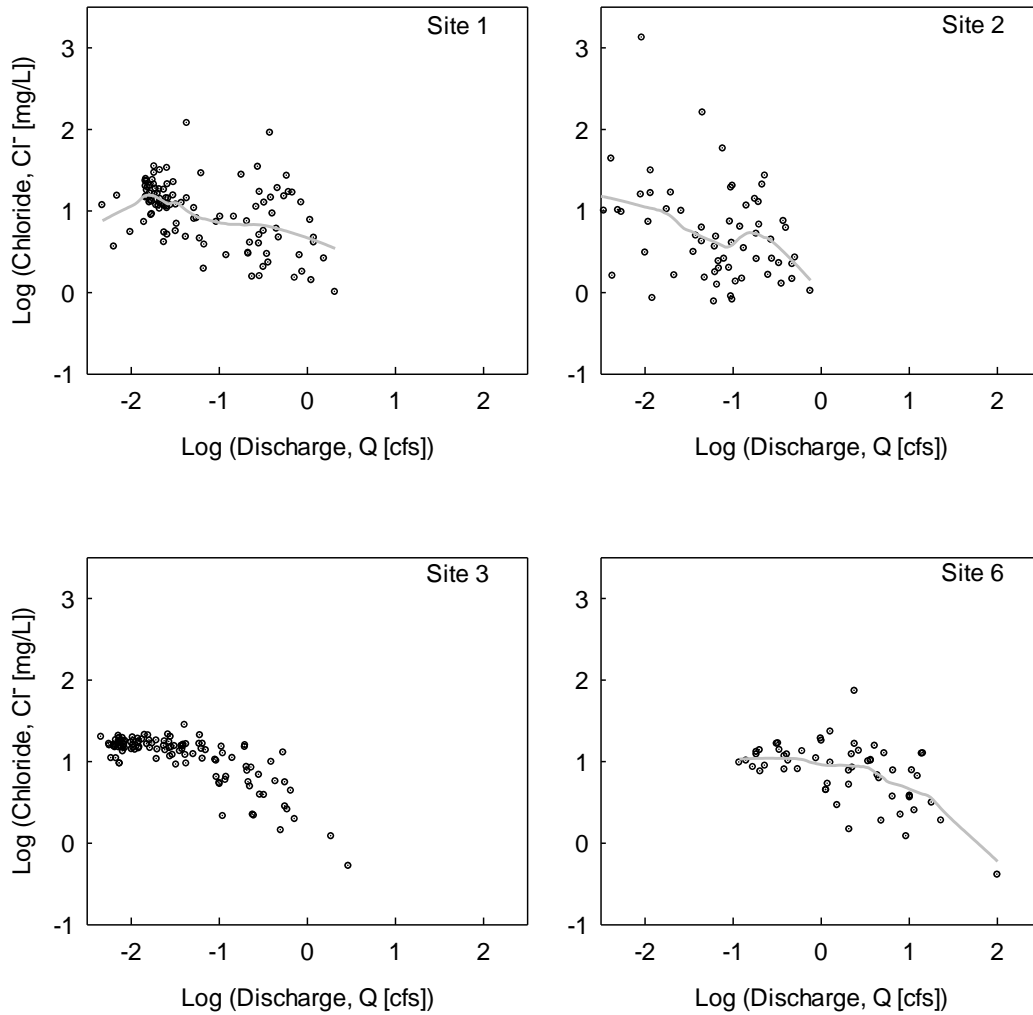
- ADEQ. 2012. Assessment of Potential Environmental Effects of Modifying Water Quality Standards for Delta Ecoregion Streams within the Bayou Meto Basin Project. Available at: <http://www.adeg.state.ar.us/regs/drafts>. Accessed 23 July 2012.
- Allert, A. L., C. L. Cole-Neal, and J. F. Fairchild. 2012. Toxicity of chloride under winter low-flow conditions in an urban watershed in Central Missouri, USA. *Bull. Environ. Contam. Toxicol.* 89: 296-301.
- ASAE Standards. 2005. D384.2: Manure production and characteristics. St. Joseph, Mich: ASAE.
- Beaulac, M. N., and K. H. Reckhow. 1982. An examination of land use – nutrient export relationships. *Water Resources Bulletin.* 16(6): 1013-1024.
- Bekele, A., and A. McFarland. 2004. Regression based flow adjustment procedures for trend analysis of water quality data. *Trans. American Soc. Agric. Eng.* 47: 1093-1104.
- Davis, G. V., M. S. Gadberry, and T. R. Troxel. 2002. Composition and nutrient deficiencies of Arkansas forages for beef cattle. *The Professional Animal Scientist.* 18: 127-134.
- EPA. 2012. United States Environmental Protection Agency Drinking Water Contaminants. Available at: <http://water.epa.gov/drink/contaminants/index.cfm#List>. Accessed 23 July 2012.
- Fissore, C., S. E. Hobbie, J. Y. King, J. P. McFadden, K. C. Nelson, and L. A. Baker. 2012. The residential landscape: fluxes of elements and the role of household decisions. *Urban Ecosystems.* 15: 1-18.
- Groffman, P. M., N. L. Law, K. T. Belt, L. E. Band, and G. T. Fisher. 2004. Nitrogen fluxes and retention in urban watershed ecosystems. *Ecosystems.* 7: 393-403.
- Haggard, B. E., P. A. Moore Jr., I. Chaubey, and E. H. Stanley. 2003. Nitrogen and phosphorus concentrations and export from an Ozark plateau catchment in the United States. *Biosystems Eng.* 86(1): 75-85.
- Hann, C. T., B. J. Barfield, and J. C. Hayes. 1994. *Design Hydrology and Sedimentology for Small Catchments.* San Diego, Ca: Academic Press, Inc.
- Harmel, R. D., D. R. Smith, R. L. Haney, and M. Dozier. 2009. Nitrogen and phosphorus runoff from cropland and pasture fields fertilized with poultry litter. *J. Soil Water Conserv.* 64(6): 400-412.
- Heichel, G. H., D. K. Barnes, and C. P. Vance. 1981. Nitrogen fixation of alfalfa in the seeding year. *Crop Science.* 21: 330-335.
- Helsel, D. R., and R. M. Hirsch. 2002. *Statistical methods in water resources: U.S. Geological Survey Techniques of Water-Resources Investigations.*
- Hill, A. R. 1996. Nitrate removal in stream riparian zones. *J. Environ. Qual.* 25: 743-755.
- Hirsch, R. M., R. B. Alexander, and R. A. Smith. 1991. Selection of methods for detection and estimation of trends in water quality. *Water Resources Res.* 5(5): 803-813.

- Jordan, T. E., D. L. Correll, W. T. Peterjohn, and D. E. Weller. 1986. Nutrient flux in a landscape: The Rhode river watershed and receiving waters. Washington DC, Smithsonian Institution Press.
- Kurz, I., C. D. O'Reilly, and H. Tunney. 2006. Impact of cattle on soil physical properties and nutrient concentrations in overland flow from pasture in Ireland. *Agriculture, Ecosystems, and Environment*. 113: 378-390.
- Lee, K. H., T. M. Isenhardt, and R. C. Shultz. 2003. Sediment and nutrient removal in an established multi-species riparian buffer. *J. of Soil and Water Conservation*. 58(1): 1-8.
- Lettenmaier, D. P., E. R. Hooper, C. Wagoner, and K. B. Faris. 1991. Trends in stream quality in the continental United States. *Water Resources Res.* 27(3): 327-339.
- Mahler, B. J., and F. L. Lynch. 1999. Muddy waters: temporal variation in sediment discharging from a karst spring. *Journal of Hydrology*. 214: 165-168.
- McLaughlin, M. R., K. R. Sistani, T. E. Fairbrother, and D. E. Rowe. Overseeding common bermudagrass with cool-season annuals to increase yield and nitrogen and phosphorus uptake in a hay field fertilized with swine effluent. *American Society of Agronomy*. 97: 487-493.
- Meals, Donald W. 1996. Watershed-scale response to agricultural diffuse pollution control programs in Vermont, U.S.A. *Wat. Sci. Tech.* 33(4-5): 197-204.
- Metson, G., R. Hale, D. Iwaniec, E. Cook, J. Corman, C. Galletti, and D. Childers. Phosphorus in Phoenix, a budget and spatial representation of phosphorus in an urban ecosystem. *Ecological Applications*. 22: 705-721.
- Migliaccio, K. W., B. E. Haggard, I. Chaubey, and M. D. Matlock. 2007. Linking watershed subbasin characteristics to water quality parameters in War Eagle Creek watershed. *Trans. American Soc. Agric. Eng.* 50(6): 2007-2016.
- Migliaccio, K. W., J. Castro, and B. E. Haggard. 2011. Water quality statistical analysis. In Y. Li and K. W. Migilaccio (editors) 'Water Quality Concepts, Sampling and Analyses' CRC Press, Taylor and Francis Group, Boca Raton, Florida.
- Nagy, R. C., B. G. Lockaby, B. Helms, L. Kalin, and D. Stoeckel. 2011. Water resources and land use and cover in a humid region: The Southeastern United States. *J. of Env. Quality*. 40: 867-878.
- Nelson, E. J., and D. B. Booth. 2002. Sediment sources in an urbanizing, mixed land-use watershed. *J. of Hydrology*. 264: 51-68.
- Owens, L. B., M. J. Shipitalo, and J. V. Bonta. 2008. Water quality response times to pasture management changes in small and large watersheds. *J. Soil Water Conserv.* 63(5): 292-299.
- Paul, M. J., and J. L. Meyer. 2001. Streams in the urban landscape. *Annu. Rev. Ecol. Syst.* 32: 333-365.
- Peter, S., R. Rechsteiner, M. F. Lehmann, R. Brankatschk, T. Vogt, S. Diem, B. Wehrli, K. Tockner, and E. Durisch-Kaiser. 2012. Nitrate removal in a restored riparian groundwater system: functioning and importance of individual riparian zones. *Biogeosciences Discuss.* 9: 6715-6750.

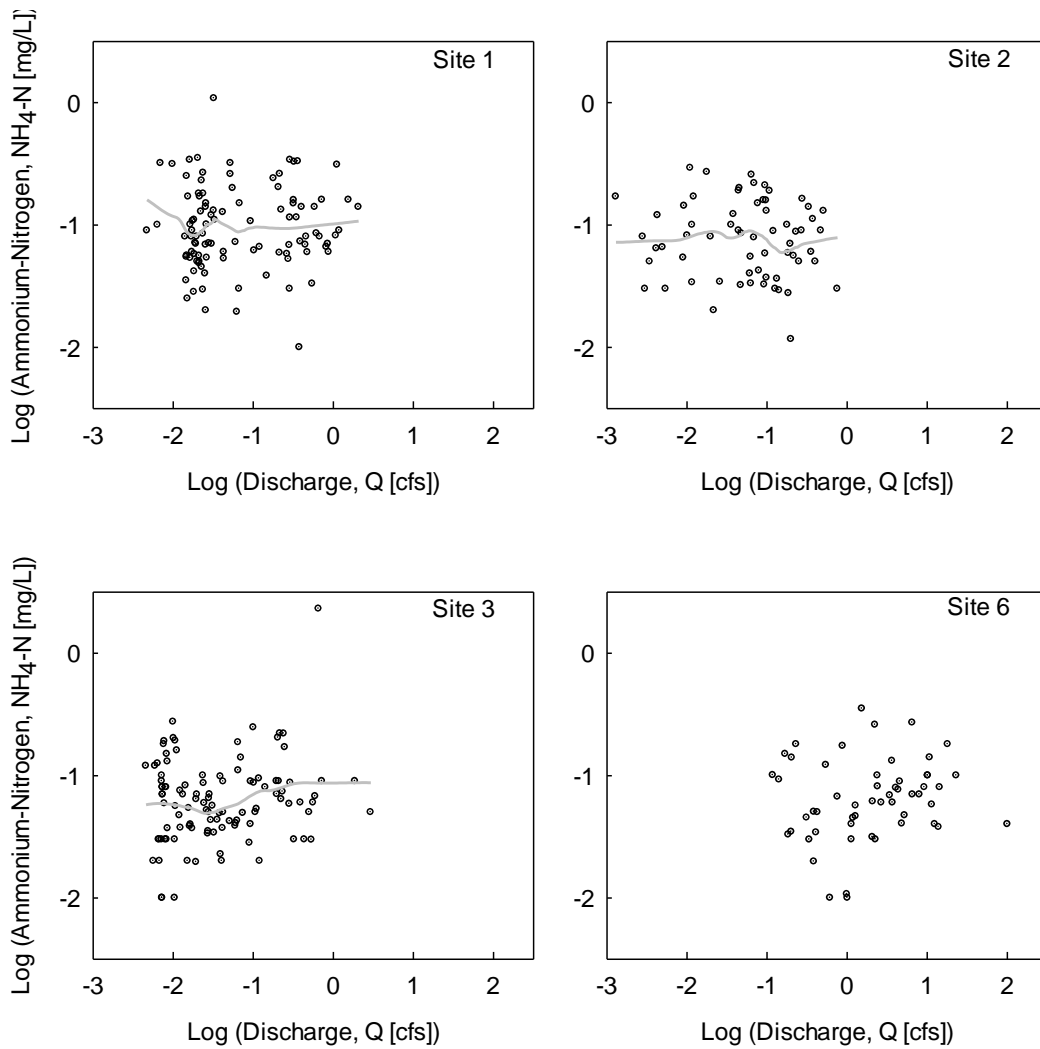
- Pionke, H. B., and J. B. Urban. 1985. Effect of agricultural land use on ground – water quality in a small Pennsylvania watershed. *Ground Water*. 23(1): 68-80.
- Russell, M. A., D. E. Walling, and R. A. Hodgkinson. 2001. Suspended sediment sources in two small lowland agricultural catchments in the UK. *J. of Hydrology*. 252: 1-24.
- Sabater, S., A. Butturini, J. C. Clement, T. Burt, D. Dowrick, M. Hefting, V. Maitre, G. Pinay, C. Postolache, M. Rzepecki, and F. Sabater. Nitrogen removal by riparian buffers along European climatic gradient: patterns and factors of variation. *Ecosystems*. 6: 20-30.
- Schilling, K. E., and R. D. Libra. 2003. Increased baseflow in Iowa over the second half of the 20<sup>th</sup> century. *J. of the American Water Resources Association*. 369(4):851-860.
- Shreve, B. R., P. A. Moore, Jr., T. C. Daniel, D. R. Edwards, and D. M. Miller. 1995. Reduction of Phosphorus in runoff from field-applied poultry litter using chemical amendments. *J. Environ. Qual.* 24: 106-111.
- Sharpley, A. N., S. J. Smith, and J. W. Naney. 1987. Environmental impact of agricultural nitrogen and phosphorus use. *J. Agric. Food Chem.* 35: 812-817.
- Sharpley, A. N., R. W. McDowell, and P. J. A. Kleinman. 2001. Phosphorus loss from land to water: integrating agricultural and environmental management. *Plant and Soil*. 237: 287-307.
- Singh, K., K. Lee, J. Worley, L. M. Risse, and K. C. Das. 2010. Anaerobic digestion of poultry litter: a review. *App. Eng. In Agric.* 26(4): 677-688.
- Smith, K. A., and J. P. Frost. 1999. Nitrogen excretion by farm livestock with respect to land spreading requirements and controlling nitrogen losses to ground and surface waters. Part 1: cattle and sheep. *Bioresource Technology*. 71(2000): 173-181.
- Sonzogni, W. C., G. Chesters, D. R. Coote, D. N. Jeffs, R. C. Ostry, and J. B. Robinson. 1980. Pollution from land runoff. *Environmental Science & Technology*. 14(2): 148-153.
- Toland, D. C., B. E. Haggard, and M. E. Boyer. 2012. Evaluation of nutrient concentrations in runoff water from green roofs, conventional roofs, and urban streams. *Trans. American Soc. Agric. Eng.* 55(1): 99-106.
- Van Breemen, N., E. W. Boyler, C. L. Goodale, N. A. Jaworski, K. Paustian, S. P. Seitzinger, K. Lajtha, B. Mayer, D. Van Dam, R. W. Howarth, K. J. Nadelhoffer, M. Eve, and G. Billen. 2002. Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern U.S.A. *Biogeochemistry*. 57/58: 267-293.
- Vories, E. D., T. A. Costello, and R. E. Glover. 2001. Runoff from cotton fields fertilized with poultry litter. *Trans. American Soc. Agric. Eng.* 44(6): 1495-1502.
- White, K. L., B. E. Haggard, and I. Chaubey. 2004. Water quality at the Buffalo National River, Arkansas, 1991-2001. *Trans. American Soc. Agric. Eng.* 47(2): 407-417.
- Wolf, L., J. Klinger, H. Hoetzel, and U. Mohrlök. 2007. Quantifying mass fluxes from urban drainage systems to the urban soil-aquifer system. *J. Soils Sediments*. 7(2): 85-95.

## APPENDIX I

Log transformed chloride concentration as a function of log transformed discharge with the LOESS regression line from samples collected at Sites 1, 2, 3, and 6 of the Watershed Research and Education Center.

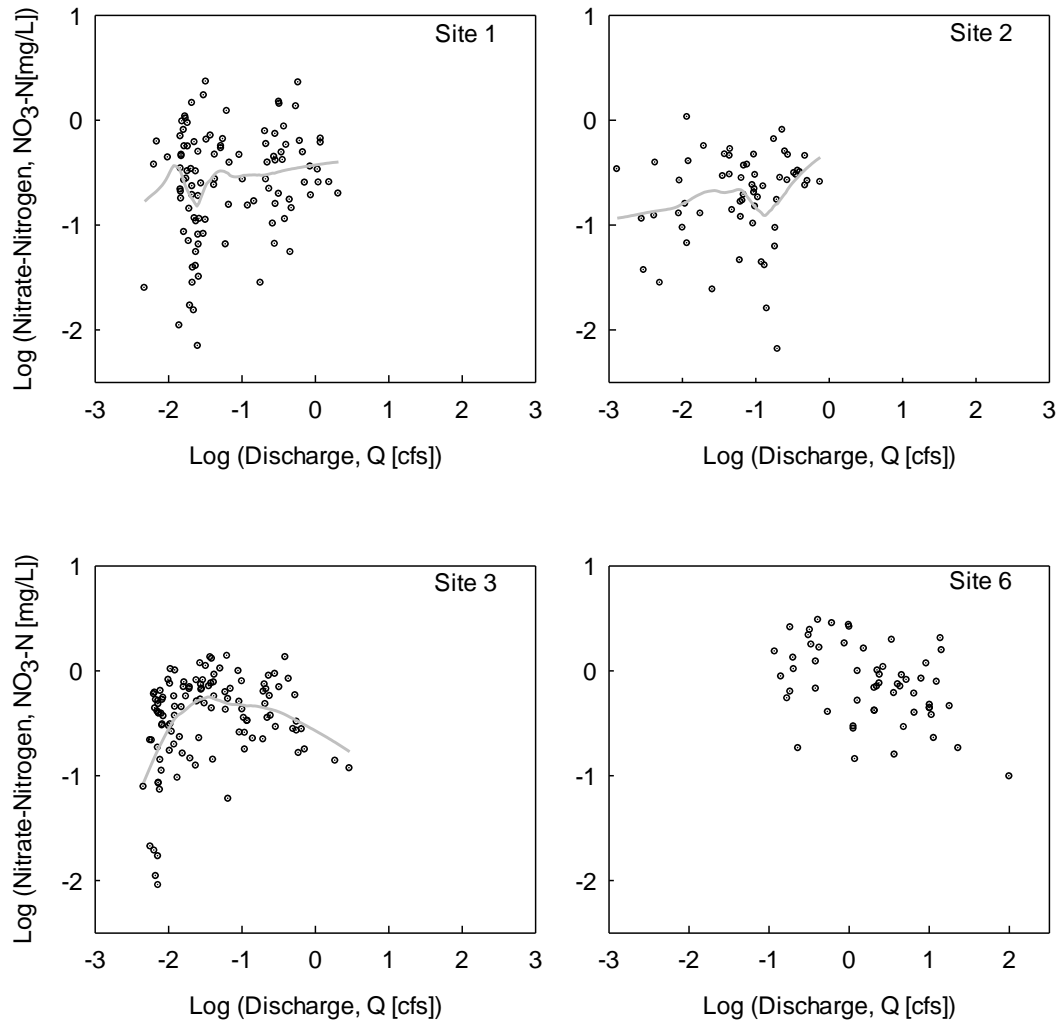


Log transformed  $\text{NH}_4\text{-N}$  concentration as a function of log transformed discharge with the LOESS regression line from samples collected at Sites 1, 2, 3, and 6 of the Watershed Research and Education Center.

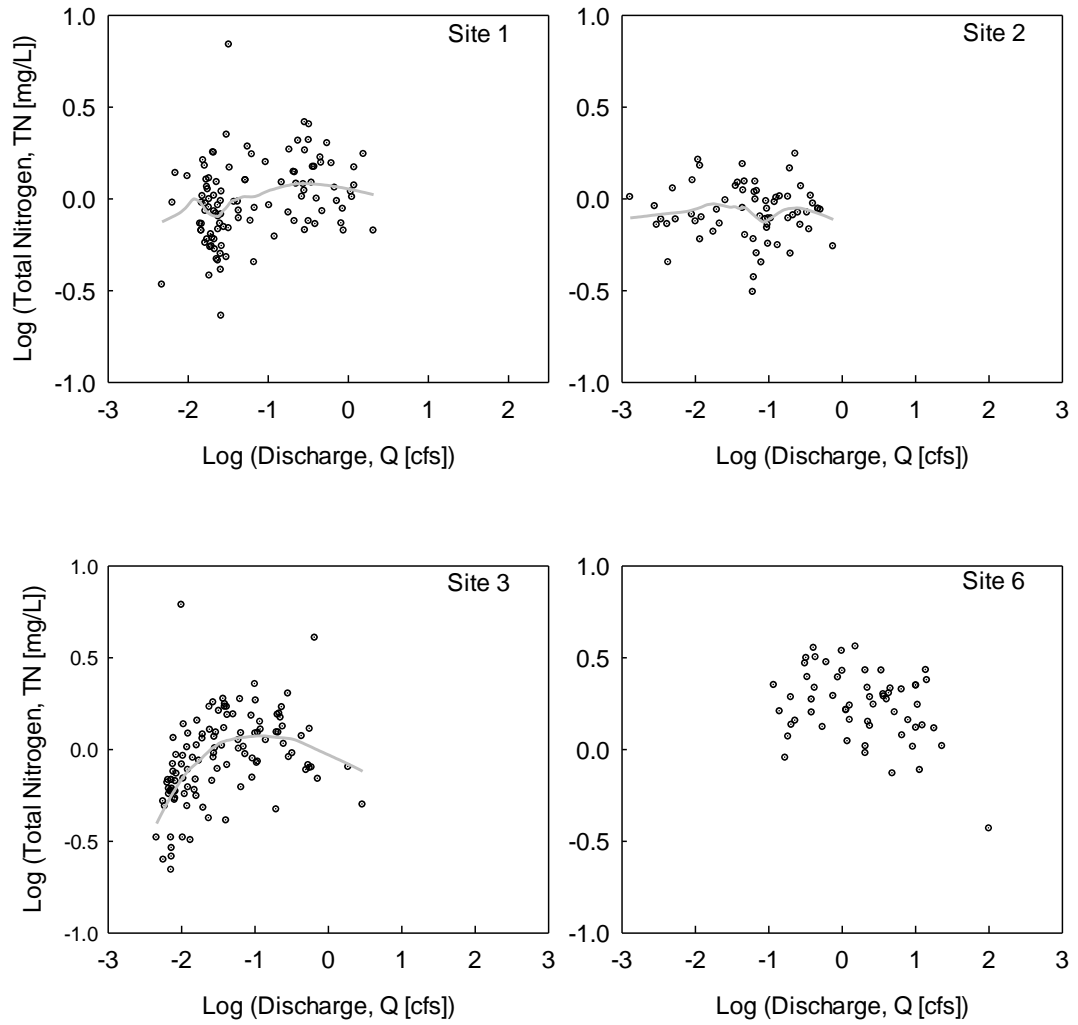




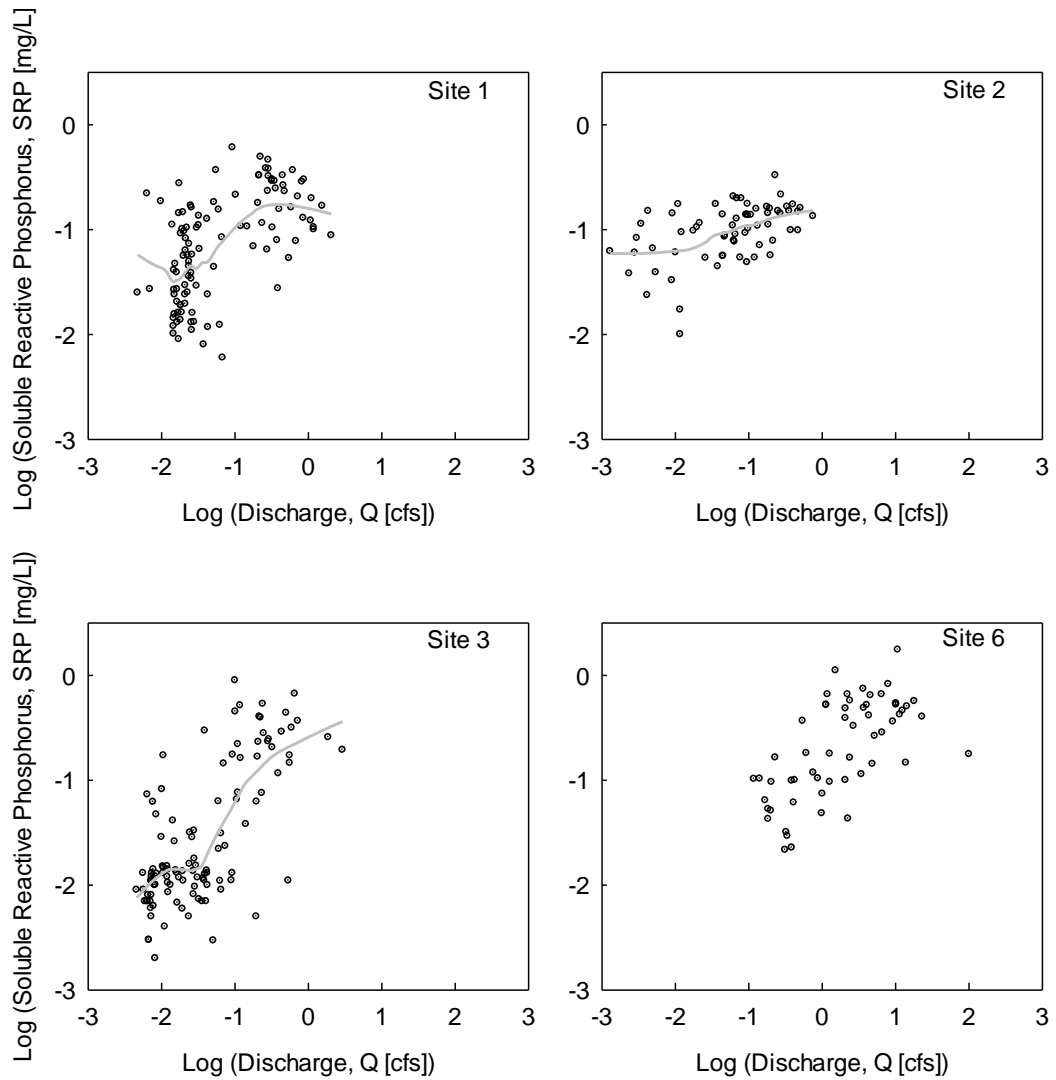
Log transformed  $\text{NO}_3\text{-N}$  concentration as a function of log transformed discharge with the LOESS regression line from samples collected at Sites 1, 2, 3, and 6 of the Watershed Research and Education Center.



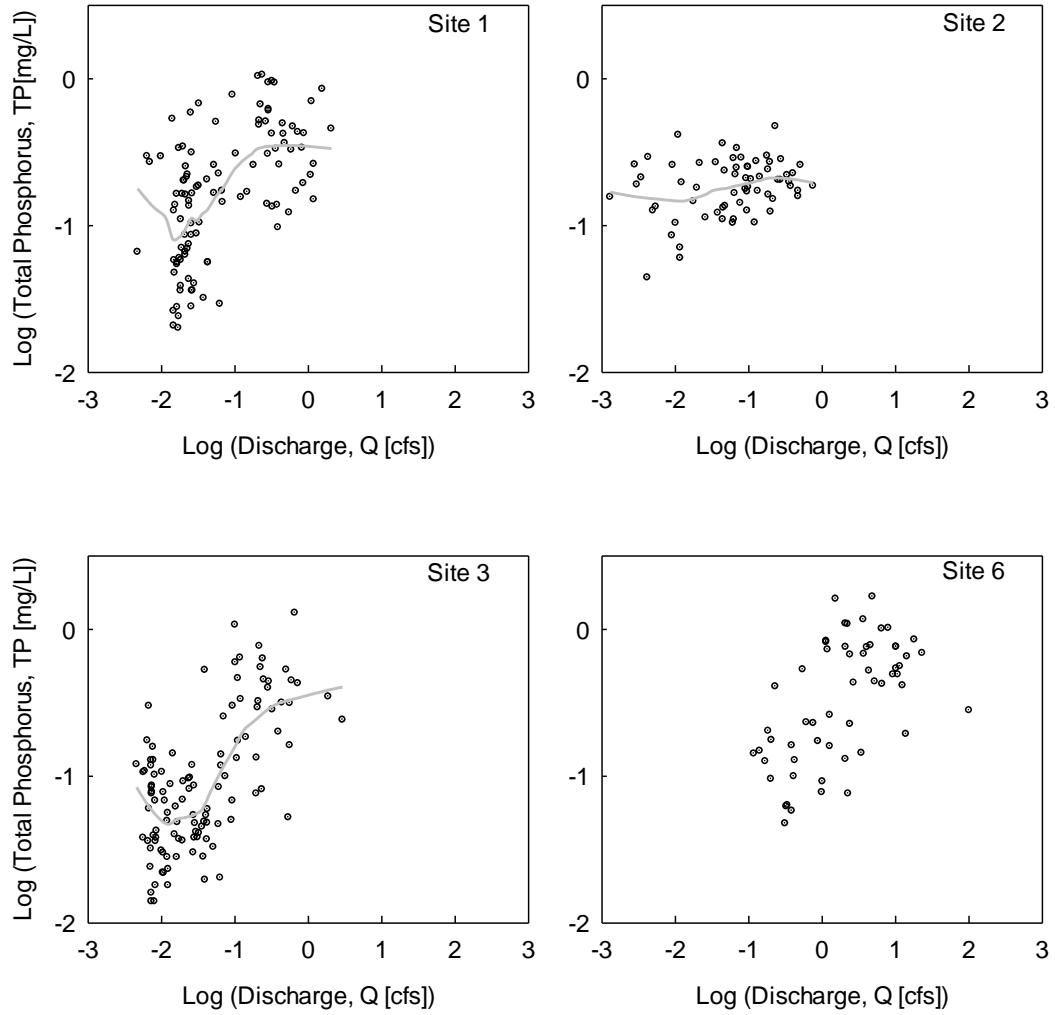
Log transformed TN concentration as a function of log transformed discharge with the LOESS regression line from samples collected at Sites 1, 2, 3, and 6 of the Watershed Research and Education Center.



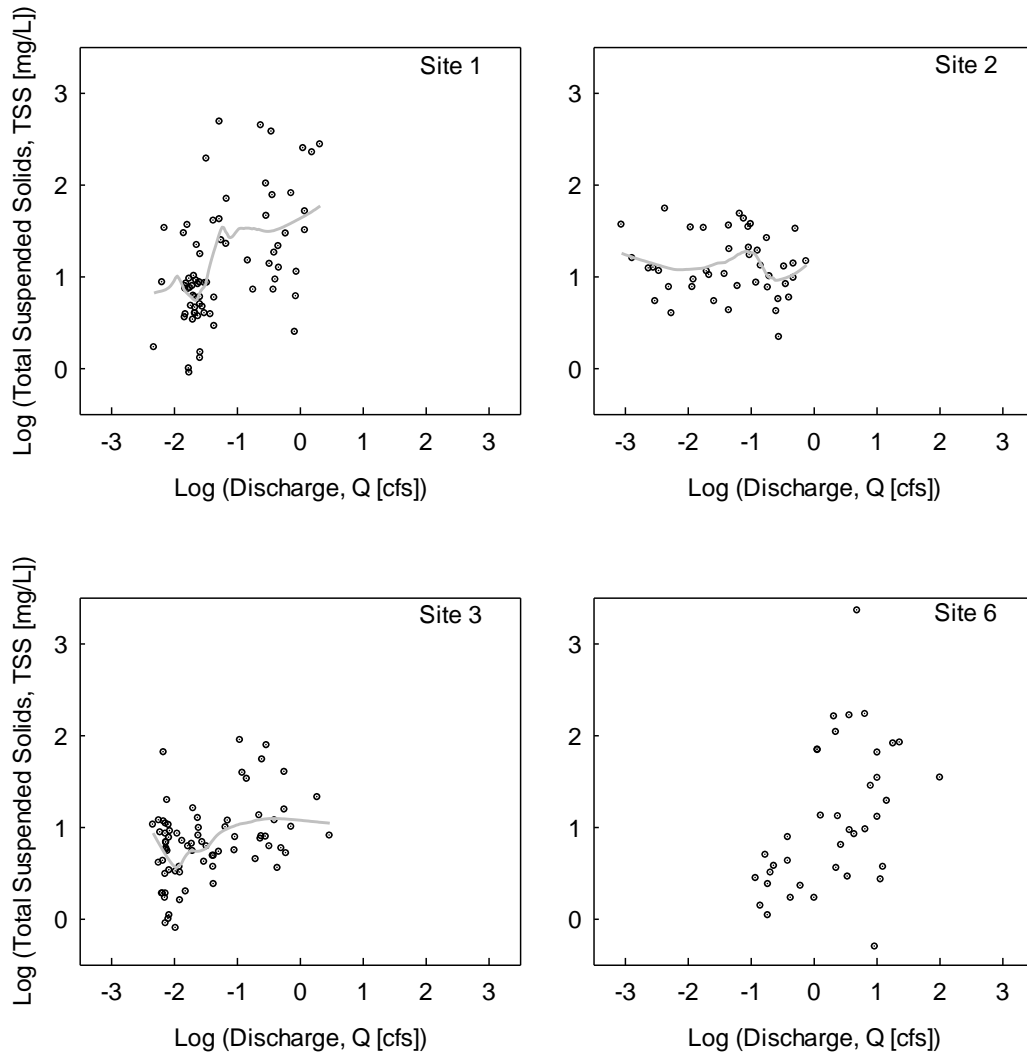
Log transformed SRP concentration as a function of log transformed discharge with the LOESS regression line from samples collected at Sites 1, 2, 3, and 6 of the Watershed Research and Education Center.



Log transformed TP concentration as a function of log transformed discharge with the LOESS regression line from samples collected at Sites 1, 2, 3, and 6 of the Watershed Research and Education Center.

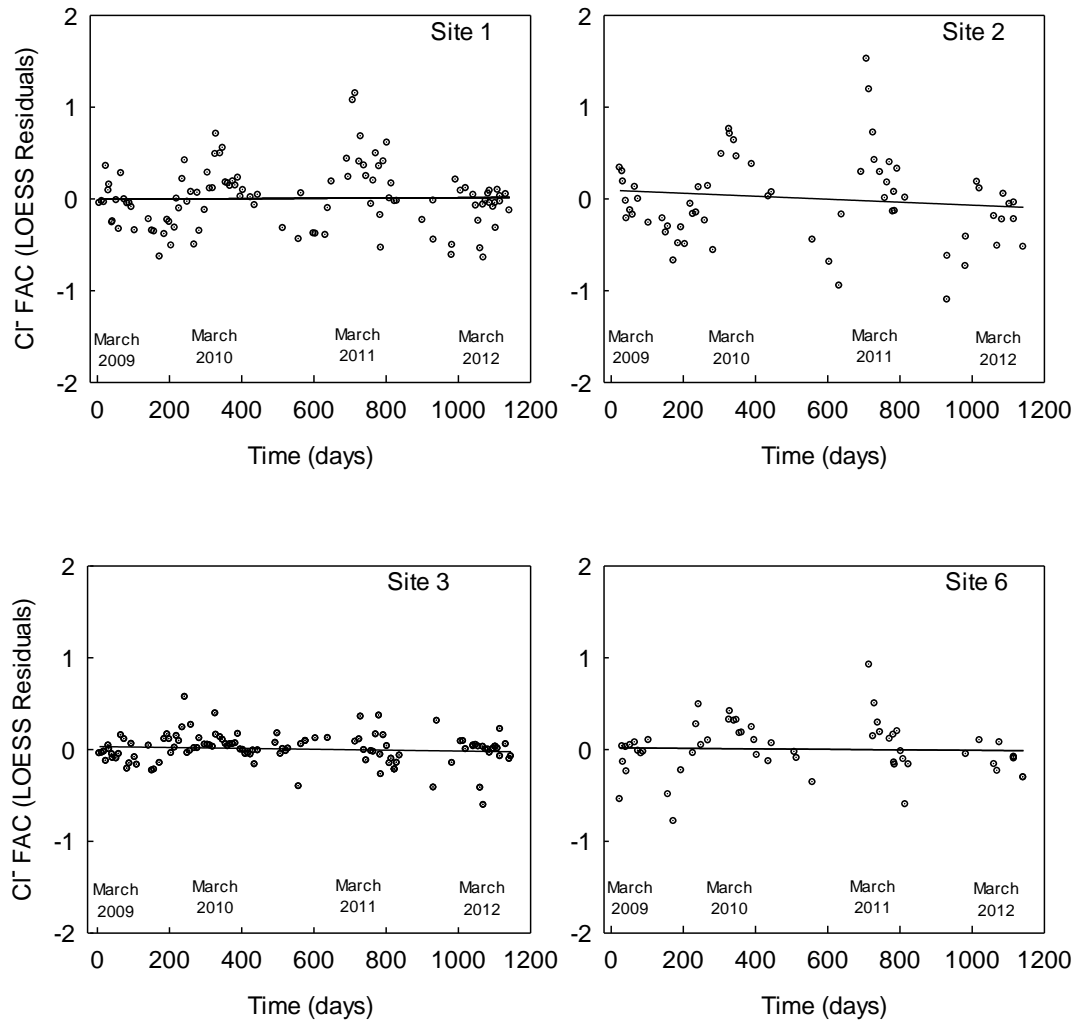


Log transformed TSS concentration as a function of log transformed discharge with the LOESS regression line from samples collected at Sites 1, 2, 3, and 6 of the Watershed Research and Education Center.

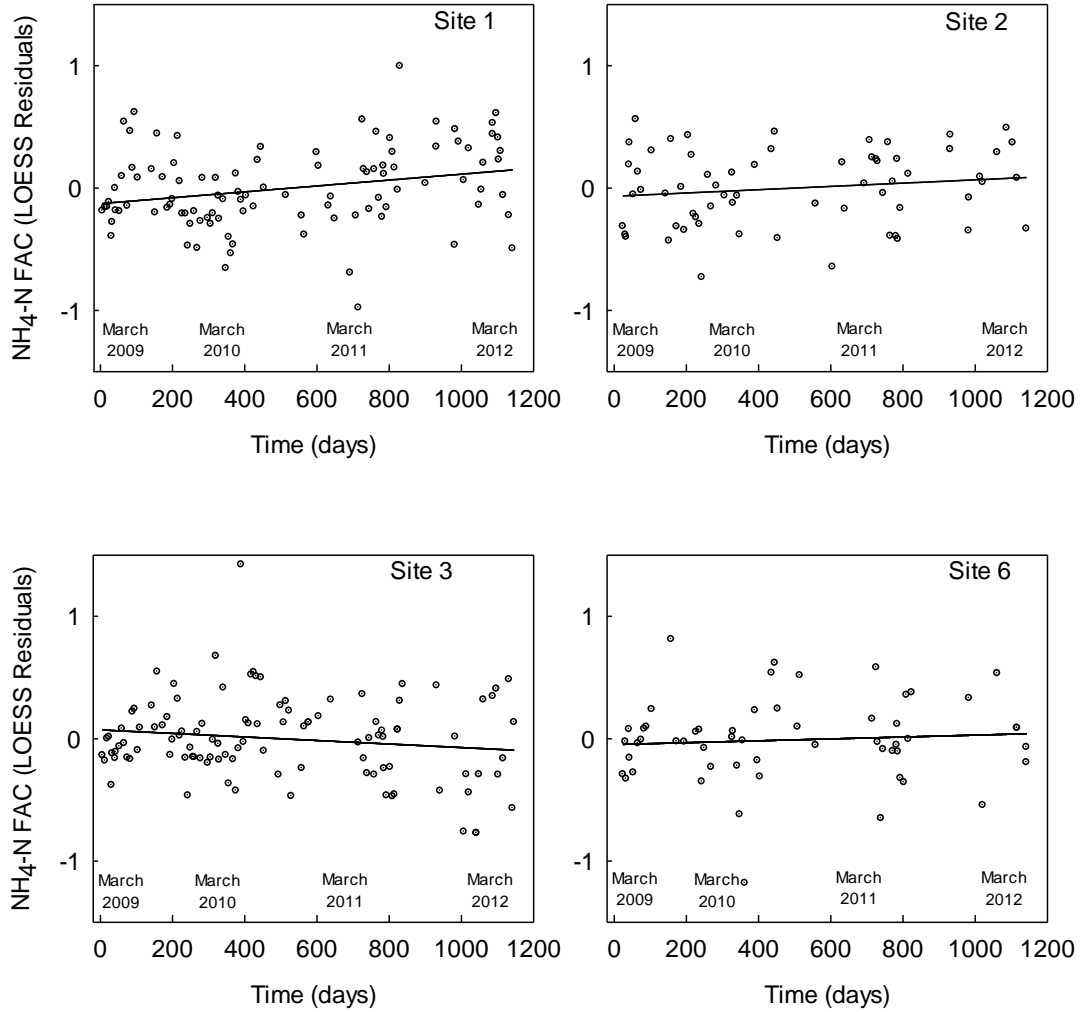


## APPENDIX II

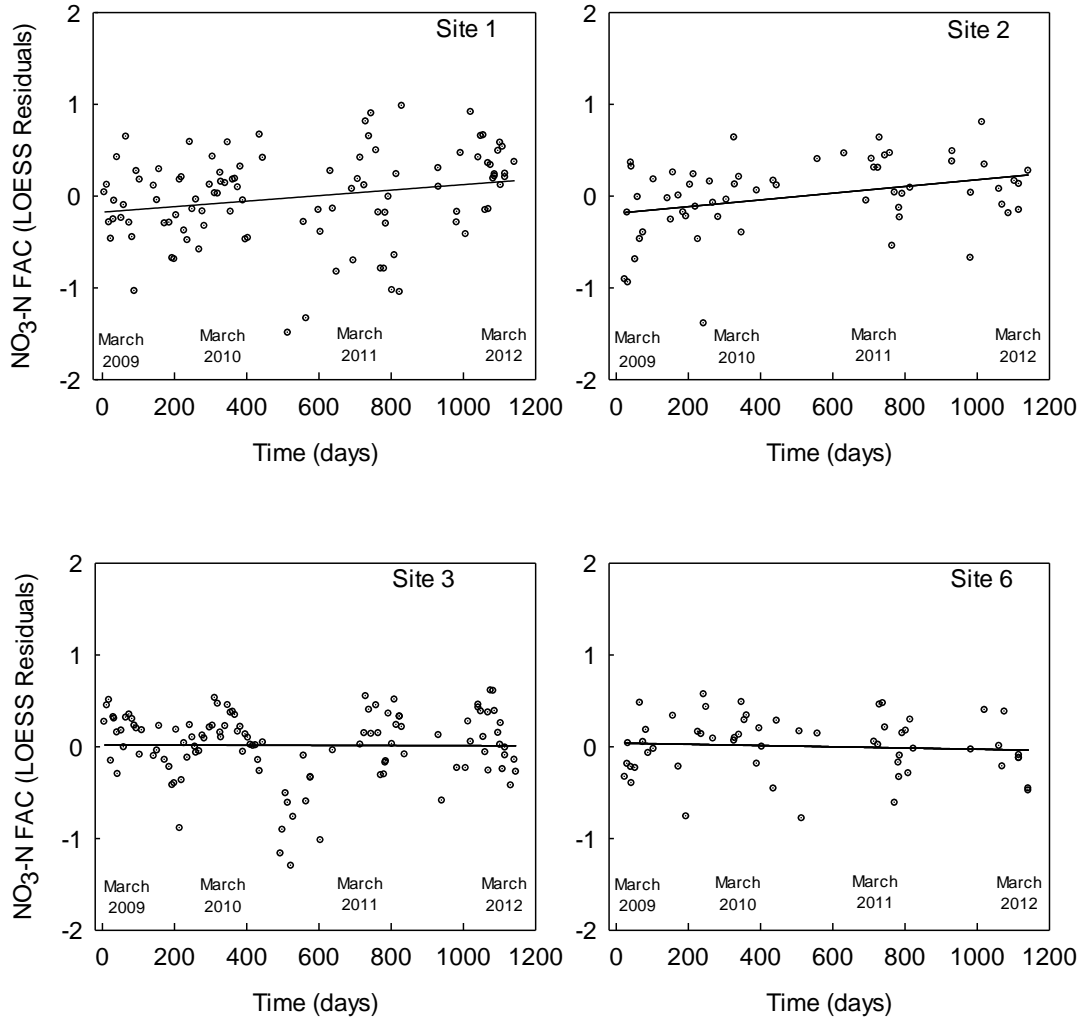
Flow adjusted concentrations for Cl at sites 1, 2, 3, and 6 of the Watershed Research and Education Center where seasonal variations were noted for site 1 and 2. Significant annual changes did not occur.



Flow adjusted concentrations for  $\text{NH}_4\text{-N}$  at sites 1, 2, 3, and 6 of the Watershed Research and Education Center where a significant annual increase ( $p=0.009$ ) was noted for site 1. Seasonal variations did not occur.

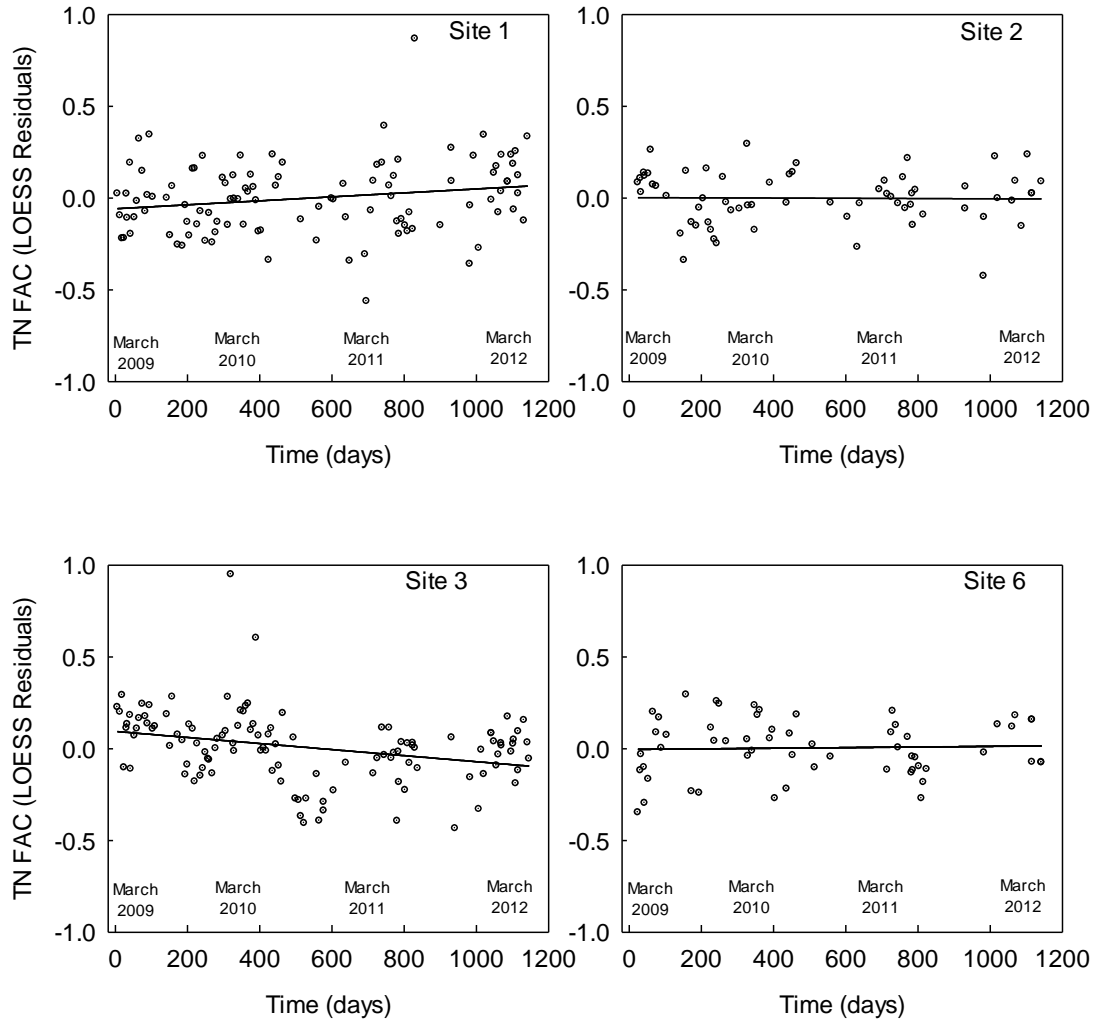


Flow adjusted concentrations for NO<sub>3</sub>-N at sites 1, 2, 3, and 6 of the Watershed Research and Education Center where a significant annual increase ( $p < 0.021$ ) was noted for sites 1 and 2, and seasonal variations occurred at site 3.

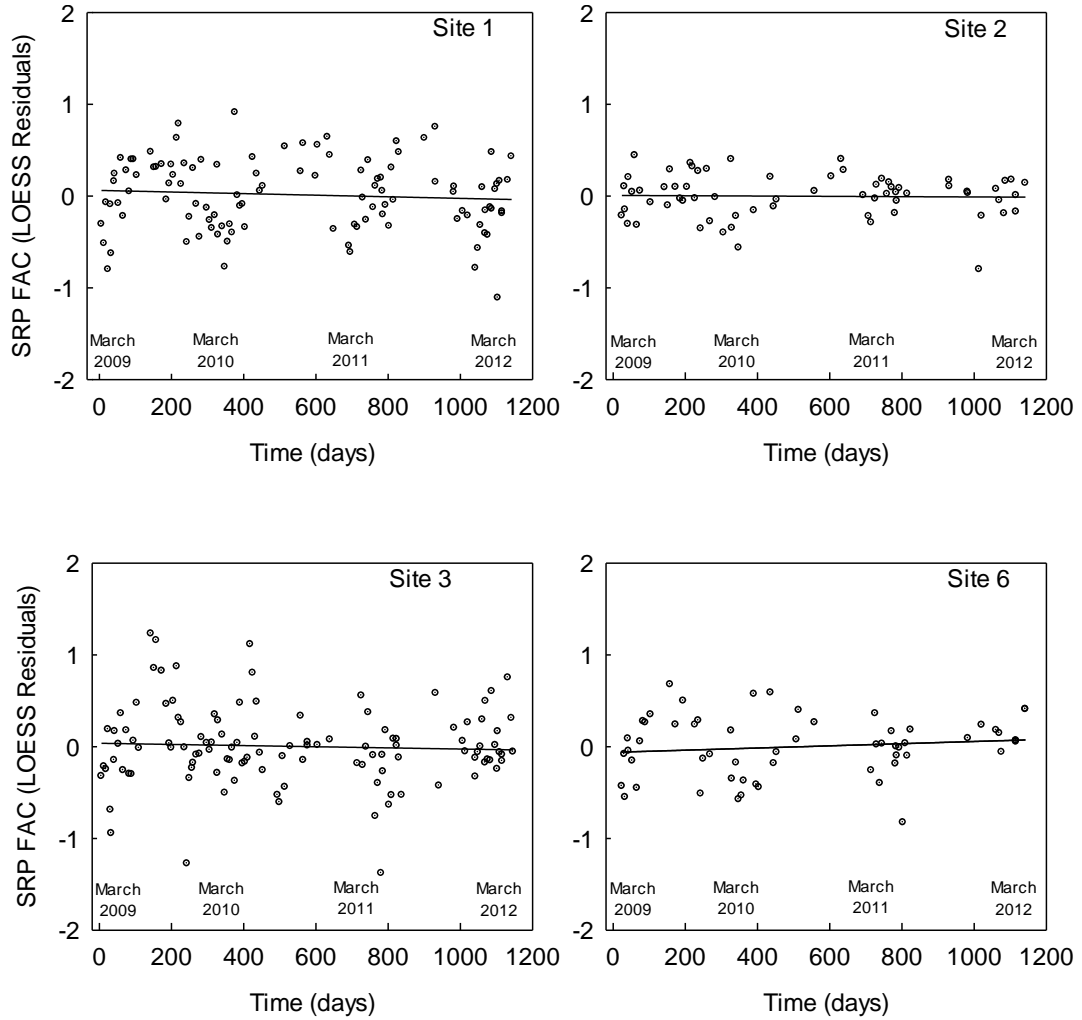




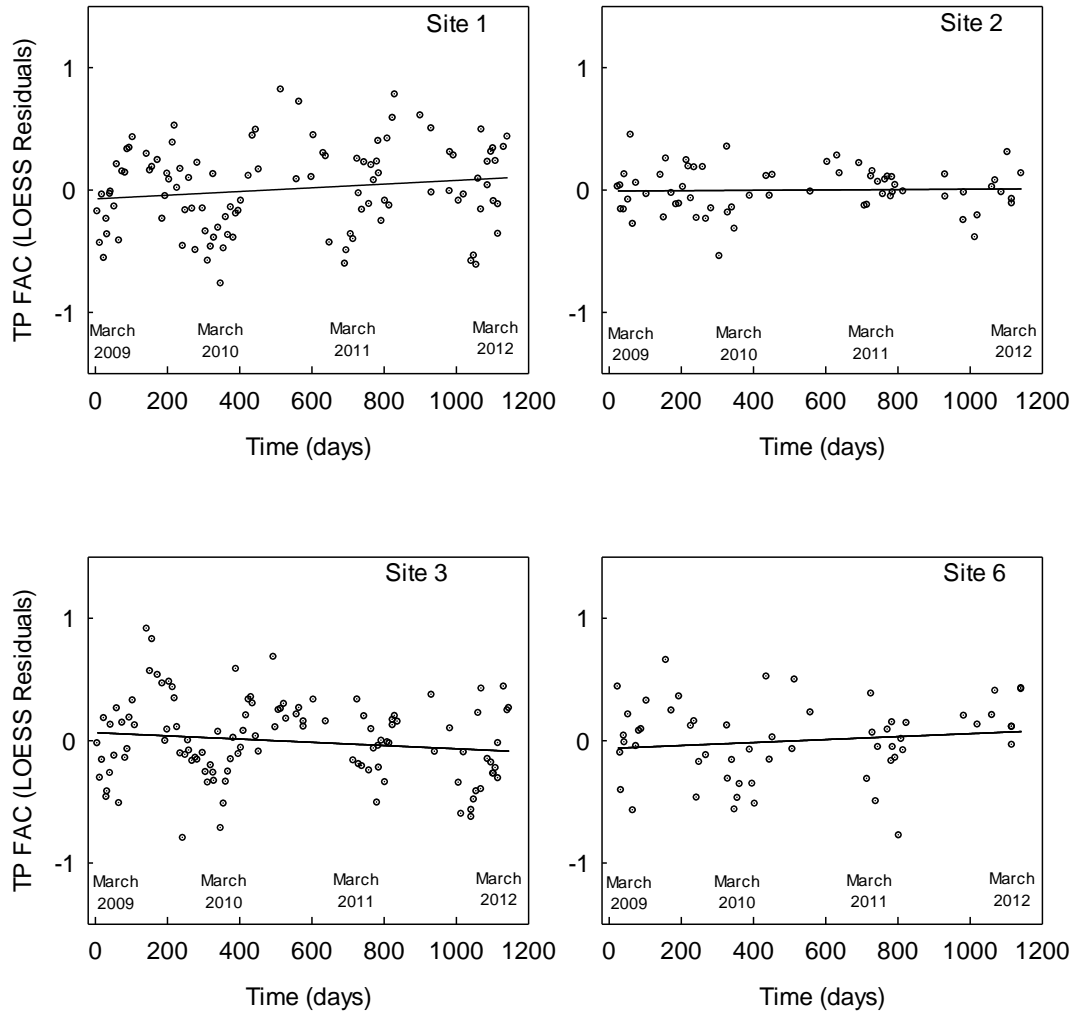
Flow adjusted concentrations for TN at sites 1, 2, 3, and 6 of the Watershed Research and Education Center where a significant annual changes ( $p < 0.044$ ) were noted for sites 1 and 3, and seasonal variations occurred at site 3.



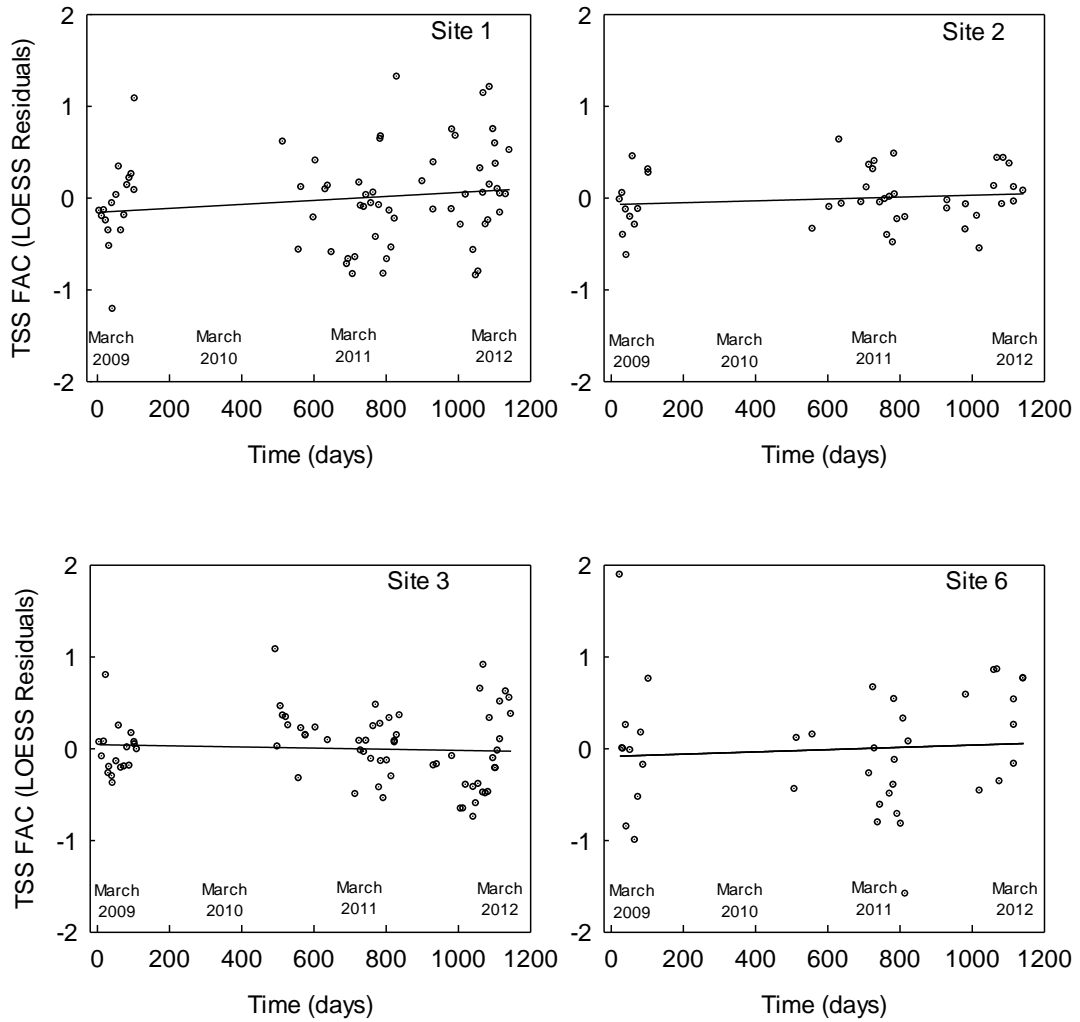
Flow adjusted concentrations for SRP at sites 1, 2, 3, and 6 of the Watershed Research and Education Center where seasonal variations were noted for sites 1 and 3. Significant annual changes did not occur.



Flow adjusted concentrations for TP at sites 1, 2, 3, and 6 of the Watershed Research and Education Center where seasonal variations were noted for sites 1 and 3. Significant annual changes did not occur.



Flow adjusted concentrations for TSS at sites 1, 2, 3, and 6 of the Watershed Research and Education Center. Significant annual changes and seasonal variations did not occur.



**APPENDIX III**

Field measurements from the USGS containing discharge (cfs) and staff gage height (m) for sites 1, 2, 3, and 6 of the Watershed Research and Education Center, 2008-2010.

| Site One              |                          | Site Two              |                          | Site Three            |                          | Site Six              |                          |
|-----------------------|--------------------------|-----------------------|--------------------------|-----------------------|--------------------------|-----------------------|--------------------------|
| Staff Height (meters) | Measured Discharge (cfs) | Staff Height (meters) | Measured Discharge (cfs) | Staff Height (meters) | Measured Discharge (cfs) | Staff Height (meters) | Measured Discharge (cfs) |
| 0.034                 | 0.005                    | 0.018                 | 0.001                    | 0.064                 | 0.006                    | -0.046                | 0.000                    |
| 0.034                 | 0.005                    | 0.024                 | 0.001                    | 0.076                 | 0.017                    | 0.210                 | 0.110                    |
| 0.046                 | 0.007                    | 0.027                 | 0.002                    | 0.082                 | 0.012                    | 0.247                 | 0.150                    |
| 0.046                 | 0.008                    | 0.049                 | 0.008                    | 0.094                 | 0.028                    | 0.277                 | 0.100                    |
| 0.055                 | 0.012                    | 0.052                 | 0.008                    | 0.094                 | 0.022                    | 0.329                 | 0.780                    |
| 0.055                 | 0.010                    | 0.055                 | 0.010                    | 0.104                 | 0.025                    | 0.411                 | 5.280                    |
| 0.064                 | 0.017                    | 0.064                 | 0.014                    | 0.113                 | 0.039                    | 0.430                 | 4.240                    |
| 0.070                 | 0.019                    | 0.073                 | 0.019                    | 0.113                 | 0.035                    | 0.442                 | 6.270                    |
| 0.122                 | 0.072                    | 0.107                 | 0.048                    | 0.122                 | 0.039                    | 0.445                 | 5.490                    |
| 0.143                 | 0.093                    | 0.165                 | 0.140                    | 0.125                 | 0.056                    | 0.448                 | 9.550                    |
| 0.146                 | 0.120                    | 0.168                 | 0.150                    | 0.143                 | 0.100                    | 0.497                 | 8.550                    |
| 0.213                 | 0.270                    | 0.171                 | 0.059                    | 0.149                 | 0.078                    | 0.536                 | 7.200                    |
| 0.226                 | 0.260                    | 0.183                 | 0.180                    | 0.158                 | 0.088                    | 0.597                 | 17.800                   |
| 0.229                 | 0.310                    | 0.201                 | 0.150                    | 0.201                 | 0.180                    | 0.637                 | 22.900                   |
| 0.244                 | 0.350                    | 0.213                 | 0.260                    | 0.232                 | 0.440                    | 0.695                 | 22.400                   |
| 0.256                 | 0.390                    | 0.213                 | 0.160                    | 0.250                 | 0.280                    | 0.756                 | 36.400                   |
| 0.277                 | 0.440                    | 0.216                 | 0.160                    | 0.262                 | 0.320                    | 0.762                 | 37.800                   |
| 0.283                 | 0.460                    | 0.226                 | 0.310                    | 0.277                 | 0.340                    | 0.774                 | 37.400                   |
| 0.293                 | 0.580                    | 0.250                 | 0.640                    | 0.311                 | 0.450                    | 0.799                 | 42.300                   |
| 0.326                 | 0.720                    | 0.256                 | 0.360                    | 0.329                 | 0.580                    | 0.805                 | 40.400                   |
| 0.351                 | 0.720                    | 0.259                 | 0.370                    | 0.360                 | 0.790                    |                       |                          |
| 0.375                 | 1.100                    | 0.259                 | 1.090                    | 0.387                 | 0.900                    |                       |                          |
| 0.411                 | 3.500                    |                       |                          | 0.390                 | 0.990                    |                       |                          |
| 0.415                 | 1.600                    |                       |                          | 0.393                 | 1.200                    |                       |                          |
| 0.415                 | 1.600                    |                       |                          | 0.405                 | 0.920                    |                       |                          |
| 0.427                 | 1.910                    |                       |                          | 0.424                 | 0.900                    |                       |                          |
| 0.454                 | 2.020                    |                       |                          |                       |                          |                       |                          |
| 0.482                 | 2.890                    |                       |                          |                       |                          |                       |                          |

