ABSTRACT

DOBBS, NICOLE ASHLEY. Hydrology and Water Quality Dynamics in Coastal Plain and Upland Watersheds with Loblolly Pine (*Pinus taeda*) and Switchgrass (*Panicum virgatum*) Intercropping in the southeastern United States. (Under the direction of Dr. François Birgand and Dr. George Chescheir).

With the increasing concern for energy security, there are efforts to investigate and develop alternative energy sources such as biofuels. The Energy Independence and Security Act of 2007 called for an increase in biofuel production to 136 million m^3 (36 billion gal) by 2022; however, with the growth of biofuel feedstocks concerns exist over competition with food-production lands and uncertain environmental impacts. A potential solution is to grow the feedstocks on marginal lands. This research looks at the potential hydrological and water quality impacts of growing switchgrass on managed forested watersheds in the southeastern United States, in coastal plain (North Carolina) and upland (Alabama) regions. Hydrology and water quality data were measured and modeled over a five-year period in order to assess immediate and lasting impacts of intercropping switchgrass with pine. Each region contained four to five watersheds ranging from 8 to 40 ha each with one of the following land covers: pine, pine and switchgrass intercropped, switchgrass only, or mature pine.

In the upland watersheds of Alabama, there were short-term impacts on sediment and nutrient exports due to operation-induced soil disturbance, but no fertilization effects. Overall nutrient exports were low; however, steep increases in sediment and total phosphorous exports, and perhaps more lasting, were detected from the intercropped sites. We hypothesize that these high sediment exports can be partially attributed to geomorphological properties of the riparian zone rather than specific operations.

In the coastal plain watersheds of North Carolina, high-frequency in-situ spectrophotometry data revealed unique water quality dynamics during various hydrological conditions. Despite efforts to minimize optical fouling of in-situ spectrophotometers and performing local calibration, only spectral data from one of the four watersheds provided acceptable continuous data for dissolved organic carbon (DOC), nitrate-nitrogen (NO_3^--N), and total dissolved nitrogen. During typical or dry antecedent conditions, we observed a dilution in DOC and an increase in NO_3^--N concentrations during flow events. During a series of large events that brought the water table near the surface for several days, a DOC concentration effect, more typical of upland watersheds, was observed. This phenomenon demonstrates the overwhelming influence of the organic horizon in DOC export. It also suggests in return that the near ditch area in these flat systems plays a particular role, specifically we hypothesize that the near ditch soil profile is highly leached due to a steeper hydraulic gradient during the rising limb of hydrographs, and is generally drier with more active organic matter mineralization. We hypothesize that both of these processes cause DOC and nitrate dilution effects followed by DOC and nitrate concentration increases likely sourced from enriched areas of the soil profile further away from the ditch.

The Agricultural Policy/Environmental eXtender (APEX) model was able to simulate hydrology of the upland watersheds in Alabama reasonably well with Nash-Sutcliffe efficiencies (NSE) for monthly outflow between 0.74 and 0.92 and percent bias (PBIAS) values between -6.6 and 6.5% during calibration and NSE values of 0.69 to 0.92 and PBIAS between -34% and -1.3% during validation. Both intercropped sites yielded the best results for simulating hydrology. The switchgrass site was the most challenging to calibrate and we hypothesize that this was due to the dramatic land cover change over the entire simulation period. Sensitive parameters included the subsurface flow factor and the order of various crop plantings within the operation schedule. Simulated sediment yield was sensitive to sand, silt, and organic carbon contents of the top soil layer and generally under predicted, with percent differences in annual loads ranging from -98% to +156%.

Hydrology and Water Quality Dynamics in Coastal Plain and Upland Watersheds with Loblolly Pine (*Pinus taeda*) and Switchgrass (*Panicum virgatum*) Intercropping in the southeastern United States

by
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DEDICATION

I dedicate this work to the Sacred Heart of Jesus through the Immaculate Heart of Mary. By the merits of His most Precious Body and Blood, may this work glorify God.

"To obey is better than sacrifice." 1 Samuel 15:22

BIOGRAPHY

Nicole Ashley Dobbs was born July 14, 1988 to Leo Edward and Caroline Minerva Dobbs in Baltimore, Maryland. At the age of two she moved to the suburbs in Harford County, Maryland. Then, at the age of 11 she moved to the countryside of Pennsylvania. Her family and teachers provided an invaluable foundation of faith and moral values, inseparable from any intellectual endeavor. From a young age, she enjoyed being outdoors and developed an appreciation for the beauty of nature. This appreciation and wonder sparked an interest in studying nature and a desire to help restore and preserve God's gift of creation. While she considered her favorite subjects to be science and mathematics, her thirst for knowledge extended to other subjects as well, seeing that each subject has its value for contributing to the overall investigation, study, understanding, and communication of the truth.

Nicole saw water as a key resource necessary to sustain all life on this planet and so she began her undergraduate career with a concentration on water resources in Environmental Engineering at the University of Delaware. She graduated from there in 2010 and moved directly to Florida where she interned with the South Florida Water Management District for the summer before beginning graduate studies for her Masters of Engineering in Agricultural and Biological Engineering at the University of Florida in Gainesville. After two semesters there, she moved to the University of Florida Tropical Research and Education Center in Homestead, Florida to finish her Masters research on water use and nutrient leaching from irrigated turfgrass. After graduating from the University of Florida in 2012, she moved directly to Raleigh, North Carolina to begin her doctoral studies in Biological and Agricultural Engineering at North Carolina State University.

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CHAPTER 1: Introduction

1.1 Project Incentive

In an effort to augment energy security, there is motivation to invest in the research and development of alternative energy sources such as biofuels. While certain biofuel feedstocks, such as switchgrass, offer a promising means to augment our energy supply, careful management strategies must be considered in order to avoid competition with food production lands (Thompson, 2012; Tomei and Helliwell, 2015). A potential solution to avoiding a “food versus fuel” conflict, is to grow biofuel feedstocks on marginal lands such as managed forests. The unused space between rows of pine where natural understory would normally exist could be used to grow a biofuel crop such as switchgrass, a practice referred to as intercropping. This practice of intercropping, in theory, would provide marginal land to grow biofuel feedstocks without competing with land needed to produce food while also providing an additional source of revenue to an already well established forestry industry (Blazier, 2009). Therefore, there are multiple incentives to investing in and researching this practice which could be applied at the national level and provide a viable solution to energy security.

Given that this practice of intercropping pine with a biofuel crop could expand throughout and beyond the southeast region of the United States, the environmental impacts of such a large-scale land use change must be assessed in order to avoid potential problems in the future. The research presented here focuses on the hydrological and water quality impacts of intercropping pine and switchgrass at the watershed scale, but it was part of a larger, multi-scale, multi-cooperator study that assessed a broad range of environmental impacts including impacts on soil, flora and fauna, as well as an energy and economic assessment.

1.2 Research objectives

At the core of this project, stands a set of replicated treatment and reference 20-40 ha watersheds. The water quality impact of switchgrass intercropping was assessed for two upland and one lowland condition across three states within the southeast United States, respectively, Alabama, Mississippi, and North Carolina. In each state, the impacts of intercropping were assessed within a gradient of switchgrass/pine management and density, following a paired watershed experimental design from adjacent watersheds (or nearby in Mississippi). The watersheds were implemented with the following land covers: young pine (control), mature pine (reference), pine and switchgrass intercropped, and switchgrass only. All watersheds were equipped to measure weather, stream discharge, water table depth, and water quality.

Data were collected over a five-year period to provide information before, during, and after treatment (i.e., land use change). The research presented here specifically focuses on the upland watersheds of Alabama and the coastal plain watersheds of North Carolina.

The first approach (reported in Chapter 2) was to evaluate the bulk water quality effect, by comparing the relative nutrient and material exports using two-minute flow data and flow-proportional composite samples for water quality analyses. By obtaining enough water quality (total suspended solids, dissolved organic carbon [DOC], total Kjeldahl nitrogen, NO_3^--N, NH_4^+-N, PO_4^{3+}-P, and total phosphorous) concentration data and two-minute flow data, there were adequate data to construct double-mass plots, i.e., cumulative load of treatment watersheds as a function of the control cumulative load. Given that climatic conditions for the control and treatment watersheds were assumed to be the same, these plots showing changes in slope corresponding to the timing of operations were taken as strong evidence of treatment impact on water quality. Additionally, changes in annual cumulative flow after the treatment phase provided evidence of hydrological impacts due to treatment.

The second approach (Chapter 3) to evaluate the water quality impact of switchgrass intercropping was the use of continuous water quality monitoring sensors, i.e., in situ ultraviolet-visual spectrophotometers. These optical sensors have the potential to offer new insights into the dynamics of nutrient exports and could fundamentally change how water quality is collected and analyzed (Langergraber et al., 2003; Rieger et al., 2006; Etheridge et al., 2013). However, there are challenges with this method of data analysis. We were able to obtain continuous concentration data for NO_3^--N and DOC for one of the coastal plain watersheds. From these data, we gained new insights into the nutrient exports of this coastal plain watershed during various hydrological conditions. By thoroughly capturing the timing and magnitude of nutrient exports (by the 15-minute sampling) and knowledge of corresponding drainage theory for these artificially drained coastal plain watersheds, we were able to hypothesize the importance of the various parts of the soil profile (e.g., the organic horizon contributing DOC during elevated water table conditions). However, due to optical fouling of these sensors in-situ, we could not obtain adequate continuous data from the three other coastal plain watersheds; therefore, a comparison among treatment watersheds could not be performed using the continuous water quality data acquisition method. Still, many valuable insights were gained from this method of water quality analysis and should be considered as a viable means of assessment.

The third approach to further understand and assess the impact of pine and switchgrass intercropping is through modeling (Chapter 4). The hydrology data measured in the upland Alabama watersheds were used to calibrate the Agricultural Policy/Environmental eXtender (APEX) model. The model has been designed for upland watersheds, similar to the experimental sites in Alabama and Mississippi. Calibration and validation results from several studies have shown the usefulness of APEX for plot, field, and small watershed scales (Gassman et al., 2006; Mudgal et al., 2010; Saleh et al., 2004; Tuppad et al., 2009; Wang et al., 2007; Wang et al., 2008; Wang et al., 2009; Williams et al., 2006; Yin et al., 2009). The model was able to simulate outflow for both intercropped watersheds in Alabama very well, but there were challenges with simulating hydrology in the switchgrass only watershed. One of the main challenges was configuring the operation schedule in a way to accurately grow the correct crop and accurately represent evapotranspiration, particularly since crops were changing throughout the warm-up, calibration, and validation periods and evapotranspiration was calculated from only one of the crops present. The model was also able to simulate sediment export comparable to our observed export values. All of these measured and modeled data provided a basis for the assessment of hydrological and water quality impacts due to climate, specific operations, and land use changes on both upland and coastal plain forested watersheds of the southeast United States.

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CHAPTER 2: Hydrology and water quality comparisons of Loblolly pine (*Pinus taeda*) and switchgrass (*Panicum virgatum*) in upland forested watersheds in Alabama, USA

2.1 Introduction

Biofuels were originally well intended to augment our energy supply, reduce greenhouse gas emissions, and promote agricultural development (Koizumi, 2015); however, biofuels have also sparked a food versus fuel debate in which potential negative impacts of converting lands from food production into fuel production are disputed (Rosillo-Calle and Johnson, 2010; Thompson, 2012; Tomei and Helliwell, 2015). The conversion of agricultural lands to grow crops for fuel production rather than food poses a threat to food security (Spangenberg, 2008). With this potential threat to food security and the Energy Independence and Security Act of 2007 calling for an increase in biofuel production to 136 million m^3 (36 billion gal) by 2022, with 58% (79 million m^3) being sourced from "advanced" biofuels (e.g., switchgrass), there is a need to grow biofuel feedstocks on marginal lands.

One potential non-agricultural area to plant biofuel feedstocks is managed forested lands. Space between rows of pine trees in managed forests could be utilized by a second biofuel crop. Typically, this unused space would fill in with natural understory. However, with modifications to the normal operation schedules on these managed forested lands, a bioenergy feedstock (i.e., switchgrass) could be planted, grown and harvested between the rows of pine. While this idea may seem straightforward, there are unknown effects and outcomes associated with this practice.

The use of switchgrass (*Panicum virgatum*) as an optimum biofuel feedstock was selected by the U.S. Department of Energy due to the well supported advantages of this species (Sanderson et al., 1996). Despite several advantages of switchgrass over other herbaceous species as a biofuel feedstock, there is economic risk associated with growing a singular crop for a newly developing market (i.e., biofuels market) (Blazier, 2009). Therefore, the notion of interplanting switchgrass with an already established marketable crop (e.g., forestry) was proposed as a more secure way of investing in the biofuels industry and/or diversifying current sources of revenue from managed forests (Blazier, 2009). While agroforest systems combining trees and grasses or other crops have been developed (Gold et al. 2000), the viability of growing switchgrass with pine is still being studied.

Other researchers have studied the interplanting of bioenergy crops in forest settings. Gruenewald et al. (2007) found that there were positive effects of intercropping *Medicago sativa* and *Robinia pseudoacacia* with regards to integrating fuelwood and crop production and enhancing soil fertility. Quinkenstein et al. (2009) reported the ecological advantages of an intercropping agroforestry system for biomass production. Wicke et al. (2013) studied greenhouse gas and economic impacts of rice-Eucalyptus *camaldulensis* and rice-wheat-Eucalyptus *tereticornis* agroforestry systems. The agroforestry system of interplanting switchgrass with pine has been studied by Blazier et al. (2012), Tian et al. (2015), Albaugh et al. (2012), Strickland et al. (2015), and Loman et al. (2013), among others. Blazier et al. (2012) obtained 80% switchgrass ground coverage by the second year after planting and found that overstory increased coverage. Still, there is limited information on the potential hydrology and water quality impacts of intercropping, specifically on forested lands; hence, the need for this research.

Concerning hydrology and water quality impacts, the Soil and Water Assessment Tool (SWAT) revealed that growing switchgrass can reduce sediment erosion compared to growing corn on agricultural lands; however, growing switchgrass in place of native grass could cause a decrease in water yield and an increase in nitrate-nitrogen load (Wu and Liu, 2011). Long-term simulated nitrogen loss from switchgrass ranged from 73% to 80% less than nitrogen loss from cotton (Sarkar and Miller, 2014). Using the Agricultural Policy/Environmental eXtender (APEX) model, Feng et al. (2015) found that converting marginal lands under corn/soybean production to switchgrass reduced water yield by 13.4% to 36.3% and improved water quality by reducing soil erosion by 27% to 98%, reducing nitrogen loss by 30% to 91%, and reducing phosphorous loss by 65% to 76%.

Typical practices of managed forestry include harvesting (i.e., felling, clearcutting and thinning), site preparation, planting, fertilization. These typical practices do impact hydrology and water quality. Soil types and nutrient content play a major role in the nutrient leaching magnitude and sediment loading (Ahtiainen and Huttunen, 1999). Disturbance to the ground surface increases nitrogen mineralization (Vitousek and Melillo 1979). Felling impacts hydrology by causing an increase in soil water content and impacts water quality by interrupting the nutrient cycle since vegetation no longer binds nutrients. Decomposition of organic matter increased total nitrogen and mineral nitrogen loads (Martin and Pierce 1980;

Martin et al. 1984). Increases in total phosphorous and phosphate were observed for three years following clearcutting in a nutrient rich basin. Protective zones surrounding a water body should be at least 30 m wide to provide adequate protection (Roby et al. 1977). However, with a typical managed forest, the majority of soil disturbance typically occurs once every 20 to 30 years with harvesting and replanting, and with an occasional thinning. With planting a second crop, such as switchgrass, there would be an increase in equipment traffic and fertilizer application, both initially with the additional operations required to establish switchgrass and annually with harvesting and fertilization.

The objectives of this research were to quantify the effects of intercropping switchgrass (*Panicum virgatum*) with loblolly pine (*Pinus taeda*) on hydrology and water quality of five small upland forested watersheds in Greene County, Alabama, USA. The impacts on hydrology and water quality were evaluated throughout the pre-treatment, treatment, and post-treatment phases.

2.2 Hypotheses

Hydrology hypothesis

Compared with the site-preparation period and given equal climatic conditions, there will be a reduction in cumulative flow during the early establishment phase of the intercropped and switchgrass only treatments as the established switchgrass causes an increase in infiltration and evapotranspiration rates compared to standard managed forestry.

Water quality hypothesis

An increase in the cumulative loading of NO_3^--N (and other nutrient species) is expected for the watersheds where fertilizer was applied to the switchgrass treatments. A decrease in total suspended solids loading relative to the conventional pine treatments is expected in the watersheds with switchgrass for this early establishment period when compared to the treatment period. This is due the absence of heavy equipment traffic used for site preparation during the treatment period. The cumulative loading of all water quality parameters (TKN, TSS, NO_3^--N, PO_4^{3+}-P, NH_4^+-N, total phosphorous, dissolved organic carbon) will be driven by the cumulative flow volume regardless of treatment. Differences among treatments after establishment will be beyond detection methods.

2.3 Methods

A paired watershed approach was used to account for the inherent watershed differences. The hydrology and water quality of three treatment watersheds were compared to a control and reference watershed for the early establishment period (04 March 2013 to 01 December 2014). As potential indicators of treatment effects, relationships were established between flow, precipitation, watershed physical parameters (i.e., slope) and cumulative loading of water quality parameters.

Site description

Five watersheds were evaluated during the early establishment period (04 March 2013 to 01 December 2014). The watersheds were located in Greene County, in western Alabama, USA, and ranged in area from 7.6 to 26.1 ha (Figure 2.1). The control and three treatment watersheds were adjacent, while a reference watershed was located 3.8 km to the southeast.

During the pre-treatment period (March 2010-March 2012), four to six-year old pine stands with natural understory existed on the control and treatment watersheds, while an older pine stand planted in 1994 was used as a reference for comparison When treatments were implemented in March 2012, GR1 (control) remained a young pine stand with natural understory; GR2 became a thinned young pine stand intercropped with switchgrass; GR3 became a newly established pine (age 0) with switchgrass intercropping; and GR4 was cleared and replanted with switchgrass only. Details and timing of field operations during the treatment (site preparation) period is shown in Table 2.2. GR1 was used as the primary control as it corresponded to current loblolly pine sylviculture, and climatic variability between the control and treatment watersheds were minimal due to close proximity of the watersheds.

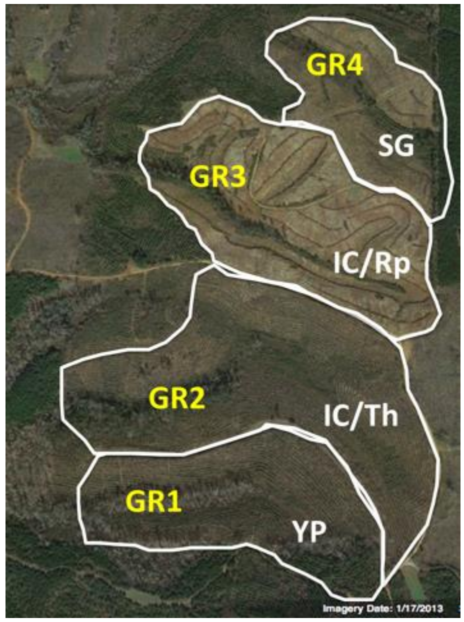

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Figure 2.1. Satellite image of four adjacent study watersheds (GR1, GR2, GR3, GR4) in Greene County, Alabama (image taken Jan 17 2013).

Soils on the hillslopes and summits were mostly Faceville fine sandy loam (Fine, kaolinitic, thermic Typic Kandiudults) with some Smithdale fine sandy loam (Fine-loamy, siliceous, subactive, thermic Typic Hapludults). The floodplain soils were Ochlockonee fine sandy loam (Coarse-loamy, siliceous, active, acid, thermic Typic Udifluvents) and Falaya fine sandy loam (Coarse-silty, mixed, active, acid, thermic Aeric Fluvaquents).

Table 2.1. Watershed area, slope, and treatments in Greene County, Alabama, USA.

Watershed	**Area** (ha)	**Avg. Slope** (%)	**Treatment**
GR1	11.3	12.7	Young pine (control)
GR2	25.1	11.9	Intercropped- thinned
GR3	24.4	12.6	Intercropped-replanted
GR4	16.5	11.4	Switchgrass only
GRREF	8.0	9.9	Mid-rotation pine (reference)

Table 2.2. Management operations implemented on Greene County Alabama study watersheds.

Year	Management	GR1	GR2	GR3	GR4	GRREF	Details
1994	Pine planting					o	
2006	Pine planting			o	o		Pine seedlings planted (1077 trees ha^{-1})
2007	Pine planting				o		02/25: Pine seedlings planted (1077 trees ha^{-1})
2008	Tree harvest	o	o				
	Offset rip	o	o				
2009	Pine planting	o	o				02/01: Pine seedlings planted (1077 trees ha^{-1})
	Pruning					o	Lower and dead branches removed
	Fertilization						Fertilizer applied by stem injection
2011	Fertilization					o	Broadcast dry fertilizer application
2012	Thinning		o				Stand thinned to 247 trees per ha on 03/12 - 03/19
	Shearing		o	o	o		Trees were sheared and debris were piled on windrows. Conducted between rows (GR2) 03/12 - 03/19; on entire field (GR3) 10/19 - 10/23; entire field (GR4) 03/12 - 03/19
	Herbicide application	o	o	o	o		04/19 (GR2, GR4); 09/07 (GR1, GR3)
	Disking and switchgrass planting		o		o		Switchgrass seeds sown approx. 0.3 cm into soil 05/10-05/13 (GR4); 05/13-05/17 (GR2)
	Offset rip			o			11/26
2013	Pine planting			o			02/17: Pine seedlings planted (1077 trees ha^{-1})
	Disking and switchgrass planting		o	o	o		05/20-05/24 (GR3 sown; GR2 and GR4 resown)

Table 2.2. Continued

2014	Fertilization		o	o	o		03/18-03/21: Broadcast fertilizer application at 56 kg N per ha (only switchgrass portion)
	Herbicide application		o	o	o		06/04-06/05: Herbicide applied (only switchgrass portion)
	Switchgrass harvest		o	o	o		10/09-10/14: Switchgrass harvested

***"o" denotes implementation of an operation for a given experimental watershed.**
**** Updated from original chart drafted by Julian Cacho.**

Hydrology data collection

The data collection period covered early establishment (04 March 2013 to 01 December 2014). Trapezoidal wooden flumes were installed at the outlet of each watershed to measure flow using the stage rating and index velocity method (Birgand et al., 2005; Levesque and Oberg, 2012). An ISCO flow meter (750 Area Velocity Flow Module, Teledyne ISCO, Lincoln, NE, USA) was used to obtain stage (m) and velocity (m s^{-1}) measurements at two minute intervals. These measurements were used to calculate flow with the known flume dimensions. Additional water stage sensors (HOBO U20 Water Level Data Logger, Onset, Cape Cod, MA, USA) were installed as backup for missing flow meter data. Sites were serviced and data was retrieved from the field every two weeks, at which time data were downloaded from the instruments and stage and flow were measured manually.

Weather data were collected using an automatic weather station (HOBO U30 Cellular Data Logger, Onset, Cape Cod, MA, USA). The station was located between watersheds GR2 and

GR3 (Figure 2.1). Data collected were precipitation, photosynthetic active radiation (PAR), atmospheric pressure, air temperature, relative humidity, and wind speed and direction. Additional tipping bucket rain gages were located at other points to measure precipitation distribution.

Hydrology data processing

The stage and velocity data were processed using the software program AQUARIUS (AQUARIUS, Aquatic Informatics, Vancouver, British Columbia, Canada). A 9-step data process derived and detailed in Bennett (2013) was established to remove outliers and noise from the raw data, correct stage drift, create rating curves, and fill in gaps when ISCO flow meters failed (Bennett et al., 2013). Stage data collected from the backup stage sensors were used to fill in the missing flow meter data. Manual stage and flow data collected every two weeks were used to correct drift in the stage data.

Velocity could not be reliably measured during low flow conditions because stage was too low for the Doppler meter to function properly. Data gaps during these periods were filled by extrapolating values from stage and velocity relationships and verifying values against manual flow data. The velocity measurements were smoothed by using moving averages. As described by Bennett et al. (2013), "relationships between the cross-sectional average velocities and the ISCO sensors or index velocities were derived from manual gauging using the velocity area method (ISO 748, 2000) and velocity measurements using a Flowmate flowmeter (Marsh-McBirney®). An additional stage correction was required since the stage where velocities were measured (10 cm upstream of the instrument) and stage at the instrument differed because of the hydraulic drop downstream of the flumes."

Hydrology data analysis

Analysis of water yield included annual cumulative discharge and discharge patterns over time and in response to rainfall as well as the relationship between slope and water yield.

$$RC = \frac{CumulQ}{CumulP} \tag{1.1}$$

Runoff coefficients (RC) were calculated using Equation 1.1. Discharge differences due to rainfall versus land cover were evaluated. To assess the variability in discharge between pre-treatment, treatment and early establishment phases, regression relationships were developed between treatment and control watersheds for daily and weekly flow volumes. Flow volumes were log transformed for the regression analyses. As in earlier research (Bennett et al., 2013), the relationship of the logarithmic transformation of the daily and weekly flow volumes was analyzed for flow volumes greater than 2% of the cumulative volume in a given period. A type of flashiness, or hydrological reactivity, indicator ($V_{2\%}$) was calculated for each watershed. This indicator corresponds to the proportion of the annual flow volume that occurred in 2% of the time corresponding to the highest flows. As reported by Bennett et al. (2013), 2% was chosen as an indicator of reactivity for our watersheds because it offered the largest discrimination among watersheds for the highest flows and had been previously used for other applications (Moatar and Meybeck, 2007). As summarized by Bennett et al., "the value was obtained by sorting flow values from highest to lowest and calculating the cumulative flow corresponding to the cumulative probability of occurrence from 1 to 100% for the individual years," obtaining then the highest flow volume that occurred in 2% of the time.

Reference ET (ET_0) was calculated using the Penman-Monteith combination equation (Allen et al., 1989) and weather data, accounting for vegetation height (details in Appendix F). Reference ET was calculated; however, this was only used as a rough comparison given that ET_0 is location specific and will be equal for the same location and only differ based on crop height input. There were shortcomings acknowledged in this approach to obtain ET_0, as this value is species specific, and we do not know crop coefficients for either loblolly pine or switchgrass. Still, the water balance for each watershed was evaluated cumulatively on a yearly basis, considering rainfall, outflow, ET_0, and change in soil storage (unknown, but representative of bypass flow or ET_0 error).

Water quality data collection and analyses

Flow proportional composite samples were collected using automatic samplers (ISCO 6712) located at the outlet of each watershed. Samplers were serviced approximately every two weeks and composite samples were analyzed for concentrations (mg L^{-1}) of nitrate (NO_3^--N), ammonium (NH_4^+-N), total Kjeldahl nitrogen (TKN), total suspended solids (TSS), phosphate (PO_4^{3-}), total phosphorous (TP), and dissolved organic carbon (DOC). Flow thresholds for the flow proportional sampling were set by watershed and season in order to best capture all the storm events in the composite sample. To minimize nutrient decay by keeping the pH below 2, the composite bottles were fit with 2 mL vials of 95-98% pure concentrated sulfuric acid, distributed vertically on a ladder and dispensed proportionally to the sample volume (every 0.5 L). the method detection limits and standard methods used are given in Table 2.3.

Table 2.3. Method detection limits and standard methods used for water quality data (copied from Carter 2016).

Water Quality Parameter	**Method Detection Limit** (mg L^{-1})	**Standard Method**
TKN	0.04	4500-N_{org} D section
Total P	0.01	4500-N_{org} D section
Ortho-Phosphate	0.01	4500-P G section
NO_3^--N	0.1	4500-NO_3^- I section
NH_4^+-N	0.1	4500-NH_3 H section

Water quality data analysis

Water quality difference between watersheds were evaluated from cumulative loads calculated over time. The cumulative load (kg ha^{-1}) for each sampling period was calculated as the product of the composite sample concentration and the cumulative flow volume calculated over the same period per watershed area. This calculation was performed for every sampling interval and summed together on a yearly basis using Equation 1.2.

$$\sum_i L_i = \sum_i \frac{0.01 V_i C_i}{SA} \qquad (1.2)$$

where i represents a sampling period; L_i is the load corresponding to the i^{th} sampling period (kg ha^{-1}); V_i is the flow volume corresponding to the i^{th} sampling period (mm); C_i is a parameter concentration (mg L^{-1}) in the composite bottle corresponding to the i^{th} sampling period; SA is the surface area of the watershed (ha); and 0.01 is a conversion factor taking into consideration unit conversions.

Water quality analyses included differences in annual cumulative load (kg ha^{-1}). The plotting methods included cumulative load over time, cumulative load versus cumulative discharge, and treatment watershed cumulative load as a function of control and reference watershed cumulative loads. The effects due to rainfall versus land cover were evaluated as well as the operations time correspondence with shifts in cumulative loading trends.

Three types of plots were used to evaluate the dynamics of cumulative loads. The first type of plot (type 1) was a simple time series plot of cumulative load which also showed flow rate, the time points when samples were taken and the time of field operations. These plots allowed for the study of the relationships between constituent loading and flow, as well as the effect of field operations on loading. However, the effects of flow on loading obscured the effects of field operations given that a particularly large event can cause a significant impact on concentrations regardless of operations. Therefore, a second plot type (type 2) was used to minimize this bias, which plotted cumulative load versus the cumulative flow and still showed the timing of field operations. This plot removed the effect of flow on the loading and better showed the effect of field operations on constituent load. It should be noted that the point to point slopes of these plots were equal to the flow weighted concentration of the constituent between the points; therefore, the amount of flow during the period between points was not taken into account. The third type of plot (type 3) was of the cumulative load from a treatment watershed versus the cumulative load of the control watershed. These plots showed relationships between the constituent loads of the treatment and control watershed and showed the effects of both constituent concentrations and the amount of flow occurring during a specified period. Daily cumulative loads were calculated by linear interpolation between measured values.

Particular attention was given to changes in the slopes of the lines in plot types 2 and 3. Abrupt increases in slope indicated increases in constituent concentrations in the case of type 2 plots or increases in loading rates in the case of type 3 plots. Such changes were noted relative to the field operations the occurred just prior to the change. We believe that these observations were a good indicator of the impact of field operations on the loading of a particular constituent. The synchrony between the inflection points and the field operations was taken as strong evidence of a causal relationship of the operation to the water quality effects.

2.4 Results and Discussion

Following previous studies (Bennett et al., 2013), the March-to-March hydrologic years were continued for post-treatment year 4 (March 2013 to March 2014) and March-to-November hydrologic period for year 5 (March 2014 to November 2014). Years 4 and 5 are considered years of treatment establishment. The cumulative precipitation for years 4 and 5 were 1245 (near average) and 897 mm, respectively. The average yearly rainfall for Greene County, AL is 1361 mm. Annual rainfall for year 4 was similar to the amount for year 2 (1498 mm) (Figure 2.2).

Hydrology

The cumulative flow, cumulative precipitation, and runoff coefficients were calculated (Figure 2.2 and Table 2.4). Watershed streams flowed between 41 and 100% of the time (Table 2.4, %Q time). The percentage of time that watersheds flowed was calculated as any flow greater than or equal to 0.0001 $m^3 s^{-1}$. Both intercropped watersheds, GR2 and GR3, flowed 100% of the time period of 2013 Mar 04 to 2014 Mar 04 (hydrological year 4), followed by GR4 (66%), GR1 (57%), and GRREF (44%). During the period 2014 Mar 04 to 2014 Dec 01 (hydrological year 5), only GR3 flowed 100% of the time, followed by GR2 (81%), GRREF (51%), and GR4 (42%).

Table 2.4. Summary of watershed hydrological characteristics in Greene County, AL, including cumulative flow (CQ), cumulative precipitation (CP), runoff coefficient (RC), percentage of time that flow occurs (>0.0001 $m^3 s^{-1}$) (%Q time), and $V_{2\%}$, for year 4 (2013 Mar 04 to 2014 Mar 04) and year 5 (2014 Mar 04 to 2014 Dec 01).

		Year 4					**Year 5**				
Watershed	Avg. Slope %	CQ (mm)	CP (mm)	RC	%Q time	$V_{2\%}$	CQ (mm)	CP (mm)	RC	%Q time	$V_{2\%}$
GR1	12.7	494	1245	0.40	57	0.19	304	897	0.34	41	0.40
GR2	11.9	425	1245	0.34	100	0.15	253	897	0.28	81	0.33
GR3	12.6	510	1245	0.40	100	0.25	319	897	0.36	100	0.52
GR4	11.4	287	1245	0.23	66	0.30	175	897	0.20	42	0.50
GRREF	9.9	230	1245	0.18	44	0.23	283	897	0.32	51	0.44

Cumulatively for year 4, GR3 (intercropped-replanted) produced the greatest flow, followed by GR1 (control, young pine), followed by GR2 (thinned, intercropped), followed by GR4 (switchgrass only), and lastly GRREF (reference mature pine) (Table 2.4). During year 4, cumulative flow from GRREF was greater than GR4 until December 2013 (Figure 2.2). During year 4, GRREF is less responsive to rainfall, as flow is relatively constant over a broad precipitation range, whereas the other watersheds show an increase in flow for the same precipitation amount (Figure 2.2). Cumulatively for year 5, GR3 still produced the greatest flow, followed by GR1, GRREF, GR2, and GR4 (Table 2.4). Over the entire study period, the highest sloped watershed (the control, GR1) produced the greatest cumulative outflow until year 4, when the one of the intercropped watersheds, with the second steepest slope (GR3), began producing the greatest cumulative outflow (Table 2.5). This was one means of indication that there was at least a short term impact on hydrology caused by intercropping operations.

Table 2.5. Summary of watershed (WS, [GR1, GR2, GR3, GR4, GRREF]) hydrological characteristics in Greene County, Alabama, including cumulative precipitation (precip., mm), cumulative flow (CQ, mm), and runoff coefficients (RC), 2010-2014.

	Year 1		**Year 2**		**Year 3**		**Year 4**		**Year 5**	
Precip. (mm)	1002		1498		1577		1245		897	
	CQ (mm)	**RC**	**CQ** (mm)	**RC**	**CQ** (mm)	**RC**	**CQ** (mm)	**RC**	**CQ** (mm)	**RC**
GR1	341	0.34	510	0.34	691	0.44	494	0.40	304	0.34
GR2	221	0.22	366	0.24	495	0.31	425	0.34	253	0.28
GR3	293	0.29	466	0.31	594	0.38	510	0.40	319	0.36
GR4	178	0.18	253	0.17	366	0.23	287	0.23	175	0.20
GRREF	260	0.26	308	0.20	465	0.29	230	0.18	283	0.32

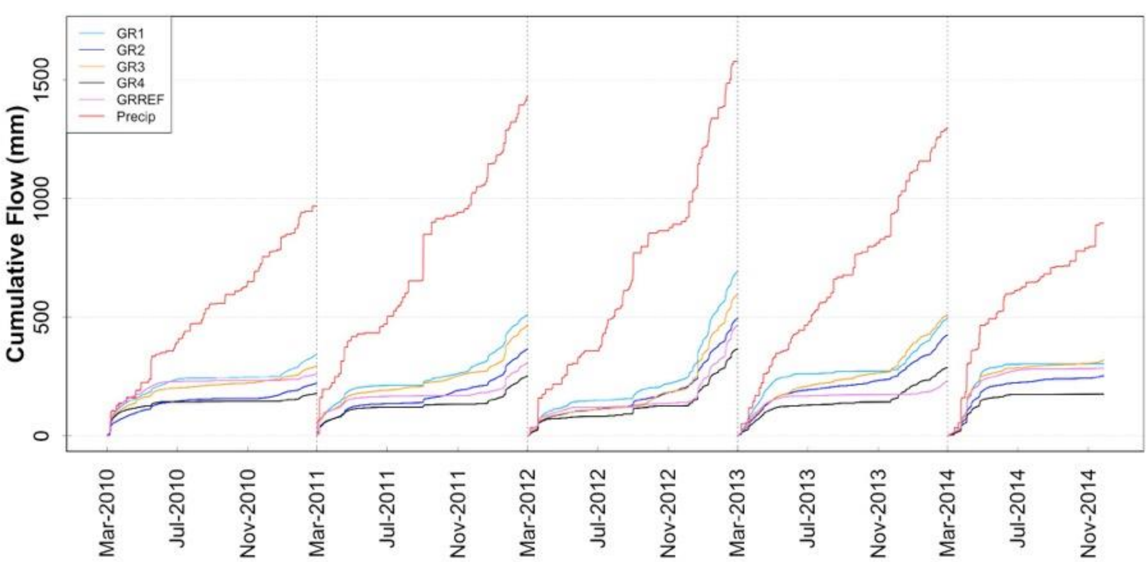

Figure 2.2. Cumulative flow and cumulative precipitation over time from March 2010 through November 2014.

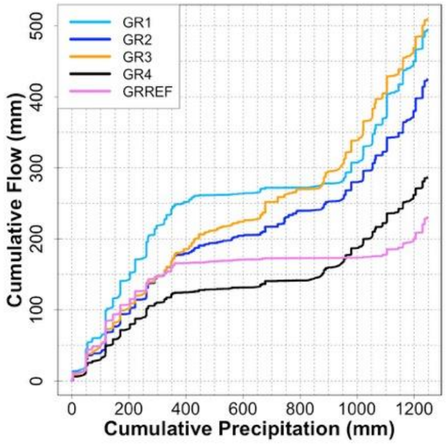

Figure 2.3. Cumulative flow as a function of cumulative precipitation for 2013 Mar 04 to 2014 Mar 04.

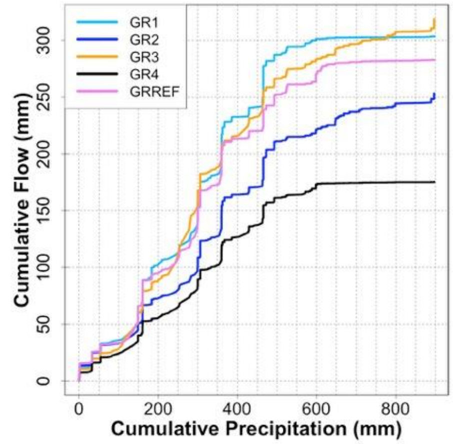

Figure 2.4. Cumulative flow as a function of cumulative precipitation for 2014 Mar 04 to 2014 Dec 01.

There was a consistent and strong relationship between cumulative flow and average slope of the watershed over the five years for all study watersheds, except for the mature reference pine stand (GRREF) (Figure 2.5).

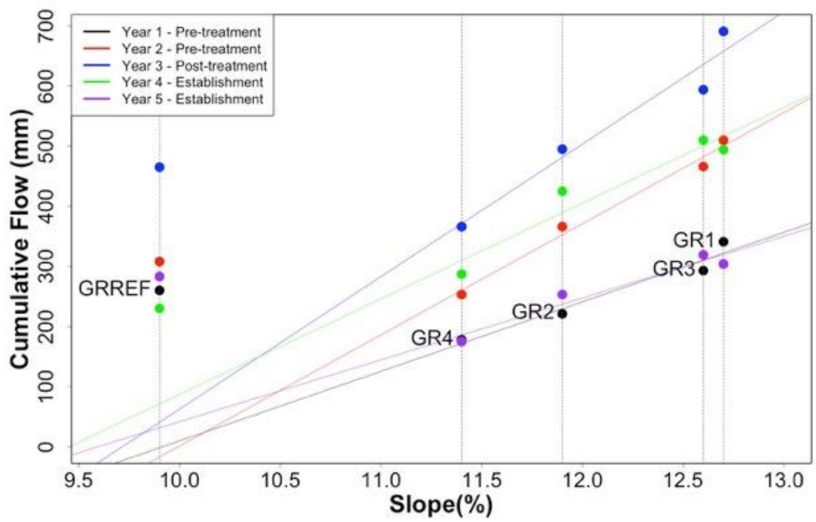

Figure 2.5. Cumulative flow as a function of average slope of the study watersheds over a five-year period.

Flow definitely varied between AL and MS (between 19 - 416 mm differences) and there were no consistencies for which treatments yielded the most outflow between years 4 and 5 (Table 2.6). During year 4 all AL watersheds except switchgrass and mature pine produced a greater cumulative flow, but in year 5 all MS watersheds except the intercropped/thinned were greater than AL. During year 4, the intercropped replanted site produced the greatest cumulative outflow in AL (510 mm), but the mature reference pine watershed produced the greatest cumulative outflow in MS (407 mm), followed by the intercropped replanted site (359 mm). During year 5, the intercropped replanted site yielded the greatest outflow in both AL (319 mm) and MS (608 mm). Although the cumulative outflow is generally greater in

MS during year 5, the hydrological year was slightly shorter in AL during year 5 (only 8 months vs. a full year in MS).

Table 2.6. Comparison of cumulative flow (mm) between Mississippi (MS) and Alabama (AL) sites for each of the watersheds: young pine (YP), intercropped/replanted (IC/Rp), intercropped/ thinned pine (IC/Th), switchgrass (SG), and mature pine (MP).

Hydrological Year	**Location**	**Watershed**				
		YP	**IC/Rp**	**IC/Th**	**SG**	**MP**
Year 4	AL	494	510	425	287	230
	MS	222	359	123	306	407
Year 5	AL	304	319	253	175	283
	MS	339	608	217	591	575

Paired relationships

The logarithmic relationship between the daily and weekly cumulative flow volumes from each watershed were compared with the cumulative daily and weekly flow from the young pine control watershed, GR1 (Figure 2.6 and Figure 2.7). The auto-regression among daily points makes this comparison less desirable; the weekly comparison is more reasonable so the assessment of significant differences will use weekly data. GR2 (thinned pine, intercropped) had the greatest correlation with the control throughout all five years ($0.71 \leq R^2 \leq 0.92$), with no significant differences detected among all five years based on the 95% confidence intervals. We can conclude from these results that there was no treatment effect on the hydrology of the thinned/intercropped site (GR2). This result is reasonable given that these two watersheds (GR1 and GR2) were adjacent and had the most similar land cover (same-age pine, both planted 2008).

Comparing the 95% confidence intervals of the slope values of weekly logarithmic cumulative flow, this GR3 slope in year 4 was significantly lower than the GR3 slope in year 1 (1.29), but there were no other significant differences among the other years, indicating a possible short-term treatment effect on hydrology in GR3. The GR4 slopes during years 4 (0.98) and 5 (1.07) were significantly lower than the GR4 slopes during years 1 (2.05) and 2 (1.82), but there were no other significant differences among the other years, indicating that this treatment (switchgrass only) did have a significant effect on the hydrology of GR4. GRREF had the greatest slope during year 4 (1.86), but was still not significantly different from the other years. GRREF had the lowest slope during year 5 (0.93) which was significantly lower than years 1 and 2. Given that there were no additional operations performed on either the control or mature reference, these hydrological differences must be attributed to inherent differences between the maturity and density of the pine and natural understory which affect the differences hydrology over time.

Considering R-squared values of the weekly logarithmic cumulative flow comparisons during year 4, all watersheds showed a decrease in correlation (lower R^2) with the control compared with year 3. Considering either daily or weekly cumulative flow, the strongest correlations (higher R^2) between the control and all other watersheds occurred during year 5 ($0.83 \leq R^2 \leq 0.92$). From the R^2 statistics we can conclude that there was a short-term effect on hydrology evident from the weak correlations between treatment and control flow during year 4; however, year 5 shows a return to hydrology that is strongly correlated with hydrology in the control. These results are reasonable given that heavy operations occurred during years 3 and 4 (i.e., disking, offset rip), but the land has relatively quickly recovered from these operations, showing a return to normal hydrology patterns, comparable to our control.

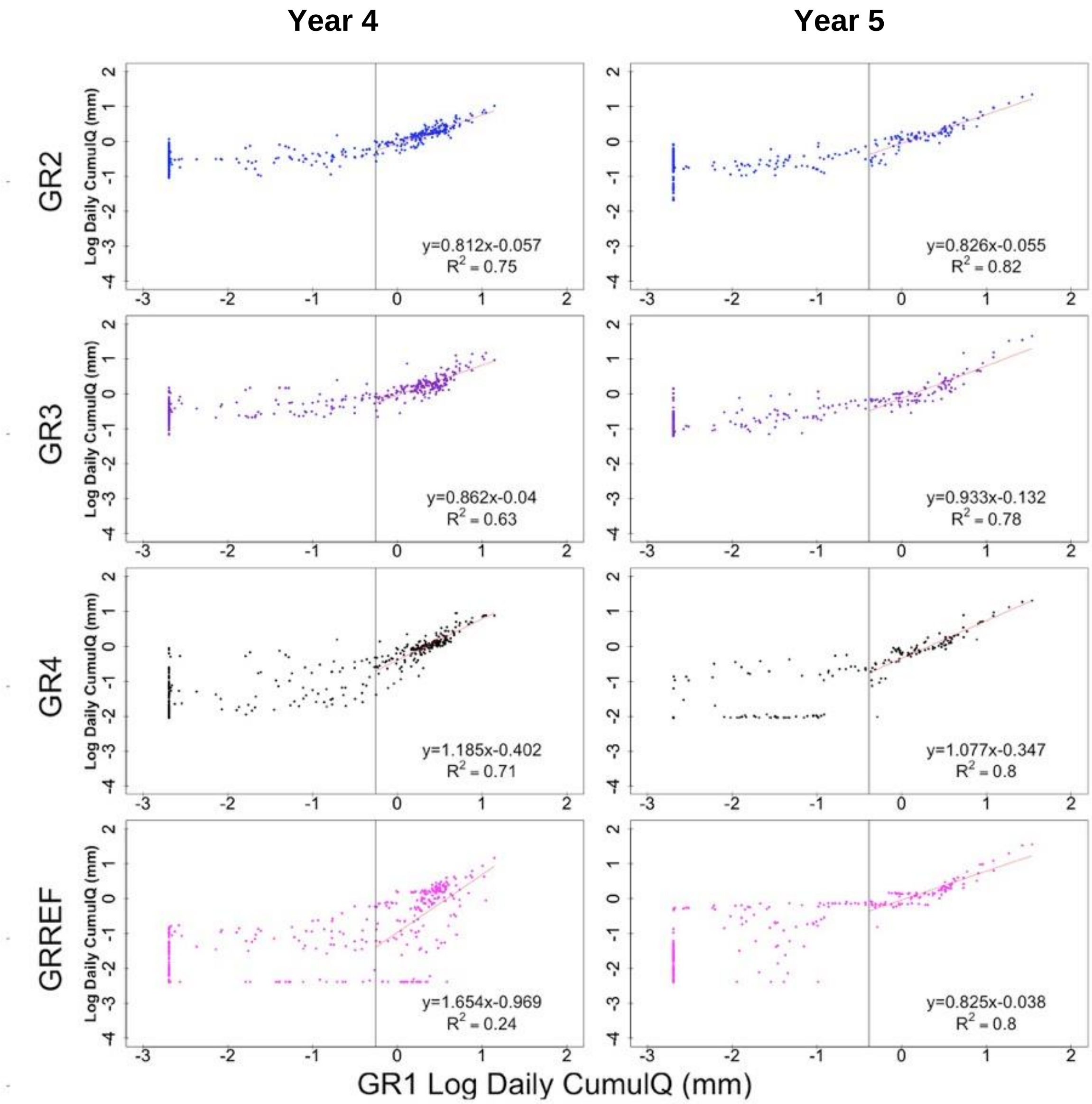

Figure 2.6. Logarithmic daily cumulative flows from the study watersheds as a function of the young pine reference GR1 watershed for 2013 Mar 04 to 2014 Mar 04 (year 4) and 2014 Mar 04 to 2014 Dec 01 (year 5) with linear regressions performed for flow corresponding to greater than 2% of the cumulative volume in a given period. The vertical line represents this threshold above which the linear regression was calculated.

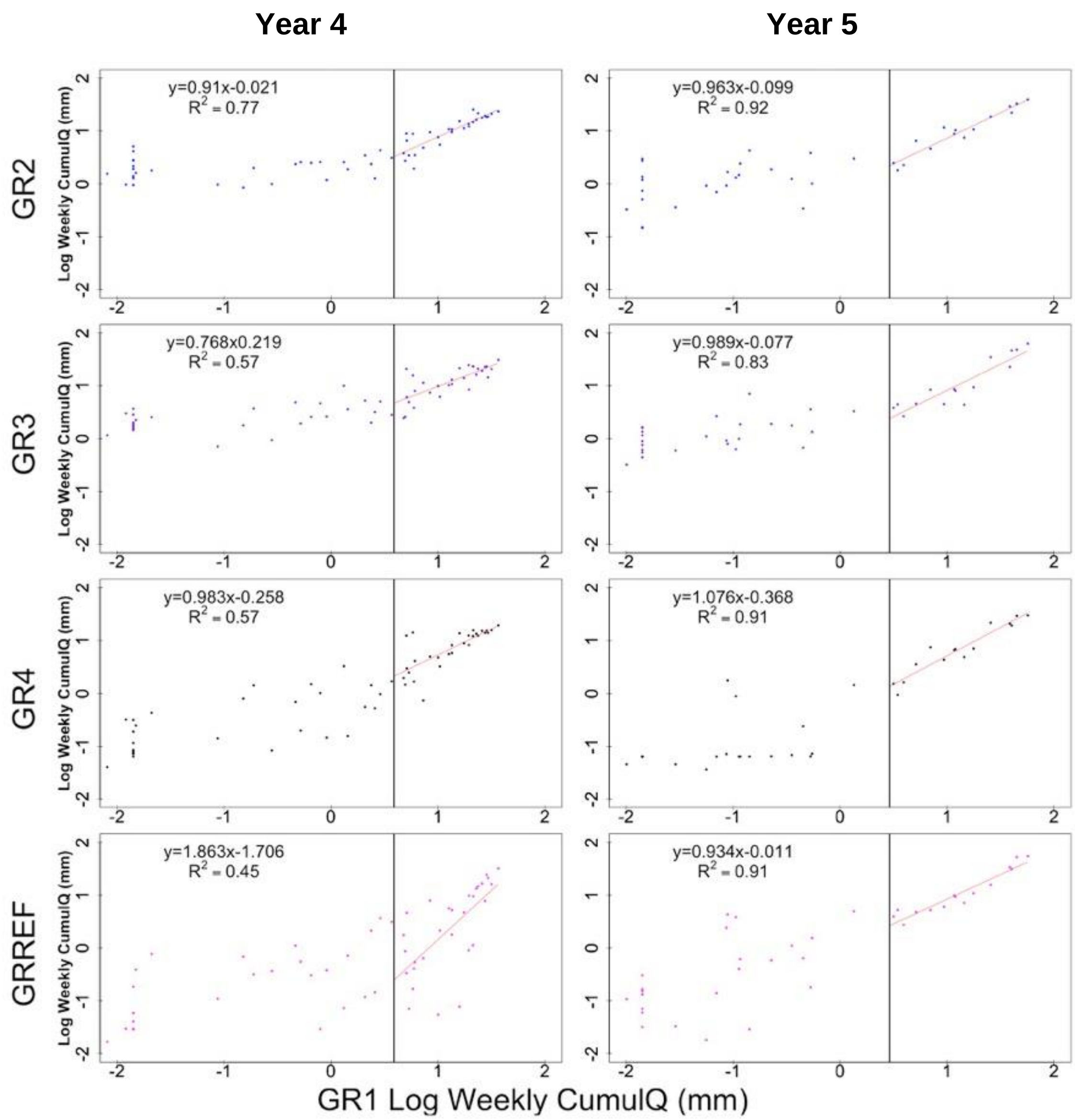

Figure 2.7. Logarithmic weekly cumulative flows from the study watersheds as a function of the young pine reference GR1 watershed for 2013 Mar 04 to 2014 Mar 04 (year 4) and 2014 Mar 04 to 2014 Dec 01 (year 5) with linear regressions performed for flow corresponding to greater than 2% of the cumulative volume in a given period. The vertical line represents this threshold above which the linear regression was calculated.

Table 2.7. Coefficients of determination (R^2) values, slope values, and 95% slope confidence intervals for linear relationships between logarithmic weekly flow volumes for each treatment watershed as a function of the control (GR1) for all five years (2010-2014).

		Year 1	**Year 2**	**Year 3**	**Year 4**	**Year 5**
GR2	$\mathbf{R^2}$	0.75	0.78	0.87	0.77	0.92
	Slope	0.95	0.93	0.86	0.91	0.96
	95% CI	(0.75, 1.15)	(0.78, 1.09)	(0.75, 0.97)	(0.72, 1.11)	(0.80, 1.13)
GR3	$\mathbf{R^2}$	0.79	0.71	0.72	0.57	0.83
	Slope	1.29	1.08	0.93	0.77	0.99
	95% CI	(1.04, 1.54)	(0.86, 1.30)	(0.73, 1.12)	(0.50, 1.03)	(0.72, 1.26)
GR4	$\mathbf{R^2}$	0.60	0.63	0.67	0.57	0.91
	Slope	2.05	1.82	1.47	0.98	1.07
	95% CI	(1.42, 2.67)	(1.37, 2.27)	(1.12, 1.81)	(0.65, 1.32)	(0.87, 1.28)
GRREF	$\mathbf{R^2}$	0.56	0.56	0.63	0.45	0.91
	Slope	1.68	1.63	1.15	1.86	0.93
	95% CI	(1.13, 2.23)	(1.15, 2.11)	(0.85, 1.44)	(1.05, 2.67)	(0.76, 1.11)

Flow relationships: treatment versus control

All treatment watersheds (GR2, GR3, GR4) exhibited an increase in flow shortly after disking and switchgrass planting, evident from the rapid increase in slope of the cumulative flow of each treatment watershed as a function cumulative flow of the control (GR1) compared with the relatively constant slope throughout the rest of the study period (Figure 2.8). Zoomed-in depictions of the hydrologic year Mar 2013 to Mar 2014 when the second disking and switchgrass planting occurred are shown in Figure 2.9, Figure 2.10, Figure 2.11, and Figure 2.12. Increases in flow following certain operations, such as disking and switchgrass planting, may be due to increased runoff rates associated with soil compaction caused by heavy equipment traffic (Jim, 1993; Kozlowski and Pallardy, 1997; Kozlowski, 1999). Soil compaction is typically paired with a soil crust that further impedes infiltration and increases runoff (Malmer and Grip, 1990). Recovery from soil compaction in warmer climates, such as the southeastern US, may be impeded due to minimal freezing and thawing (Mitchell et al., 1982). The top 30 cm, which occupies the majority of the root mass, is most susceptible to compaction, thus potentially impeding water uptake by the plant (Wingate-Hill and Jakobson, 1982). Even if the soil is not highly trafficked, most soils become compacted after only a few vehicle passes (Lockaby and Vidrine, 1984; Shetron et al., 1988). Several factors may influence the degree of compaction including soil texture, soil moisture content, ground pressure, and vehicle vibration (Greacen and Sands, 1980; Ole-Meiludie and Njau, 1989; Jim, 1993).

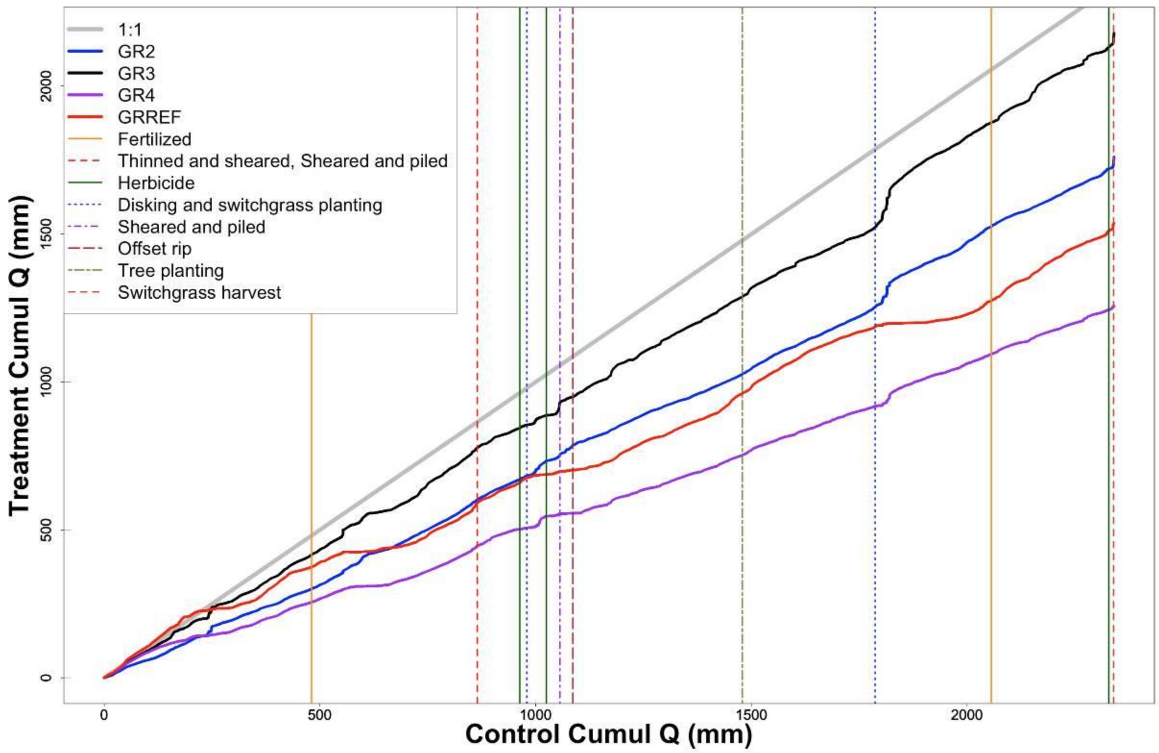

Figure 2.8. Cumulative flow (Q, mm) of each watershed (GR2, GR3, GR4, GRREF) as a function of the control watershed (GR1) in Greene County, Alabama. Operations are depicted by colored and patterned vertical lines.

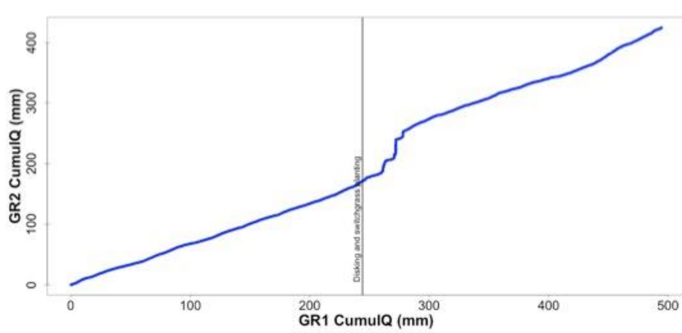

Figure 2.9. Cumulative flow relationship of GR2 as a function of GR1, 2013 Mar 04 to 2014 Mar 04 (vertical line represents disking and switchgrass planting).

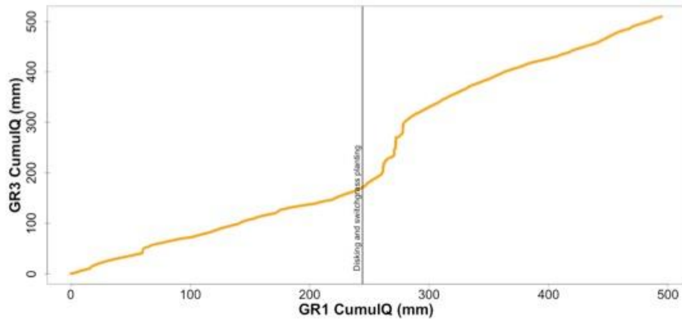

Figure 2.10. Cumulative flow relationship of GR3 as a function of GR1, 2013 Mar 04 to 2014 Mar 04 (vertical line represents disking and switchgrass planting).

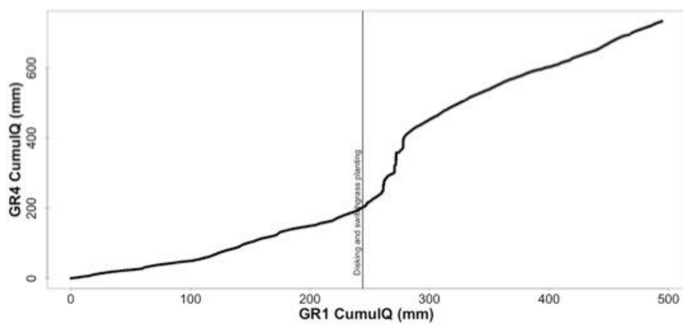

Figure 2.11. Cumulative flow relationship of GR4 as a function of GR1, 2013 Mar 04 to 2014 Mar 04 (vertical line represents disking and switchgrass planting).

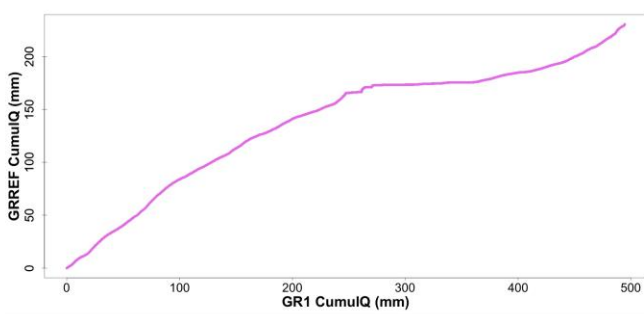

Figure 2.12. Cumulative flow relationship of GRREF as a function of GR1, 2013 Mar 04 to 2014 Mar 04.

During the following period, 2014 Mar 04 to 2014 Dec 01, fertilizer and herbicide were applied to the treatment watersheds (GR2, GR3, and GR4). From plots of cumulative flow of each of the treatment watersheds as a function of the control (GR1) (Figures E.1 to E.3 in Hydrology Appendix E), fertilization did not have an impact on cumulative outflow from GR2, GR3, or GR4. Herbicide did seem to have an impact on cumulative flow leaving GR2 and GR3 judging from the steep increase soon after this operation, but not on GR4 given the relatively constant slope that year. However, this steep increase in flow leaving GR2 and GR3 may be due to other unknown factors given that herbicide application would not be expected to impact outflow so intensely.

Water Quality

Overall cumulative loadings

Cumulative loadings for each water quality parameter measured for each hydrological year (2011 to 2014) are reported in Table 2.8 and shown graphically in Figure 2.13, Figure 2.14, Figure 2.15, Figure 2.16, Figure 2.17, Figure 2.18, and Figure 2.19. Disking and switchgrass planting was the only major operation performed on the treatment watersheds (GR2, GR3, GR4) during year 4 (2013). During this year, the intercropped-thinned (GR2) yielded the greatest cumulative loadings of TSS, DOC, TKN, PO_4^{3-}, and TP. Both intercropped sites yielded exceptionally high loads of TSS, particularly during year 4. The intercropped-thinned (GR2) yielded the greatest cumulative TSS loading (7259 kg ha^{-1}), followed by the intercropped-replanted (GR3) (2474 kg ha^{-1}), switchgrass only (GR4), the control (GR1), and lastly GRREF. A similar trend in DOC was observed with GR2 yielding the greatest cumulative load (39 kg ha^{-1}), followed by GR1, GR3, GR4, and lastly GRREF. GRREF yielded the least cumulative load for TSS, NO_3^--N, and DOC.

In year 5 (2014), treatment watersheds were fertilized, herbicided, and switchgrass harvested. The intercropped-thinned site (GR2) again produced the greatest cumulative loadings in TSS (2367 kg ha^{-1}), TKN (3.81 kg ha^{-1}), and TP (3.27 kg ha^{-1}). The intercropped-replanted site (GR3) produced the greatest DOC loading (28.3 kg ha^{-1}), followed by GR2 (24.3 kg ha^{-1}), GR1 (22.7 kg ha^{-1}), GRREF (19.0 kg ha^{-1}), and GR4 (17.1 kg ha^{-1}). Overall, nutrient loadings were relatively low. The intercropped-replanted site (GR3) produced the greatest cumulative loading of NH_4^+-N (1.75 kg ha^{-1}), followed by the control (GR1) (1.20 kg ha^{-1}), the intercropped-thinned site (GR2) (1.13 kg ha^{-1}), the switchgrass only site (GR4) (0.91 kg ha^{-1}), and lastly the mature reference (GRREF) (0.45 kg ha^{-1}). The switchgrass (GR4) produced the greatest cumulative loading of NO_3^--N (1.08 kg ha^{-1}), followed by the control (GR1) (0.93 kg ha^{-1}), intercropped-replanted (GR3) (0.90 kg ha^{-1}), intercropped-thinned (GR2) (0.46 kg ha^{-1}), and GRREF (0.43 kg ha^{-1}).

Table 2.8. Cumulative loading (kg ha^{-1} yr^{-1}) of water quality parameters for all study watersheds for hydrological years 2, 3, 4, and 5 (2011-2014).

WS	**Year**	**TSS**	**NH_4^+-N**	**NO_3^--N**	**TKN**	**PO_4^{3-}**	**TP**	**DOC**
GR1	2	394	0.253	0.176	2.53	NA	0.933	38.5
	3	681	3.69	0.488	0.984	NA	1.68	63.8
	4	312	2.12	0.82	5.86	0.16[a]	2.99	28.8
	5	347	1.20	0.93	3.08	0.15	1.41	22.7

Table 2.8 Continued.

GR2	2	497	0.132	0.152	5.02	NA	0.234	23.9
	3	1435	1.78	0.376	2.28	NA	0.869	38.4
	4	7259[c]	2.14[c]	0.76[c]	7.04[c]	1.41[b]	3.72[d]	39.0[c]
	5	2367	1.13	0.46	3.81	0.45	3.27	24.3
GR3	2	252	0.179	0.610	11.4	NA	0.372	21.3
	3	1899	3.12	1.02	1.86	NA	1.36	58.4
	4	2474	2.49	1.15	NA	0.31[a]	2.28[a]	23.4
	5	1857	1.75	0.90	NA	0.42	2.29	28.3
GR4	2	96	0.292	0.363	1.56	NA	0.214	17.1
	3	814	5.86	0.835	1.29	NA	0.353	22.0
	4	590	1.28	0.63	2.95	0.08[a]	1.46[a]	16.4
	5	485[f]	0.91[f]	1.08[f]	1.91[f]	0.33[f]	1.95[f]	17.1[f]
GRREF	2	109	0.168	0.172	5.71	NA	0.283	21.4
	3	389	0.488	0.188	0.21	NA	0.164	20.7
	4	107	1.49	0.37	4.60[e]	NA	NA	10.3
	5	502	0.45	0.43	NA	0.16	1.18	19.0

[a]Data from 2013-08-26 to 2014-02-13.
[b]Data from 2013-09-18 to 2014-02-18.
[c]Data from 2013-03-12 to 2014-02-18.
[d]Data from 2013-11-18 to 2014-02-18.
[e]Data from 2013-03-12 to 2013-05-20.
[f]Data from 2014-03-14 to 2014-06-24.

Table 2.9. Cumulative loading (kg ha^{-1} yr^{-1}) of water quality parameters for all watersheds in Mississippi and Alabama for post-treatment years 4 and 5.

WS	**NH_4^+-N Annual Load**				**NO_3^--N Annual Load**			
	Year 4		**Year 5**		**Year 4**		**Year 5**	
	AL	**MS**	**AL**	**MS**	**AL**	**MS**	**AL**	**MS**
YP	2.12	0.80	1.20	0.40	0.82	0.65	0.93	0.52
IC/Th	2.14	0.49	1.13	0.40	0.76	0.13	0.46	0.39
SG	1.28	1.86	0.91	1.70	0.63	0.69	1.08	0.92

Table 2.9 Continued.

IC/Rp	2.49	1.50	1.75	1.18	1.15	1.06	0.90	0.73
MP	1.49	1.24	0.45	0.74	0.37	0.59	0.43	0.52
WS	**TSS Annual Load**				**TP Annual Load**			
	Year 4		**Year 5**		**Year 4**		**Year 5**	
	AL	**MS**	**AL**	**MS**	**AL**	**MS**	**AL**	**MS**
YP	312	270	347	199	2.99	1.47	1.41	0.78
IC/Th	7259	537	2367	128	3.72	0.81	3.27	0.46
SG	590	1083	485	379	1.46	2.13	1.95	1.97
IC/Rp	2474	1716	1857	801	2.28	2.30	2.29	1.89
MP	107	1402	502	394	NA	1.42	1.18	1.17
WS	**TKN Annual Load**				**DOC Annual Load**			
	Year 4		**Year 5**		**Year 4**		**Year 5**	
	AL	**MS**	**AL**	**MS**	**AL**	**MS**	**AL**	**MS**
YP	5.86	2.21	3.08	0.70	28.8	15.8	22.7	25.6
IC/Th	7.04	1.13	3.81	0.90	39.0	10.5	24.3	25.8
SG	2.95	4.73	1.91	1.55	16.4	38.4	17.1	78.8
IC/Rp	NA	5.39	NA	0.95	23.4	38.0	28.3	84.7
MP	4.60	4.63	NA	0.97	10.3	37.5	19.0	60.6

Comparing the Alabama and Mississippi sites during the post-treatment years: During year 4 (Mar 2013-Mar 2014), annual NH^{4+}-N loads were slightly greater in all AL watersheds except the switchgrass watershed. The intercropped/thinned was 4.4 times greater in AL (2.14 kg ha^{-1} yr^{-1}) than MS (0.49 kg ha^{-1} yr^{-1}). The intercropped/replanted produced the greatest annual NH^{4+}-N load during year 4 from the AL site; whereas the switchgrass produced the greatest NH^{4+}-N load from the MS site. TKN values were typically greater in AL, with AL yielding the greatest load from the intercropped/thinned watershed in year 4 (~6x greater than MS).

NO_3^--N loads: during year 4, the intercropped/thinned watershed produced about 6 times greater NO_3^--N load in AL than in MS, while other watersheds produced comparable loads between both states. During year 5, the NO_3^--N loads were comparable among all watersheds in both states.

TSS loads from the intercropped/thinned were nearly 14 times greater in AL than MS during year 4 and nearly 19 times higher during year 5. TSS loads were about twice as high in AL for the young pine and intercropped/replanted during year 5, but comparable during year 4. One hypothesis for this extreme difference in TSS values is the difference in the stream management zones in AL and MS. During year 5, in addition to the higher TSS loads from the intercropped/thinned in AL, loads from intercropped/replanted in AL were over twice as much as those in MS, while the other watersheds were relatively comparable between AL and MS. Still, compared to other managed forests, TSS values from the young pine in AL and MS were relatively low (199-347 kg ha^{-1} yr^{-1} vs. 744-18,00 kg ha^{-1} yr^{-1} in other managed forests). Even with the particularly high TSS exports from GR2 and GR3, we cannot conclude that there was a treatment effect given that same operations were performed on GR4 which exported much less TSS. Therefore, we conclude that the higher TSS values were likely associated with the erodibility of the stream management zone (i.e., flood plain or riparian zone) unique to each watershed.

Table 2.10. Comparison of sediment yield (kg ha^{-1} yr^{-1}) from forested and agricultural catchments (copied and modified from Bennett et al. [in press]).

Catchment	**Location**	**Land use**	**Area (ha)**	**Sediment yield (kg ha^{-1} yr^{-1})**	**Reference**
GR1	Alabama	Young pine	11.6	394 - 681	This article
GR2	Alabama	Thinned intercropped young pine	26.7	497 - 1435	This article
GR3	Alabama	Newly established pine with switchgrass intercropping	25.9	252 - 1899	This article
GR4	Alabama	Switchgrass establishment	16.5	96 - 814	This article
GRREF	Alabama	Mature managed forest	8.0	109 - 389	This article
Mørdre	Norway	Agriculture, croplands	680	1450 – 3000	Øygarden et al. (2003)
Skuterud	Norway	Agriculture, croplands	450	1000 - 2500	Øygarden et al. (2003)
Moulinet	France	Agriculture, grass- and croplands	453	254	Lefrançois et al. (2007)
Violette	France	Agriculture, grass- and croplands	225	360	Lefrançois et al. (2007)
Jubilee	England	Agriculture, croplands	31	1310	Walling et al. (2002)
Belmont	England	Agriculture, croplands	150	819	Walling et al. (2002)
Lower Smisby	England	Agriculture, croplands	260	803	Walling et al. (2002)
New Cliftonthorpe	England	Agriculture, croplands	96	640	Walling et al. (2002)
Stanley Cars	England	Mixed pastures and urban	455	936	Goodwin et al. (2003)
Literature review	England	Upland low impact	<10 km²	1090	Walling et al. (2008)
Literature review	England	Upland Agriculture	<10 km²	270	Walling et al. (2008)
Literature review	England	Lowland low impact	<10 km²	70	Walling et al. (2008)
Literature review	England	Lowland Agriculture	<10 km²	510	Walling et al. (2008)

Table 2.10 Continued.

Literature review	England	Lowland urban	<10 km²	100	Walling et al. (2008)
Clem	Victoria, Aus.	Planted pine	46	744	Hopmans and Bren (2007)
San Salvador	Spain	Natural forest	9.2	12,000	García-Ruiz et al. (2008)
Literature review	Western USA	Forested watersheds before fire	-	78 - 1100	Moody et al. (2009)
Literature review	Western USA	Forested watersheds after fire	-	8200	Moody et al. (2009)
Clem	Victoria, Aus.	Planted pine after fire	46	18,000 - 4,500*	Smith et al. (2011)
Mangaotama	New Zealand	Indigenous forest	268	970 ± 390	Hughes et al. (2012)
Whakakai	New Zealand	Mixed pine and pasture	311	600 ± 220	Hughes et al. (2012)
El Salado	Spain	Mixed forest and agriculture	670	1800	Zuazo et al. (2012)

Table 2.11. Comparison of nitrate-nitrogen (NO_3^--N) yield (kg ha^{-1} yr^{-1}) from forested and agricultural watersheds.

Catchment	**Location**	**Land use**	**Area (ha)**	**Nitrate yield (kg ha^{-1} yr^{-1})**	**Reference**
GR1	Alabama, USA	Young pine	11.6	0.18 - 0.93	This article
GR2	Alabama, USA	Thinned intercropped young pine	26.7	0.15 - 0.76	This article
GR3	Alabama, USA	Pine with switchgrass intercropping	25.9	0.61 - 1.15	This article
GR4	Alabama, USA	Switchgrass	16.5	0.36 - 1.08	This article
GRREF	Alabama, USA	Mature managed forest	8.0	0.17 - 0.43	This article
Little River Watershed	Georgia, USA	Agricultural/Forest	1735	0.14 -0.24*	Asmussen et al. 1979
Various watersheds	USA	Forested land	NA	0.7 - 8.8	Loehr, 1974

*Nitrate and nitrite combined

DOC loads were typically greater in MS, with two exceptions during year 4 when the young pine and the intercropped/thinned watersheds yielded higher DOC loads in AL. DOC loads were relatively comparable during both years with the exception of DOC being nearly 5 times higher in MS on the switchgrass watershed, and about 3 times greater in MS from the intercropped/replanted and mature pine during year 5. Still, all values from both states were within reasonable range of reported values (Hobbie and Likens, 1973; Dillon and Molot, 1997).

Table 2.12. Comparison of dissolved organic carbon (DOC) yield (kg ha^{-1} yr^{-1}) from forested and agricultural watersheds.

Catchment	**Location**	**Land use**	**Area (ha)**	**DOC yield (kg ha^{-1} yr^{-1})**	**Reference**
GR1	Alabama, USA	Young pine	11.6	22.7 - 63.8	This article
GR2	Alabama, USA	Intercropped/ thinned	26.7	23.9 - 39.0	This article
GR3	Alabama, USA	Intercropped/ replanted	25.9	21.3 - 58.4	This article
GR4	Alabama, USA	Switchgrass	16.5	16.4 - 22.0	This article
GRREF	Alabama, USA	Mature managed forest	8.0	10.3 - 21.4	This article
Watershed 6	New Hampshire, USA	Deciduous Forested	13.2	8.51	Hobbie and Likens, 1973
Watershed 2	New Hampshire, USA	Deforested	15.6	4.84	Hobbie and Likens, 1973
BC1	Ontario, Canada	Forested	20.4	9.9	Dillon and Molot, 1997
CB1	Ontario, Canada	Forested	59.7	22.9	Dillon and Molot, 1997
CB2	Ontario, Canada	Forested	126	60.2	Dillon and Molot, 1997
CN1	Ontario, Canada	Forested	456.3	43.6	Dillon and Molot, 1997

Table 2.12 Continued.

DE10	Ontario, Canada	Forested	78.9	65.7	Dillon and Molot, 1997
DE11	Ontario, Canada	Forested	76.3	0.11	Dillon and Molot, 1997
DE5	Ontario, Canada	Forested	30	73.1	Dillon and Molot, 1997
DE6	Ontario, Canada	Forested	21.8	90.8	Dillon and Molot, 1997
DE8	Ontario, Canada	Forested	67	68.1	Dillon and Molot, 1997
HP3	Ontario, Canada	Forested	26	45.6	Dillon and Molot, 1997
HP3A	Ontario, Canada	Forested	19.7	19.3	Dillon and Molot, 1997
HP4	Ontario, Canada	Forested	119.5	29.9	Dillon and Molot, 1997
HP5	Ontario, Canada	Forested	190.5	55.8	Dillon and Molot, 1997
HP6	Ontario, Canada	Forested	10	32.8	Dillon and Molot, 1997
HP6A	Ontario, Canada	Forested	15.3	32.7	Dillon and Molot, 1997
PC1	Ontario, Canada	Forested	23.3	48.6	Dillon and Molot, 1997
RC1	Ontario, Canada	Forested	133.6	19	Dillon and Molot, 1997
RC2	Ontario, Canada	Forested	27	62.2	Dillon and Molot, 1997
RC3	Ontario, Canada	Forested	70.5	41.7	Dillon and Molot, 1997
RC4	Ontario, Canada	Forested	45.5	34.7	Dillon and Molot, 1997

Table 2.13. Comparison of total phosphorous (TP) yield (kg ha^{-1} yr^{-1}) from forested and agricultural watersheds.

Catchment	**Location**	**Land use**	**Area (ha)**	**TP (kg ha^{-1} yr^{-1})**	**Reference**
GR1	Alabama, USA	Young pine	11.6	0.93 - 2.99	This article
GR2	Alabama, USA	Intercropped/thinned	26.7	0.23 - 3.72	This article

Table 2.13 Continued.

GR3	Alabama, USA	Intercropped/replanted	25.9	0.37 - 2.29	This article
GR4	Alabama, USA	Switchgrass	16.5	0.21 - 1.95	This article
GRREF	Alabama, USA	Mature managed forest	8.0	0.16 - 1.18	This article
Watershed 6	New Hampshire, USA	Deciduous Forested	13.2	0.009	Hobbie and Likens, 1973
Watershed 2	New Hampshire, USA	Deforested	15.6	0.020	Hobbie and Likens, 1973
BC1	Ontario, Canada	Forested	20.4	0.018	Dillon and Molot, 1997
CB1	Ontario, Canada	Forested	59.7	0.033	Dillon and Molot, 1997
CB2	Ontario, Canada	Forested	126	0.082	Dillon and Molot, 1997
CN1	Ontario, Canada	Forested	456.3	0.075	Dillon and Molot, 1997
DE10	Ontario, Canada	Forested	78.9	0.072	Dillon and Molot, 1997
DE11	Ontario, Canada	Forested	76.3	1.39	Dillon and Molot, 1997
DE5	Ontario, Canada	Forested	30	0.255	Dillon and Molot, 1997
DE6	Ontario, Canada	Forested	21.8	0.197	Dillon and Molot, 1997
DE8	Ontario, Canada	Forested	67	0.063	Dillon and Molot, 1997
HP3	Ontario, Canada	Forested	26	0.111	Dillon and Molot, 1997
HP3A	Ontario, Canada	Forested	19.7	0.039	Dillon and Molot, 1997
HP4	Ontario, Canada	Forested	119.5	0.083	Dillon and Molot, 1997
HP5	Ontario, Canada	Forested	190.5	0.096	Dillon and Molot, 1997
HP6	Ontario, Canada	Forested	10	0.069	Dillon and Molot, 1997
HP6A	Ontario, Canada	Forested	15.3	0.04	Dillon and Molot, 1997
PC1	Ontario, Canada	Forested	23.3	0.041	Dillon and Molot, 1997

Table 2.13 Continued.

RC1	Ontario, Canada	Forested	133.6	0.044	Dillon and Molot, 1997
RC2	Ontario, Canada	Forested	27	0.05	Dillon and Molot, 1997
RC3	Ontario, Canada	Forested	70.5	0.068	Dillon and Molot, 1997
RC4	Ontario, Canada	Forested	45.5	0.077	Dillon and Molot, 1997
WTH	Vilppula, Finland	Forested	0.75-1.12	0.030	Kaila et al., 2014
WTH+S	Vilppula, Finland	Forested	1.05-1.07	0.115	Kaila et al., 2014
CC	Vilppula, Finland	Forested	0.90-1.05	0.244	Kaila et al., 2014

TP loads were about 7 times greater in AL during year 5 from the intercropped/thinned watershed (3.27 kg ha^{-1} yr^{-1} in AL vs. 0.46 kg ha^{-1} yr^{-1} in MS), but comparable between AL and MS for all other watersheds during years 4 and 5. Comparing the cumulative annual loading of TP in AL among all the years, we can conclude that there was a treatment effect on TP as there was an increase in the annual cumulative loading in all the treatment watersheds (GR2, GR3, and GR4), but not the control or the mature reference pine. The lowest annual TP loads for the treatment watersheds were obtained in year 2 (first year of water quality data) and the TP loads increased in year 3 (when heavy operations occurred) for all treatment watersheds and remained high throughout the study period into year 5 (considered post-treatment), indicating a lasting treatment effect on TP.

Figure 2.13 shows that the control (GR1) had the greatest cumulative DOC, followed by GR3, GR2, GR4, and lastly GRREF. A steep increase in DOC in GR1 does coincide with a rather large event, which may contribute to the overall higher cumulative load (see Figure G.22 in Appendix G). Figure 2.14 shows GR3 and GR4 had the greatest cumulative load of NH_4^+-N, followed by GR1, GR2, and lastly GRREF. Figure 2.15 shows GR3 had the greatest cumulative load of NO_3^--N, followed by GR4, GR1, GR2, and lastly GRREF. Figure 2.16 shows GR2 had the greatest cumulative load of PO_4^{3+}, followed by GR3, then GR4 (although, GR4 had missing data beyond June 2014). Figure 2.17 shows GR2 had the greatest cumulative load of TKN, followed by GR1, GR4, GRREF, and lastly GR3 (although GR3 data was missing beyond March 2013). Figure 2.18 shows GR2 had the greatest cumulative load of TP, followed by GR1, GR3, GR4, and lastly GRREF. Figure 2.19 shows GR2 had the greatest cumulative load of TSS, followed by GR3, GR4, GR1, and lastly GRREF (although GR4 data was missing beyond June 2014). Considering all water quality parameters, GRREF had consistently the least cumulative load over the four years for all parameters except TKN. Among the other watersheds, there was inconsistency among the cumulative load of the various parameters.

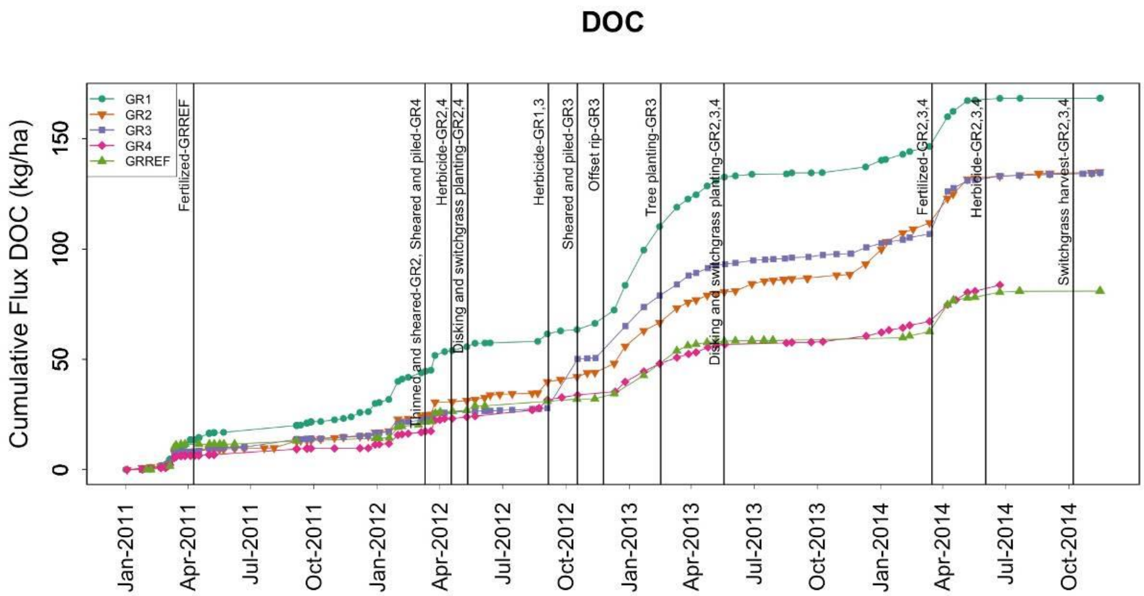

Figure 2.13. Cumulative load (kg ha^{-1}) of DOC over time (2011-2014) for all watersheds in Greene County, Alabama.

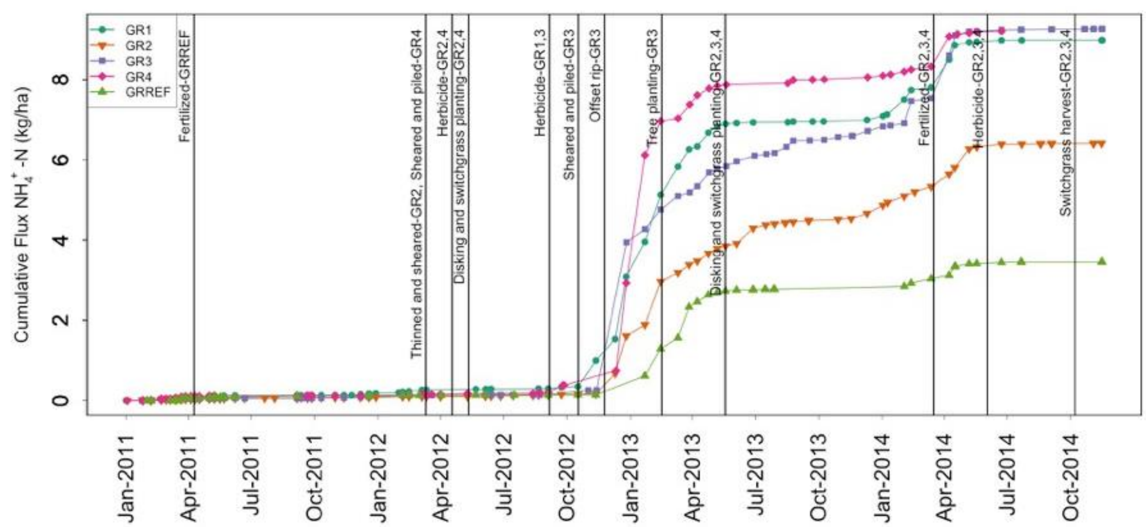

Figure 2.14. Cumulative load (kg ha^{-1}) of NH_4^+-N over time (2011-2014) for all watersheds in Greene County, Alabama.

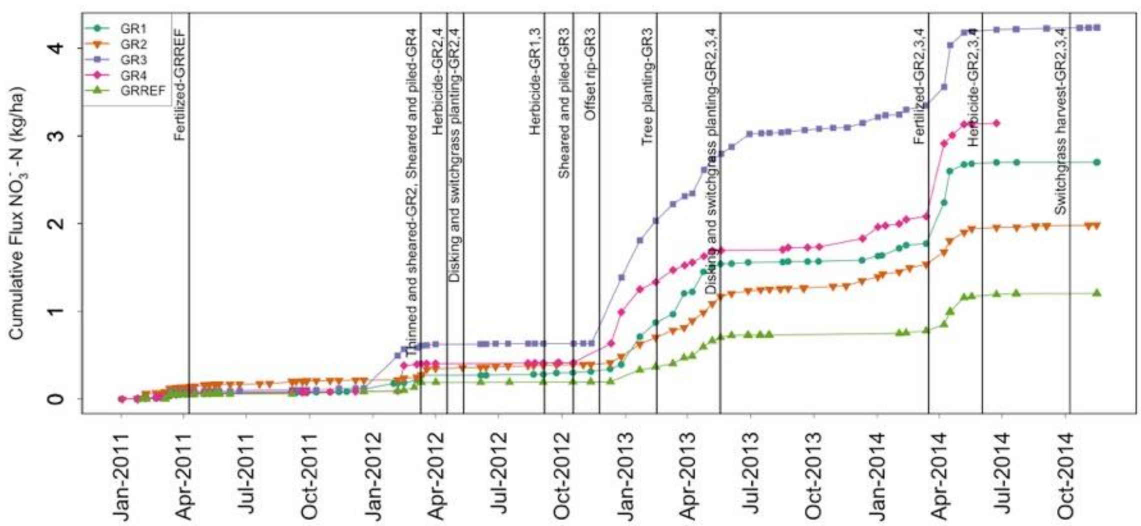

Figure 2.15. Cumulative load (kg ha^{-1}) of NO_3^--N over time (2011-2014) for all watersheds in Greene County, Alabama.

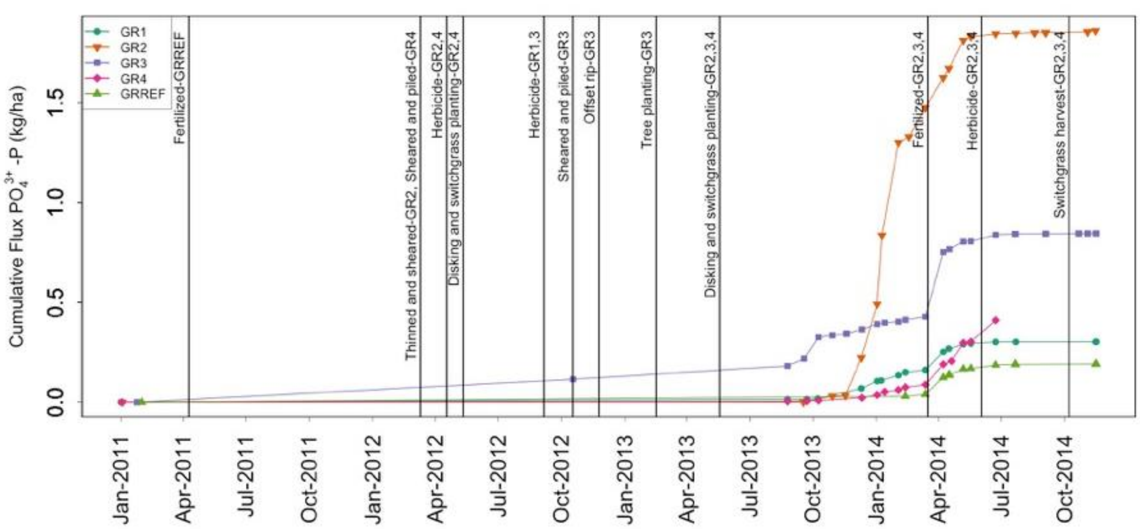

Figure 2.16. Cumulative load (kg ha^{-1}) of phosphate (PO_4^{3+}-P) over time (2011-2014) for all watersheds in Greene County, Alabama.

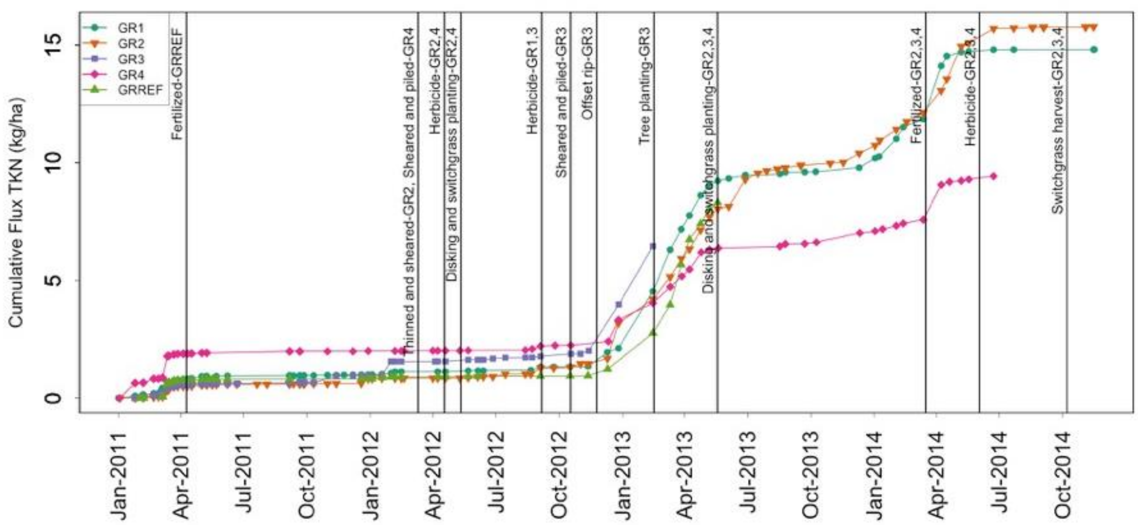

Figure 2.17. Cumulative load (kg ha^{-1}) of total Kjeldahl nitrogen (TKN) over time (2011-2014) for all watersheds in Greene County, Alabama.

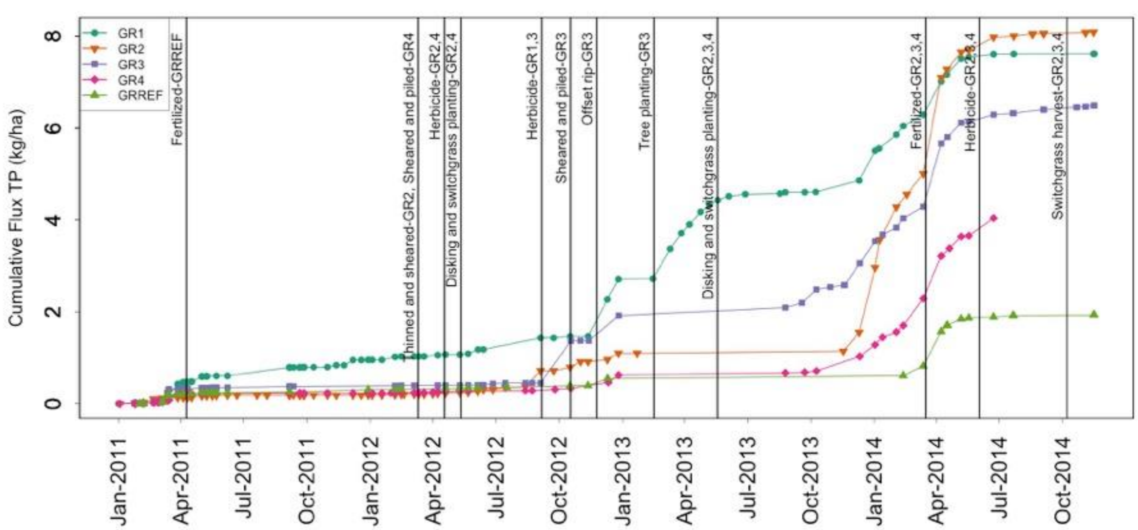

Figure 2.18. Cumulative load (kg ha^{-1}) of total phosphorous (TP) over time (2011-2014) for all watersheds in Greene County, Alabama.

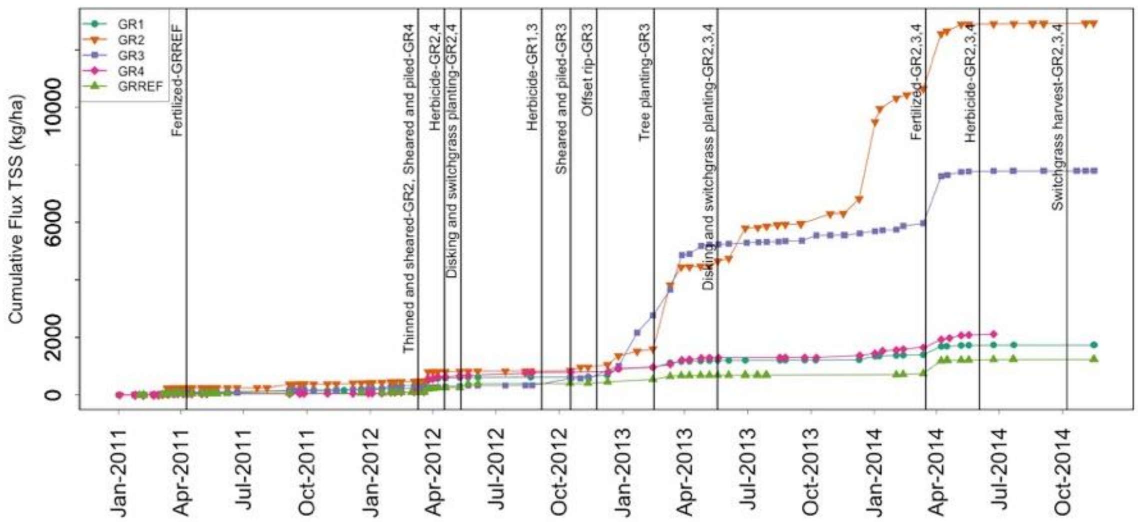

Figure 2.19. Cumulative load (kg ha^{-1}) of TSS over time (2011-2014) for all watersheds in Greene County, Alabama.

Cumulative load over time plotted together with the hydrograph for each water quality constituent in each watershed are shown in the Appendix G. An example of cumulative NO_3^--N export over time from watershed GR3 is shown in Figure 2.22. This type of plot also includes the hydrograph for that watershed, the timing of operations (labeled on vertical lines) and the timing of a water sample collection by the autosampler (black tick marks, i.e., “rug” along bottom of plot). Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler. In order to more accurately assess whether changes in material exports were due to operations rather than flow events, cumulative loads (kg ha^{-1}) were plotted as (1) a function of the cumulative volume of each watershed and as (2) a function of the cumulative load of the control watershed (in the event that extreme rainfall patterns caused a bias on the first type of plot). Slope changes suggest changes in material export (Peu et al., 2007; Brown et al., 2013). That is, a slope increase suggests an increase in the export of a constituent, a constant slope indicates no change, and a slope decrease indicates a decrease in the export of a constituent. These plots also compare relative differences among watersheds. The paired watershed design with the control watershed (without operations) allowed for an assessment of the impacts of operations on the treatment watersheds. The following sections discuss the impacts of operations on each water quality constituent (except PO_4^{3+}-P due to lack of earlier data) within each treatment watershed from the beginning of the water quality monitoring period, 2011, through 2014 using the plotting methods described previously. Larger images of the plots below are available in Appendix G. The discussion will focus on impacts the operations during years 4 and 5, specifically disking and switchgrass planting during year 4 (2013) and fertilization during year 5 (2014).

Total suspended solids

The effects of land operations were most apparent in changes in TSS export given that these operations (i.e., harvesting, offset rip, disking) cause a disturbance to and loosening of the soil surface, thus increasing erosion, as observed in similar studies (Lowrance et al., 2007). Cumulative TSS load as function of cumulative volume showed that early site preparation activities caused increases in TSS from both intercropped sites. Disking and switchgrass planting did cause an increase in the TSS export for the intercropped-thinned site (GR2), but not the intercropped-replanted (GR3) or switchgrass only site (GR4), thus indicating that this increase was not caused by that particular operation. There is no clear explanation why GR2 would have the greatest cumulative load of TSS, as this site was thinned and intercropped;

whereas, GR3 was clearcut and intercropped. GR4 was also clearcut and planted with switchgrass only, but that watershed did not exhibit such dramatic increase in TSS export. Field observations suggest that the buffer areas adjacent to the streams, or stream management zone, may have differing capacities for trapping sediment before it reaches the stream. Studies have shown the importance of the stream management zone on water quality (Witt et al., 2013; Hughes, 2016; Osborne and Kovacic, 1993). Another explanation could be that the thinning of the pine produced more mobile litter on the GR2 site, compared with clearcutting and piling in windrows, where the material was made less mobile from being compacted in windrows on the GR3 site.

The tree planting (only on GR3) had a relatively large effect on TSS export from GR3. Looking at cumulative load as a function of cumulative load of the control, the curves for both intercropped watersheds (GR2, GR3) lie well above the 1:1 line, indicating that these watersheds export much greater rates of TSS compared with the control. Since the steep increase from GR3 occurred almost simultaneously with the disking and switchgrass planting, this increase was likely linked to the earlier operation, tree planting. Fertilization did not have a prominent impact on TSS export from any of the watersheds.

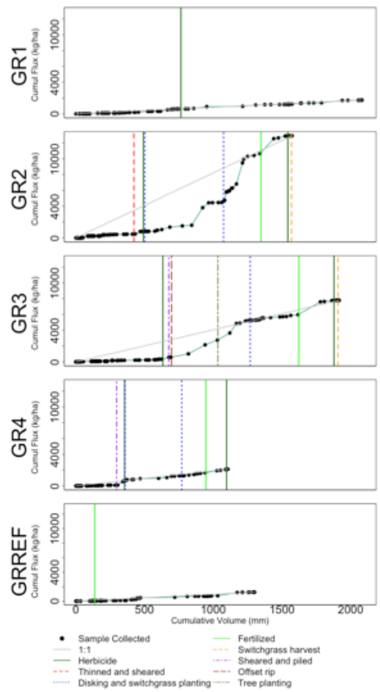

Figure 2.20. Cumulative total suspended solids (TSS**)** load (kg ha^{-1}) as a function of cumulative flow volume (mm) of each watershed (GR1, GR2, GR3, GR4, GRREF) during Jan 2011 to Nov 2014.

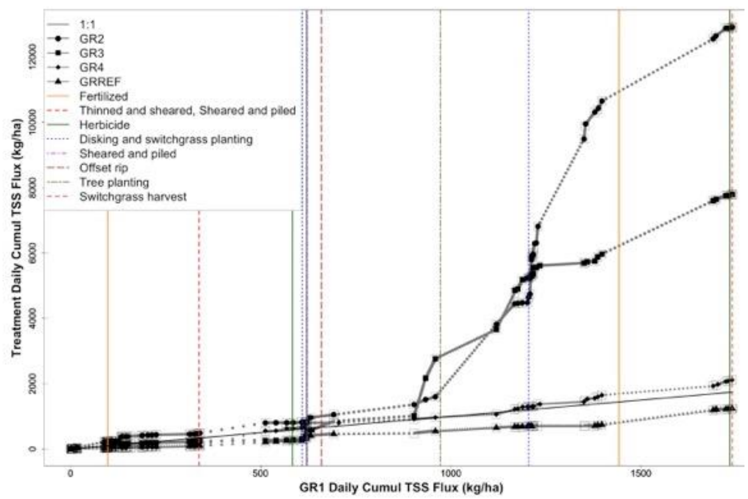

Figure 2.21. Cumulative load of TSS from each of the watersheds as a function of cumulative load of TSS from the control watershed (GR1) in Greene County, Alabama from 2011 to 2014.

NO_3^--N

Both plot types show that earlier site preparation activities caused an increase in NO_3^--N export from the intercropped-replanted (GR3) and switchgrass (GR4) sites. From the cumulative load versus cumulative volume plots, disking and switchgrass planting did not appear to increase NO_3^--N export from the intercropped-replanted (GR3) and switchgrass (GR4) sites. Cumulative NO_3^--N load as a function of the control load showed that the intercropped-thinned site (GR2) slope remained relatively consistent pre- and post-disking and switchgrass planting; however, the intercropped-replanted (GR3), showed a steep slope increase following disking and switchgrass planting. This increase could be attributed to a priming effect in which the soil disturbance causes an increase in aerobic microbial activity as previous belowground soil organic matter (i.e., organic nitrogen) is now exposed to the atmosphere and mineralization rates increase (Jenkinson and Rayner, 1985). Following fertilization, the cumulative load of NO_3^--N from the intercropped-thinned site (GR2) actually decreased with respect to the control and there was no drastic change for the intercropped-replanted site (GR3).

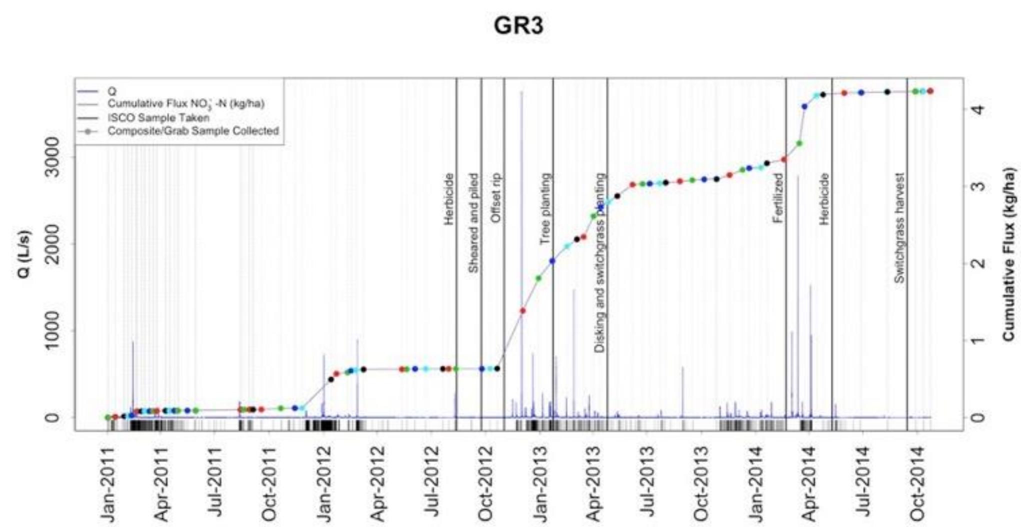

Figure 2.22. Cumulative NO_3^--N load over time (Jan 2011 to Nov 2014) in watershed GR3, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

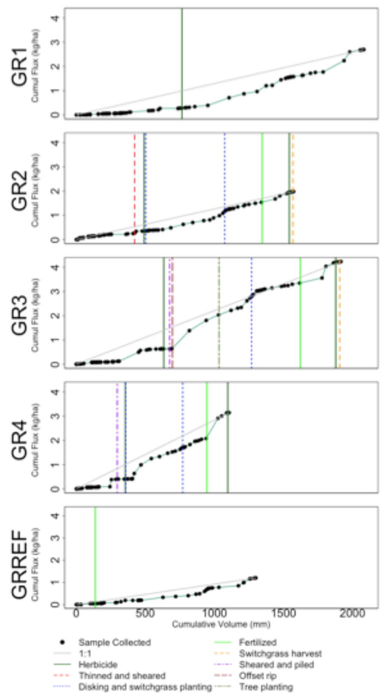

Figure 2.23. Cumulative nitrate-nitrogen (NO_3^--N**)** load (kg ha^{-1}) as a function of cumulative flow volume (mm) of each watershed (GR1, GR2, GR3, GR4, GRREF) during Jan 2011 to Nov 2014.

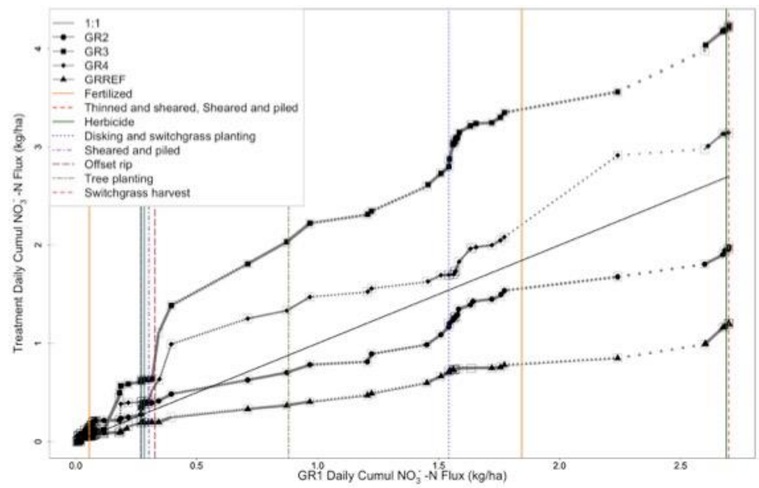

Figure 2.24. Cumulative load of nitrate-nitrogen (NO_3^--N) from each of the watersheds as a function of cumulative load of NO_3^--N from the control watershed (GR1) in Greene County, Alabama from 2011 to 2014

NH_4^+-N

Early site preparation activities caused a steep increase in NH_4^+-N export from all treatment watersheds, evident in both plot types. With cumulative NH_4^+-N load versus volume, there are slight increases following disking and switchgrass planting for both intercropped sites (GR2 and GR3); these increases become more pronounced when plotting cumulative NH_4^+-N load versus the control load. These increases in NH_4^+-N export can be attributed to the priming effect in which the soil disturbance caused an increase in microbial activity which increased mineralization rates (Jenkinson and Rayner, 1985). While there was no apparent increase observed from the switchgrass site (GR4) following disking and switchgrass planting when plotted versus volume, there was actually a slight increase when plotted versus control load. Although GR2, GR3, and GR4 underwent the same operation of disking and switchgrass planting at the same time, both intercropped sites exhibited more pronounced increases in NH_4^+-N export. This difference may be explained by differences in microbial communities that develop within a more biologically diverse environment (i.e., two crops versus one crop). Additionally, at this point, the switchgrass was not established in GR4 yet as this was the second attempt to get the switchgrass to establish; meanwhile, there were trees already planted in both the intercropped sites, thus supporting a more developed microbial community, thus increasing mineralization rates (Zak et al., 2003; Hooper and Vitousek, 1998; Lavelle et al., 1997). There were no major increases post fertilization.

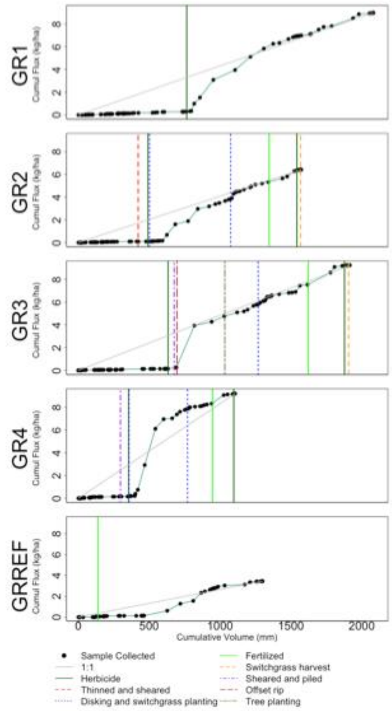

Figure 2.25. Cumulative ammonium-nitrogen (NH_4^+-N) load (kg ha^{-1}) as a function of cumulative flow volume (mm) of each watershed (GR1, GR2, GR3, GR4, GRREF) during Jan 2011 to Nov 2014.

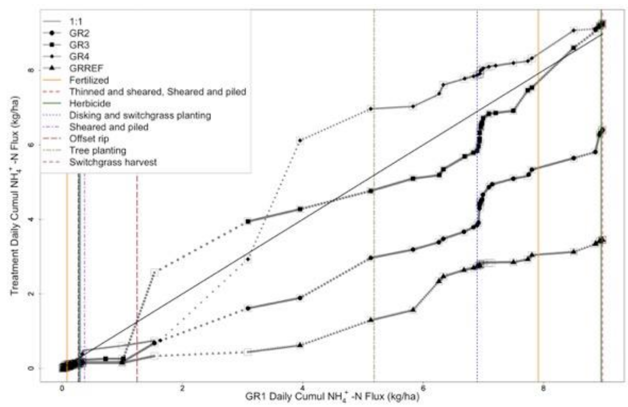

Figure 2.26. Cumulative load of ammonium-nitrogen (NH_4^+-N) from each of the watersheds as a function of cumulative load of NH_4^+-N from the control watershed (GR1) in Greene County, Alabama from 2011 to 2014.

Total Kjeldahl nitrogen

Early site preparation activities caused a steep increase in TKN export from all watersheds, evident in both plot types. Again, this increase may be attributed to a priming effect in which microbial activity increases as soil disturbance increases the lability of soil organic matter (Jenkinson and Rayner, 1985). Similar to the NH_4^+-N export patterns, disking and switchgrass planting had a prominent impact on TKN export from the intercropped-thinned site (GR2), but only a slight effect on the switchgrass only site (GR4), which again may be attributed to greater plant diversity being correlated with increased microbial activity, thus increased mineralization rates (Zak et al., 2003; Hooper and Vitousek, 1998; Lavelle et al., 1997). There was no apparent impact on TKN export immediately following fertilization, although there may have been a delayed effect as a steep increase occurred several months later in the intercropped-thinned (GR2), which would also be attributed to a priming effect (Jenkinson and Rayner, 1985). For GR3, TKN data was missing during the post-treatment years (Mar 2013 to Nov 2014).

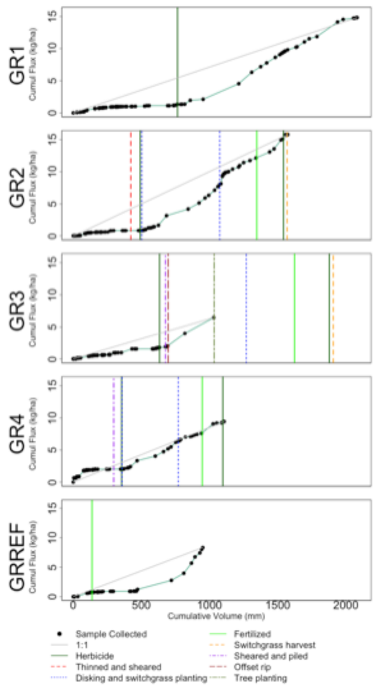

Figure 2.27. Cumulative total Kjeldahl nitrogen (TKN) load (kg ha^{-1}) as a function of cumulative flow volume (mm) of each watershed (GR1, GR2, GR3, GR4, GRREF) during Jan 2011 to Nov 2014.

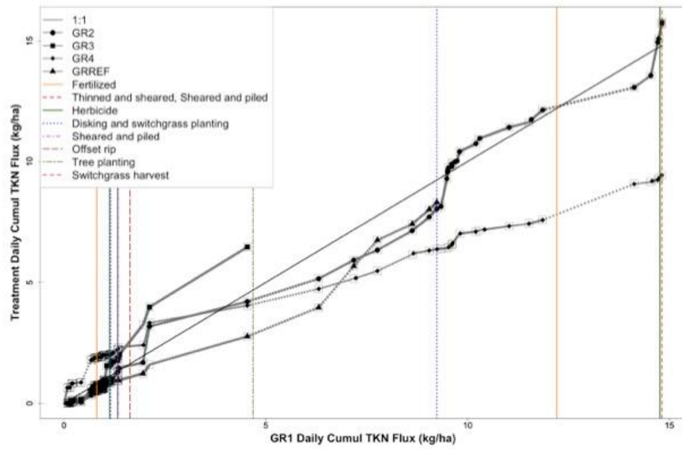

Figure 2.28. Cumulative load of total Kjeldahl nitrogen (TKN) from each of the watersheds as a function of cumulative load of TKN from the control watershed (GR1) in Greene County, Alabama from 2011 to 2014.

Total phosphorous

Disking and switchgrass planting perhaps had the most dramatic impact on TP, with sharp increases in TP export from all treatment watersheds following this operation. However, the steep slope increase may seem more pronounced because of the lack of data prior to disking and switchgrass planting. While slope is dramatically steep immediately following disking and switchgrass planting, export remains relatively constant post-fertilization. The greatest increase was from the intercropped/thinned watershed (GR2), which also had the greatest increase in TSS export following that operation. Therefore, the higher TP loads are likely associated with the geochemistry and erodibility of the sediments in a particular watershed rather than being directly caused by a specific operation (Grobler and Silberbauer, 1985; Vighi et al., 1991). Overall, the TP loads from all the watersheds, including the control were high (0.93 - 2.99 kg ha^{-1} yr^{-1} from the control) compared to other reported values which were generally <0.1 kg ha^{-1} yr^{-1} (Hobbie and Likens, 1973; Dillon and Molot, 1997; Kaila et al., 2014). The TP loads may be higher in these watersheds due to the P sorption capacity of the soils; soils lacking mineral soil components (i.e., Al and Fe) tend not to adsorb P effectively (Patrick and Khalid, 1974; Richardson, 1985; Bruland and Richardson, 2005). Given the substantial increase in TP following disking and switchgrass planting and the relatively greater values compared to other forested watersheds, this operation may have a more lasting impact on TP export.

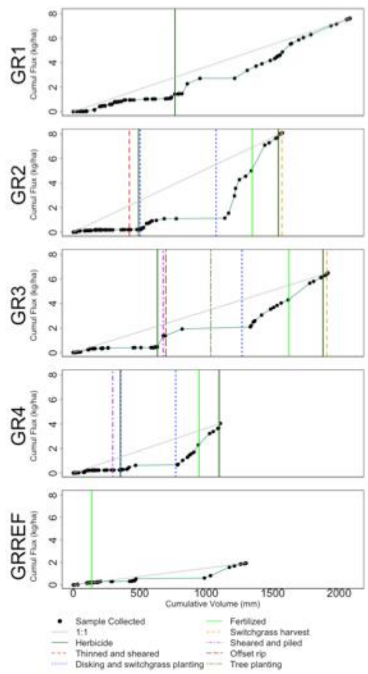

Figure 2.29. Cumulative total phosphorous load (kg ha^{-1}) as a function of cumulative flow volume (mm) of each watershed (GR1, GR2, GR3, GR4, GRREF) during Jan 2011 to Nov 2014.

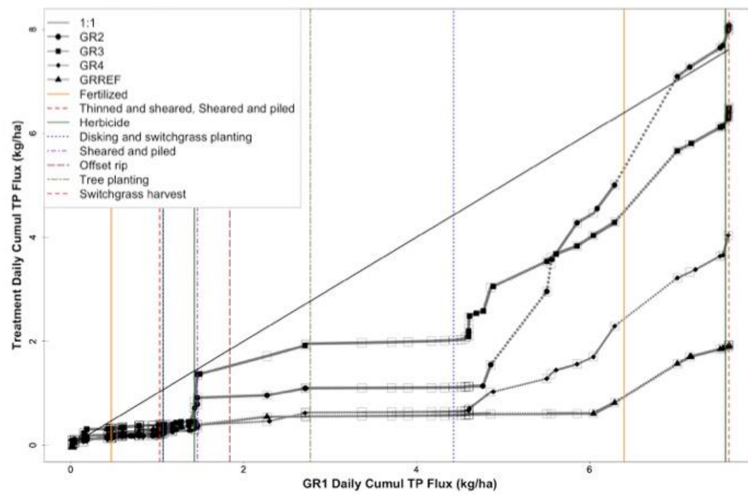

Figure 2.30. Cumulative load of total phosphorous (TP) from each of the watersheds as a function of cumulative load of TP from the control watershed (GR1) in Greene County, Alabama from 2011 to 2014.

Dissolved organic carbon

The disking and switchgrass planting occurred during low flow conditions so the operation does not appear to cause a prominent increase in the cumulative DOC load when plotted over time. Fertilization appeared to cause a greater increase in cumulative load of DOC, but this increase was biased by the large flow events that followed this operation. Only in GR2, the cumulative load as a function of cumulative volume of flow (Figure 2.27) shows a more prominent change in slope post disking and switchgrass; however, there is not a change in slope post fertilization. For all the treatment watersheds, cumulative DOC load versus the load from either the control or mature reference pine verified that disking and switchgrass planting caused an increase in DOC and that fertilization had no effect on DOC export. Increases in DOC due to similar forest disturbances have been reported by others (Hobbie and Likens, 1973; Tate and Meyer 1983; Johnson et al., 1995). Overall, the changes in DOC exports were non-threatening and remained within the normal range of DOC exports from forests (Dillon and Molot, 1997; Hobbie and Likens, 1973).

On all treatment watersheds, there was physical soil disturbance shortly after the 2012 herbicide application so that it is difficult to attribute the DOC increase to one particular operation. On watersheds GR2 and GR4, disking and switchgrass planting occurred shortly after herbicide application; on watershed GR3, trees were sheared and piled in windrows shortly after herbicide application. When load is plotted as function of either the control or mature reference pine load, watershed GR3 showed a steep increase in DOC almost simultaneously with the shearing operation, which occurred about a month after herbicide application. There is strong evidence that the physical soil disturbance had a more substantial impact on DOC export than the herbicide application. On GR3 when the disking and switchgrass planting occurred, there was another sharp increase in DOC when plotted as a function of GRREF and at least a slight increase when plotted as function of the control, but no increase after the second herbicide application; similarly, there were steep increases in DOC export following disking and switchgrass plantings on GR2 and GR4, but no change following the second herbicide application. Yamashita et al. (2011) identified DOC as being mostly from soil-derived sources in forested headwater streams which would support an increase in DOC export following soil disturbance such as disking.

Still the increase in DOC following the 2012 herbicide application may be explained by the increase in surface litter that ensues, which provides labile material (Meyer et al., 1998). The effect of herbicide may have been greater for GR3, compared with GR2 and GR4 because of the density and maturity of vegetation present at the time of herbicide application and the seasonal timing of application. At the time of herbicide application on GR2 (April 2012), the previous stand had been cleared and trees planted more recently in GR2 compared with GR3 (September 2012). Additionally, the GR2 stand was thinned and sheared just prior to herbicide application and a post-emergent herbicide was sprayed as a preventative measure. In contrast, GR3 was herbicided to remove competing hardwoods and understory from an older stand (6-year old trees), which had no other operations for six years prior. Therefore, this herbicide application may have resulted in availability of more labile organic matter compared with the other watersheds, evident in the increase in DOC export. Additionally, the season in which the herbicide was applied may have affected the differences in DOC export, given that DOC derived from leaf litter tends to be greater in autumn compared to spring (Meyer et al., 1998).

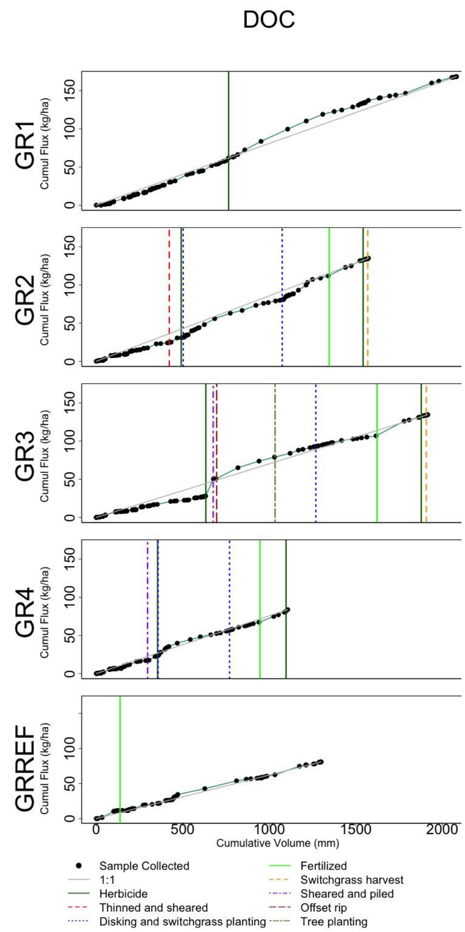

Figure 2.31. Cumulative dissolved organic carbon (DOC) load (kg ha-1) as a function of cumulative flow volume (mm) of each watershed (GR1, GR2, GR3, GR4, GRREF) during Jan 2011 to Nov 2014.

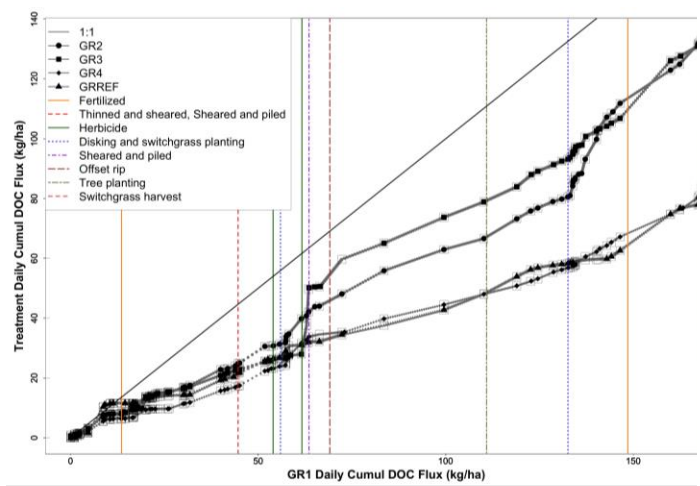

Figure 2.32. Cumulative load of DOC from each of the watersheds as a function of cumulative load of DOC from the control watershed (GR1) in Greene County, Alabama from 2011 to 2014.

PO_4^{3+}-P

There was little or no PO_4^{3+}-P data for the time period pre-disking and switchgrass planting; however, both intercropped sites (GR2, followed by GR3) exported a much greater amount of PO_4^{3+}-P relative to the control and other watersheds (Figure 2.34). Although the intercropped and the switchgrass only site underwent similar operations, there was much less PO_4^{3+}-P export from the switchgrass only watershed. Again, this difference between the intercropped sites and the switchgrass only watershed may be explained by differences in microbial communities that develop within a monoculture versus an intercropped system. The switchgrass also established later as there was second attempt to get the switchgrass to establish; while there were at least trees already planted in both the intercropped sites, thus a more mature plant community (i.e., greater carbon source) enabling the microbial community to solubilize P more readily (Hameeda et al., 2006; Patel et al., 2008).

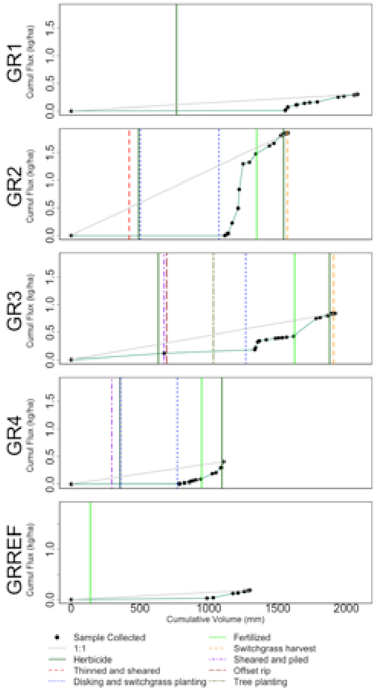

Figure 2.33**.** Cumulative PO_4^{3+}-P load (kg ha^{-1}) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

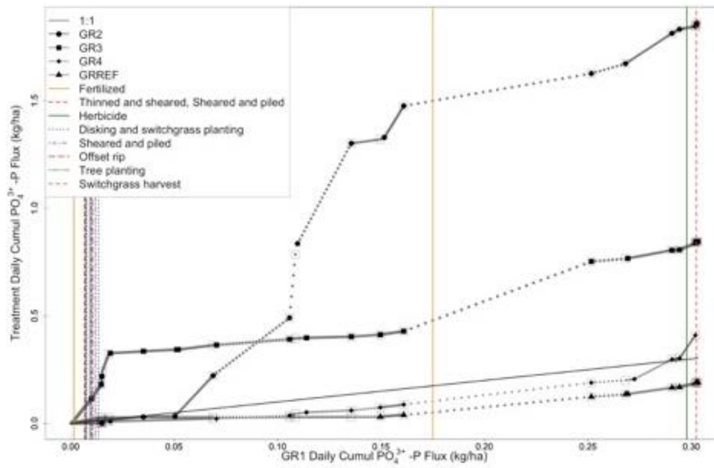

Figure 2.34. Cumulative load of PO_4^{3+}-P from each of the watersheds as a function of cumulative load of PO_4^{3+}-P from the control watershed (GR1) in Greene County, Alabama from 2011 to 2014.

Overall, disking and switchgrass planting had a greater impact on the cumulative load of water quality constituents than fertilization. The disking and switchgrass planting is a rather intensive operation, in an effort to get the switchgrass seed to germinate. However, this operation typically only has to be done once and then the switchgrass will establish. Once the switchgrass is established, the other major operation that will occur is harvesting (annually or bi-annually). Due to overturning of the soil associated with disking, there may be an increase soil aeration, increase in soil temperature as lower layers are exposed to sunlight, and an increase in the infiltration rate. Some processes that may be at play here include mineralization, where the organic nitrogen in the soil is being transformed into mobile forms of NH_4^+-N and NO_3^--N.

2.5 Conclusions

There was evidence of effects on both hydrology and water quality from intercropping switchgrass with pine, particularly due to early site preparation activities and disking and switchgrass planting. With regards to hydrology over the five-year study period, there was a change in the watershed yielding the greatest cumulative flow after the treatment period, from the control to the intercropped, replanted site. Additional evidence of effects on hydrology was revealed by the steep increase in cumulative flow shortly after disking and switchgrass planting for all treatment watersheds when plotted as a function of control cumulative flow. Also, considering log daily cumulative flow of each of the treatment watersheds as a function of the control, there were more indications of treatment impacts on hydrology. Correlations (R^2) between treatment and control flow decreased during year 4 following treatment, but were the greatest during year 5, indicating a short-term effect on hydrology from this perspective. Comparing changes in slopes of these regressions, there were significant differences detected for the intercropped replanted and switchgrass sites. For the intercropped replanted site, the slope during year 4 was significantly lower than year 1. For the switchgrass only site, the slope during years 4 and 5 were significantly different from years 1 and 2. Additionally, the slope of the mature pine reference stand during year 5 was significantly lower than years 1 and 2, indicative of flow differences caused by differences in pine maturity and density. Comparing treatment replicates between Alabama and Mississippi,

Regarding water quality impacts, following site preparation activities, there were increases in TSS loads from both intercropped sites, increases in NO_3^--N from the intercropped-replanted and switchgrass only sites, increases in NH_4^+-N, TKN, and TP from all treatment watersheds. Following disking and switchgrass planting, both intercropped sites exhibited steep increases in the exports of DOC, NO_3^--N, and TP. The intercropped-thinned site also exhibited steep increases in the cumulative loads of TKN and TSS following disking and switchgrass planting, with particularly high increases in TSS export. Disking and switchgrass planting on the switchgrass watershed showed impacts on some nutrient exports including NO_3^--N and TKN, but did not have an effect on TSS export.

We hypothesize that a portion of the increases in TSS export following operations were caused by the operation-induced soil disturbance and associated increase in erosion susceptibility, but we cannot exclusively attribute these high TSS exports to treatment impacts due to the unique conditions of the stream management zone (i.e., riparian zone) within these watersheds. Given that TP exports follows patterns similar to TSS export, TP loads are likely associated with the geochemistry and erodibility of the sediments in a particular watershed rather than being directly caused by a specific operation. Increases in DOC were attributed to soil-derived sources given that increases occurred after operation-induced soil disturbances. Increases in nutrient exports (i.e., NO_3^--N, NH_4^+-N, TKN, PO_4^{3+}-

P), were explained by a priming effect causing an increase in mineralization rates. Increases in some nutrients (e.g., NH_4^+-N, PO_4^{3+}-P) from both intercropped sites, but not the switchgrass only site, were attributed to greater microbial diversity which developed in a more biologically diverse environment on the intercropped sites, compared with the switchgrass only site, thus supporting greater mineralization rates on the intercropped sites. There is strong evidence that the physical soil disturbance had a more substantial impact on DOC export than the herbicide application. There were no apparent fertilization effects. Overall, cumulative nutrient exports remained relatively low, although TSS and TP exports became substantially greater for both intercropped sites. Therefore, operations associated with intercropping may have a more lasting impact on TSS and TP exports, but relatively short-term impacts on other nutrient exports.

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CHAPTER 3: In situ ultraviolet-visual spectroscopy to obtain high temporal resolution water quality dynamics within coastal plain watersheds with Loblolly Pine (*Pinus taeda*) and Switchgrass (*Panicum virgatum*) intercropping in North Carolina

3.1 Introduction

The recent availability of continuous optical sensors for water quality has opened the possibility to obtain high frequency water quality data which can reveal concentration dynamics that were not available until now (e.g., Langergraber et al., 2003; Rieger et al., 2006; Etheridge et al., 2013). This is potentially a true revolution as it will fundamentally change how water quality is collected and analyzed, has the potential to dramatically lower uncertainties on concentrations and loads, and reveal undetected effects, nature and source of biogeochemical processes.

With traditional infrequent time-based sampling methods, there is high probability to miss or misrepresent the transport of nutrients and materials in streams and rivers that occur following rainfall events. As most nutrients and materials transport occurs in this disproportionally small portion of the time, misrepresenting concentration values and their dynamics during flow events is at the source of the large uncertainties on nutrient and material load in watersheds (e.g., Birgand et al., 2010; Moatar et al, 2012).

However, these instruments are relatively new and a very limited return on experience is currently available for guidance. In particular, it is unclear whether these field spectrophotometers can be used in watersheds of the lower coastal plain, where reduced conditions in water are common. Etheridge et al. (2014, 2015) and Grayson and Holden (2016) have shown that these instruments are subject to optical fouling, likely due to Fe and Mn precipitation on the optics. Various ways to minimize lens fouling have been proposed. In salt rich coastal and sea-waters, passive and active electrolysis can be used to reduce fouling on the optics (respectively, Tait et al., 2015, and Xue et al., 2015). Manufacturers usually offer automatic scrubbers or sudden release of compressed air. In the latter case, however, the sudden exposure of reduced water to a burst of oxygen has been shown to increase chemical fouling (Etheridge et al., 2014). One solution proposed by Etheridge et al. (2014) is to remove the instrument from the target in-situ environment (e.g., stream) and pump water to the instrument to reduce the exposure time of the optics to the water, and to quickly rinse the lenses with clean tap water on a programmed timed basis after each water sample measurement. Despite these efforts and although reduced, Etheridge et al. (2014) found that in a salt marsh of North Carolina, fouling was still significant after two-week deployments and that manual scrubbing and lens cleaning using a chemical solvent (i.e., 2% HCl) was required.

Etheridge et al. (2014) and Birgand et al. (2016) have shown that it was possible to use spectrophotometers to measure concentrations of parameters not known to absorb light. These authors have essentially proposed to create water quality rating curves where the spectrophotometer absorbance data are used as index data from which concentrations of a suite of parameters can be calculated using a rating curve, itself generated using Partial Least

Square Regression (PLSR) statistical methods (Etheridge et al., 2015). This method also serves to further correct for the optical fouling. It is unclear whether the guidelines proposed by these authors do apply, and/or by how much they might differ in coastal freshwater watersheds where reduced conditions in soil and water prevail.

The objectives of this chapter are thus to document the potential challenges encountered while using these instruments in this part of the world, present the solutions found to address these challenges, and show the insight gained from such instruments on the nutrient and sediment dynamics in forested coastal plain watersheds in North Carolina.

3.2 Hypotheses

The goal of this work was to assess the ability and performance of *in situ* spectrophotometers to measure water quality on a continuous high frequency basis in artificially drained lower coastal plain watersheds. Given that organic matter and NO_3-N contribute to absorbance, the covariance between absorbance and the concentration of various water quality parameters can be tested using partial least squares regression. Partial least squares regression was hypothesized to be an effective method for correlating continuous absorbance data with discrete laboratory water quality measurements, including DOC, NO_3-N, and TDN, and to correct for anticipated fouling. Showing how the absorbance data can be correlated with particular concentrations as well as the associated problems are necessary to enrich guidance in the use of such instruments and improve the methods used to interpret the absorbance data.

3.3 Methods

Site description

In Carteret County, North Carolina (34°48’, 76°42), in the lower coastal plain, four watersheds were instrumented with continuous water quality sensors (details below). These four watersheds are part of a project designed to measure the hydrology and water quality impacts of switchgrass intercropping in managed forests. The four watersheds instrumented include a traditionally managed pine stand, planted in 2010 (D0); a young pine stand with switchgrass intercropped (D1) planted the same year; a reference mature, thinned pine stand planted in 1996 (D2); and switchgrass only seeded in 2011 (D3) (Figure 3.1, Table 3.1). All four watersheds are located on very flat (slope <0.02%) coastal plain soils (soil type: Deloss), artificially drained by open ditches installed 100 m apart, and where the typical roughness of soil surface in forested settings creates enough surface storage to almost eliminate completely surface runoff. Trees were removed (clear cut) in 2009 from watersheds D0, and D1, and seedlings were planted on these three sites in 2010. Switchgrass was sown in D3 in years 2011, and again in 2012 as switchgrass did not establish well the first year. The older reference pine stand (D2) was planted in 1996 and thinned in 2009. An Aborite®CUF 39-9-0 fertilizer was applied to sites D1, D2, and D3 on June 3 and 4, 2014 (nitrogen application rates are given in Table 3.2).

Figure 3.1. Plan view of treatment watersheds in Carteret County, North Carolina.

Table 3.1. Site characteristics and operations performed on watersheds in Carteret County, North Carolina.

Watershed	**Land Cover**	**Area (ha)**	**Tree birth year**	**Switchgrass planted**	**Fertilizer applied**
D0	Young pine	24.0	2010	NA	NA
D1	Young pine/switchgrass intercropped	24.7	2010	Aug 2011 Apr 2012	June 4-5 2014
D2	Mid-rotation pine	23.6	1996	NA	June 4-5 2014
D3	Switchgrass	26.8	NA	Aug 2011 Apr 2012	June 4-5 2014

Table 3.2. Nitrogen application rates in Carteret County, North Carolina.

Watershed	Amount N applied ($lbs\ ac^{-1}$)	Amount N applied ($kg\ ha^{-1}$)
D0	NA	NA
D1	58.5	65.6
D2	156	175
D3	58.5	65.6

Hydrology data

For each watershed, upstream and downstream stages were measured every 12 minutes using In-situ® 500 pressure transducers, one upstream and one downstream of the weir, and data logged using a Campbell Scientific® CR200 logger. Flow rates at the watershed outlet were estimated using standard weir equations for 120° v-notch weir (equations in Appendix I). Water table data was measured hourly at two wells (~3 m deep), located at the midpoint between the lateral ditches, one closer (1/4 distance from front to back of plot) and one further from the main canal (3/4 distance from front to back of plot). A single HOBO® tipping bucket rain gauge collected 15-minute rain data for all four watersheds. Weather data was collected using a HOBO® weather station.

Instrumentation

Water quality data was collected for approximately one year (Nov 12 2013 to Nov 30 2014) from each of the four watersheds, including continuous (15 min) absorbance spectra data and discrete (14 h interval) water samples. At the outlet of each watershed, water was pumped from the canal every 15 minutes into a spectrophotometer probe (s::can spectro::lyser™, s::can Measuring Systems, Vienna, Austria) to a flow-through cuvette (Figure 3.2). The s::can spectro::lyser™ (s::can) was placed outside of the canal with water pumped to it in order to reduce lens fouling (i.e., buildup of both chemical and biological films), which had been observed in a previous study (Etheridge, 2013). The s::can was housed inside a plastic encasement to reduce the impact of sunlight on the absorbance measurement.

The s::can with a 5mm measurement pathlength obtained an absorbance spectrum for a range of wavelengths (210 different wavelengths from 220 to 742.5 nm at 2.5 nm intervals) passing through the water sample. The water sample was held within a plastic sleeve encasing the measurement path long enough for the s::can to take a measurement (approximately 20 sec). The solar-powered automatic pumping/rinsing system was controlled by an Arduino Uno microcontroller (Arduino, Ivrea, Italy) which triggered a sequence of events upon a 12V signal from the spectrophotometer, originally designed to trigger the compressed-air antifouling. Every 15 minutes a peristaltic pump (obtained from old Sigma® autosamplers), pumped water to the s::can probe fitted with an overflow sleeve. Pump time was long enough to rinse the sleeve at least 5 times its volume. Several seconds after pumping had stopped, the probe took a measurement, after which a valve located below the sleeve opened to drain water from the sleeve. The lenses were then rinsed with tap water stored in a 38 L tank using a windshield washer pump for 3-5 seconds. The polarity at the peristaltic pump was then reversed using an H-bridge to purge water left in the sleeve and in the pump tubing, back to the canal. More details of the pumping system can be found in Etheridge (2013).

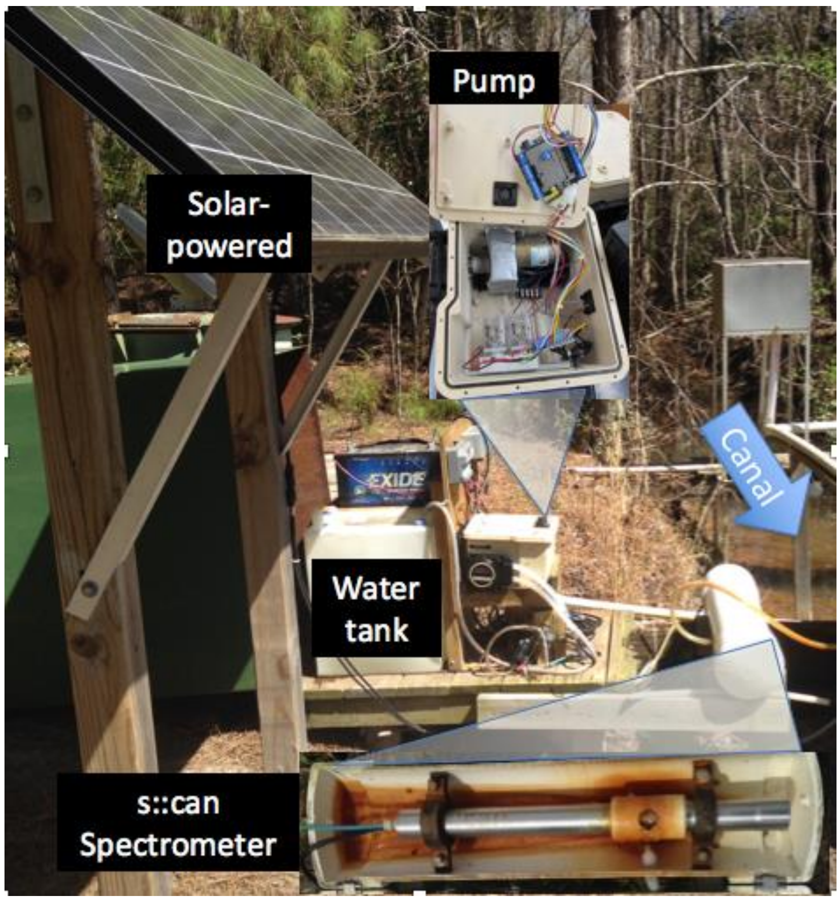


Figure 3.2. Example of setup of data collecting instrument (s::can spectrophotometer) and pumping system at a watershed outlet (D2) in Carteret County, North Carolina.

Lens fouling and maintenance

Field servicing was set as biweekly (15 d), as the probe memory capacity would fill and the water tank empty within that time. Very significant optical fouling occurred within that time (details below), which required lens cleaning. Before cleaning the s::can, absorbance values were measured in air (ambient) and in DI water to assess the level of fouling that had accumulated over the past two weeks, with higher absorbance values in the UV range indicating greater fouling. After measuring the absorbance of air first, the sleeve surrounding the lenses was filled with DI water and absorbance measured. The sleeve was then removed, DI water drained, and the s::can cleaned with a cotton swab soaked in 2 or 5% HCl used to scrub and allowed to set for a period of time (approximately 3 to 20 min depending on severity of fouling) on the lenses, followed by rinsing with DI water and drying with a cloth. The absorbance spectra of air and DI water were then retaken post-cleaning to ensure that these absorbance values had returned to initial values measured at the time of installation. If needed, the cleaning process was repeated until acceptable absorbance values were obtained. At times when the fouling was particularly severe, a dilute surfactant (i.e., diluted Dawn® dish soap) was used to further clean the lenses.

Discrete data collection

To calibrate the probe, an automatic 24-bottle discrete sampler collected canal water samples (~900 mL) every 14 hours (no flow conditions were possible). These discrete samples were non-acidified in order to be comparable to measurements taken by the s::can and used for calibrating s::can measurements. In order to assess any potential degradation effects of the discrete samples, two grab samples (1000mL each) were also collected during the field servicing visit. One grab sample was left inside the discrete sampler at the site to observe degradation effects over the two-week period, while the other grab sample, along with the discrete samples, were put on ice in the field and stored at 5°C for future analysis. A paired T-test was used to detect if concentrations were significantly different after remaining in the discrete sampler in the field for two weeks.

Laboratory analysis

Of the original set of discrete samples collected in the field, a subset was selected for analysis based on the timing of events and corresponding patterns within the absorbance spectra obtained at each site. The high cost of laboratory analyses was one particular reason for limiting the number of samples analyzed, but also only a subset of the total set of samples collected was necessary for calibrating the s::can. The subset included samples for which the s::can detected some concentration increase/spike and also samples taken during flow events for which s::can data was missing. For the grab samples and selected discrete samples, 40 mL were filtered in the laboratory; approximately 12 mL were acidified with sulfuric acid and analyzed for total dissolved nitrogen (TDN) and DOC; a non-acidified, filtered 12 mL was analyzed for NO_3-N, ammonium (NH_4-N), and phosphate (PO_4-P). The unfiltered portion (~500 mL) was analyzed for total kjeldahl nitrogen (TKN) (Standard Methods 4500Norg B [1998]), total phosphorous (TP) (Standard Method 4500-P F [1998]), and TSS (Standard Methods 2540 D).

Table 3.3. Measured parameters of the two data acquisition methods.

Data Source	**Sampling Interval**	**Measurement Type**	**Measured Parameter**
s::can spectro::lyser™ spectrophotometer	15 min	Instantaneous	Absorbance, correlated with turbidity, NO_3-N, TOC, DOC
Automatic discrete sampler	14 h	Laboratory analysis	TSS, TKN, TP, TDN, DOC, NO_3^--N, NH_4^+-N, and PO_4^{3-}-P

Local calibration using Partial Least Squares Regression (PLSR)

The s::can software uses a global calibration (proprietary) to correlate absorbance spectra (fingerprint data) with various parameter concentrations including turbidity (NTUeq), NO_3-N (mg L^{-1}), total organic carbon (TOC, mg L^{-1}), and dissolved organic carbon (DOC, mg L^{-1}). These concentration values are output into a parameter (PAR) file by the s::can software using the global calibration. Ideally, these instruments would be able to provide reliable real-time continuous concentration data; however, lens fouling rendered these instrument-calculated concentrations unreliable. To create local calibrations, partial least squares regression (PLSR) was used to correlate absorbance spectra to concentrations from the discrete and grab samples. The various parameter concentrations obtained from each watershed was calibrated separately. PLSR is a chemometric technique that in this application reduces the dimension of absorption spectra measurements from hundreds of wavelengths to a smaller number of components, which have maximal correlation with nutrient concentrations. The PLSR components are used to describe the whole absorption spectrum, not to identify important wavelengths for use in a linear regression.

The pls package (Mevik et al., 2011) in the software R (R Core Team, 2013) was used to perform PLSR and develop calibrations for DOC, TDN, and NO_3^--N concentrations, following the procedure described in detail in Etheridge et al. (2014). Among all 15-min spectra, a subset of absorbance data was first generated corresponding to laboratory measured concentration data based on the time of the absorbance measurement and the time that the discrete sample was taken by the automatic sampler. From this set of data, PLSR correlated laboratory concentration data with corresponding raw spectral data using a large number of components (i.e., 20). The root mean square error of prediction (RMSEP) was plotted as a function of the number of components. Following Etheridge et al. (2014), the 'best' model for calibration was selected based as the one containing the least number of components at or near the minimum RMSEP, i.e., the smallest number of components where there is less than 1ess than 10% improvement in the RMSEP between two consecutive RMSEP values. Based on the selected model, continuous concentrations were predicted from the complete original absorbance spectrum. Once a final optimum PLSR model was selected, concentration values were predicted for a given absorbance spectrum.

The effort to limit fouling with the pumping and rinsing system came at the cost of mechanical and electronic failures which at times resulted in unintentional air measurements as no water was present between the lenses. Some of these readings corresponded to discrete sample measurements and had to be taken out of the calibration data set pool. For this purpose, a semi-automatic method was devised to identify these air measurements. The original DOC concentrations directly from the instruments were found to be good indicators of malfunctioning. They were imported into the AQUARIUS software (AQUARIUS, Aquatic Informatics™, Vancouver, British Columbia, Canada) and obvious outliers were 'cleaned' and removed of 'noise' (Figure 3.3, Figure 3.4). In the end, a second subset of the original fingerprint (absorbance) data, now containing no outliers corresponding to sampling malfunctioning, was correlated with the laboratory data corresponding to those times so that the PLSR calibration included only data when the s::can was functioning properly. This subset of the original data was used as the starting dataset for obtaining the final model. The poor quality of the initial results forced adding additional steps described in the Results and discussion section.

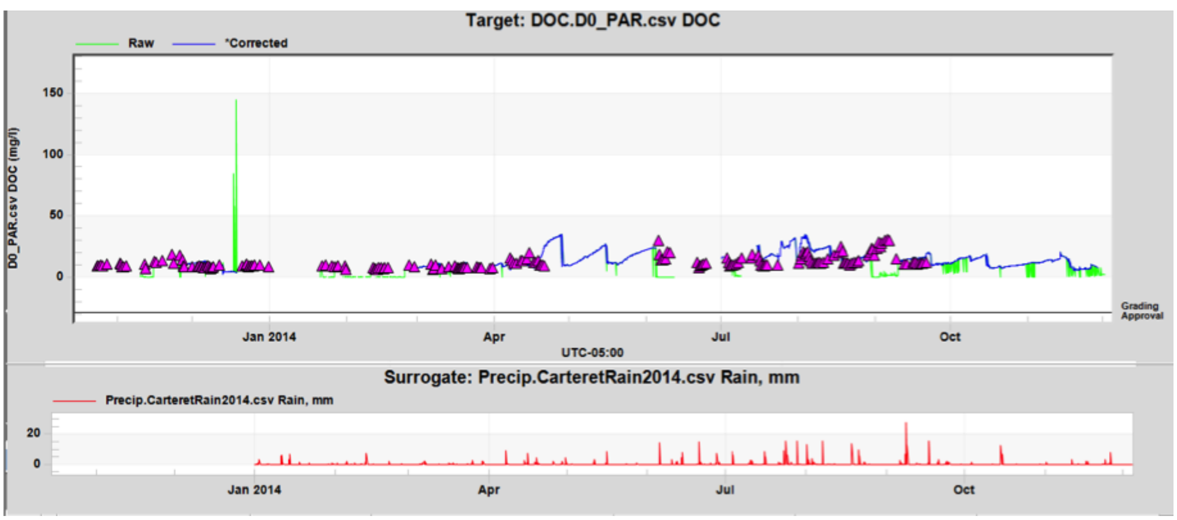


Figure 3.3. Screenshot of a corrected PAR file using AQUARIUS software for dissolved organic carbon (DOC) in watershed D0. The green colored data indicates the raw data that was removed. The blue colored data was exported as the cleaned PAR file. The pink triangle points are discrete measurements of DOC.

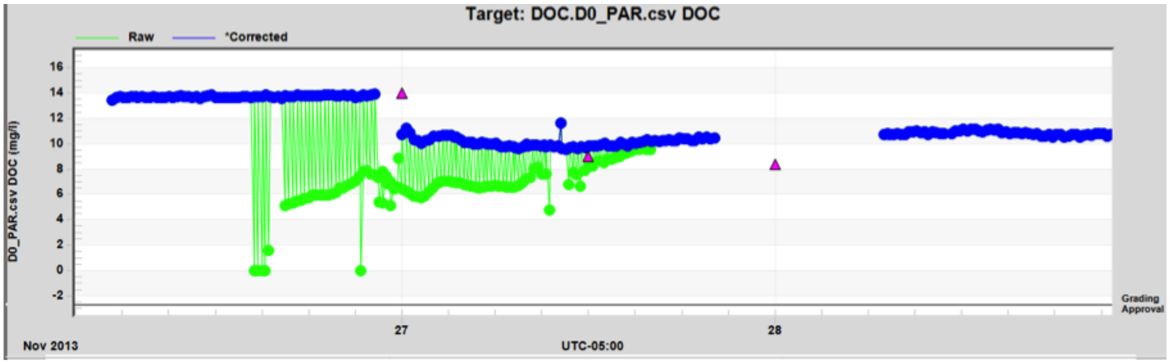


Figure 3.4. Zoomed screenshot of a section of a corrected PAR file using AQUARIUS software for dissolved organic carbon (DOC) in watershed D0. The green colored data indicates the raw data that was removed. The blue colored data was exported as the cleaned PAR file. The pink triangle points are discrete measurements of DOC.

3.4 Results and Discussion

Very high fouling observed for three of the watersheds

Despite the sampling scheme devised to minimize fouling, very significant fouling was observed at all sites (e.g., Figure 3.5), although less so at the D0 station (Table 3.4). Absorbance spectra in air and DI water are supposed to be at less than 10 m-1 for all wavelength values. On Figure 3.5, although in air and in DI water, absorbance values much greater than 10 can be observed, are highest in the UV range, and diminish sharply afterwards.

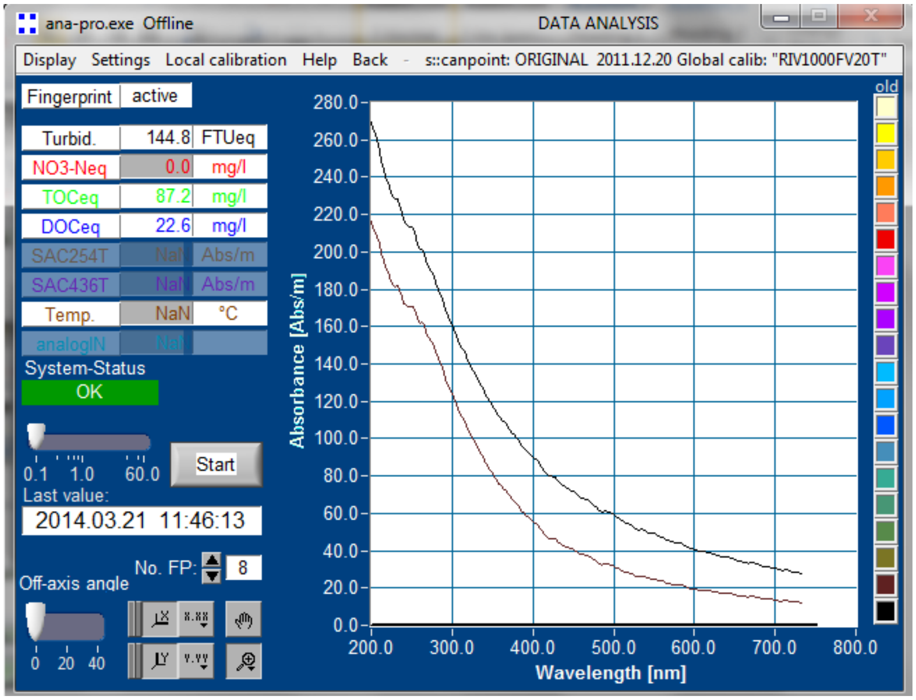


Figure 3.5. Screen shot of absorbance spectra in air (black line) and DI water (brown line) as given by the S::CAN software as a function of wavelength for watershed D2 after operating two-weeks in the field before cleaning optics during the spring (March 21, 2014).

Applying cotton swabs soaked in 2% HCl was efficient is abating the absorbance spectra, back to desirable levels described above. However, in the case illustrated in Figure 3.6, it took in March 21, 2014 at the D2 station, four trials of applying the solution onto the optics 5 min at a time, to obtain absorbance spectra that were ‘flat’ and within desirable values.

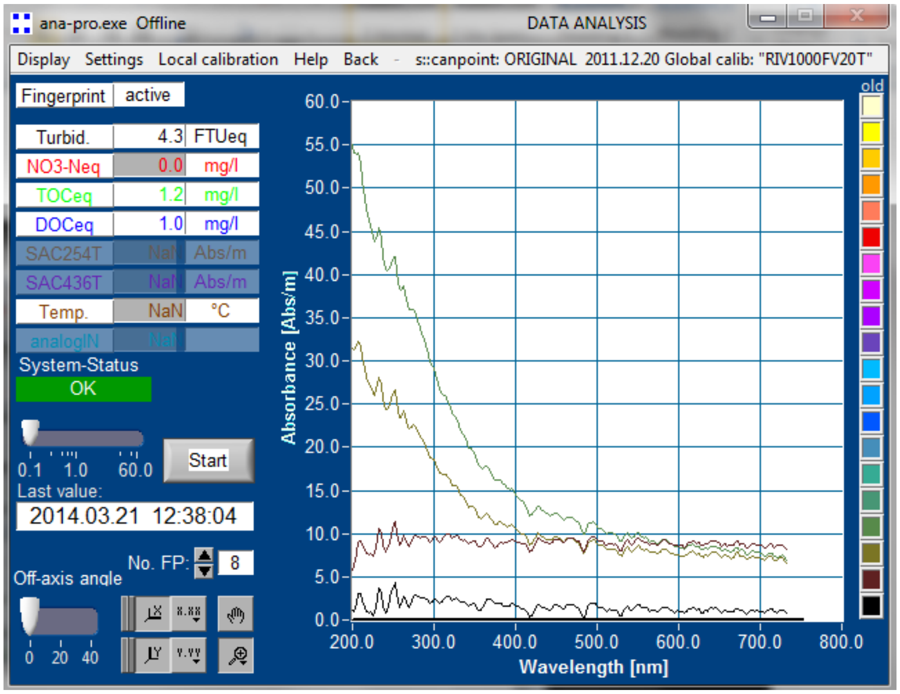


Figure 3.6. Screen shot of absorbance spectra in air as a function of wavelengths for watershed D2 during and after cleaning optics during field servicing visit during the spring (March 21, 2014).

Table 3.4. Maximum absorbance values before and after cleaning s::can lenses in watersheds D0, D1, D2, D3 throughout 2014.

			Watershed			
Season	**Date**	**Cleaning Status**	**D0**	**D1**	**D2**	**D3**
Winter	2014 Jan 27	Before	15	135	140	50
		After	11.5	12	12.5	36*
Spring	2014 Mar 21	Before	28	325	270	57*
		After	10.5	11.2	32	38*
Summer	2014 Aug 14	Before	66	426	530	376
		After	11.2	139	60	66
Fall	2014 Oct 21	Before	22.1	112	67	33
		After	10.9	26.5	11.5	25

*Absorbance increases with increasing wavelength (different trend from others).

Although in most cases, it was considered that the HCl cleaning during servicing was able to remove the fouling, the levels of fouling for the D1, D2 and D3 stations that occurred after two weeks were much higher than the ones observed in the tidal marsh (located 7 miles east of the study site) by Etheridge et al. (2013). The consequences of fouling were very poor correlation between the lab and the instrument concentrations.

Unreliable concentration values calculated by the instrument 'Global Calibration'

The s::can spectro::lyser™ uses a proprietary algorithm, referred to as the Global Calibration, to calculate concentrations from the absorbance spectra. Despite biweekly optics cleaning, and probably because of fouling, the global calibration algorithms yielded totally unreliable concentrations (e.g., Figure 3.7, Figure 3.8). Not surprisingly, the calculated chemographs for NO_3^--N and DOC in the same figures show sudden breaks, corresponding to the time when cleaning was performed. Concentrations were based on a global calibration; however, these show that these predictions do not align well with the discrete samples. On the other hand, the continuous NO_3^--N and DOC concentrations calibrated using PLSR do align well with the discrete samples (shown later in Figure 3.17 and Figure 3.18), thus supporting the need for local calibration. For DOC, the s::can PAR DOC concentration follows the PLSR calibrated continuous concentration more closely immediately following a cleaning of the instrument lens (values more closely align after field servicing on August 14). For both NO_3^--N and DOC, s::can PAR values tend to be much greater than the laboratory measured values, which correspond more closely to the values predicted using PLSR for local calibration.

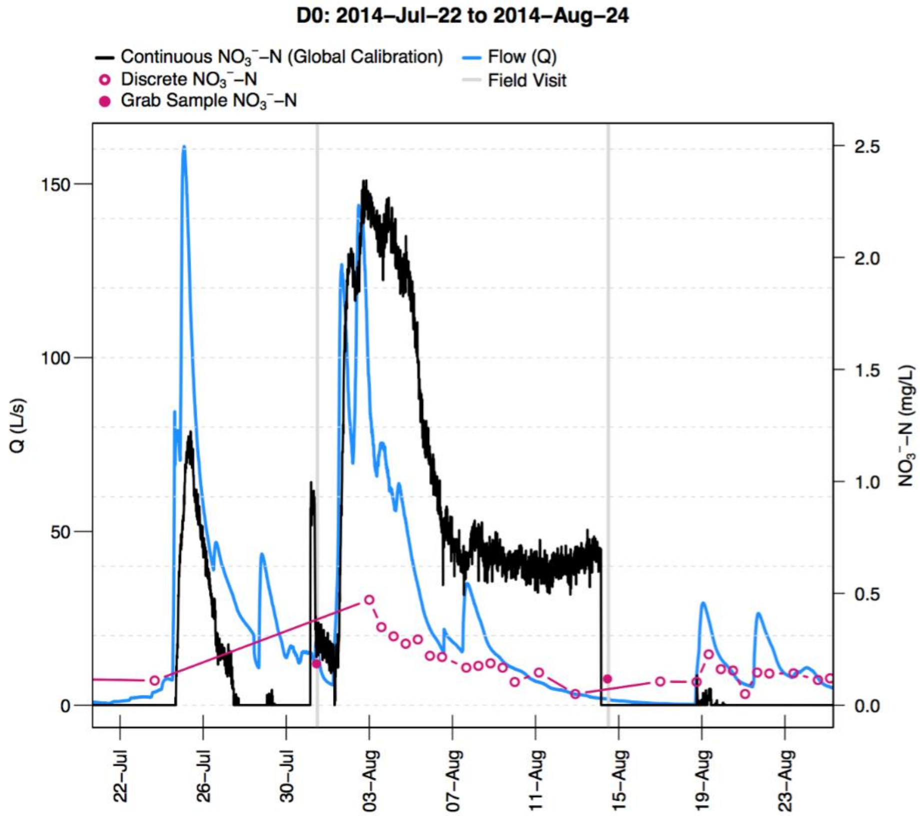


Figure 3.7. Hydrograph (blue line) and nitrate (NO_3^--N) chemograph (black line) calculated from the instrument global calibration and discrete, and grab sample concentrations (mg L^{-1}) (2014 July 22 to August 24). Vertical lines correspond to 12:00 pm of the day when servicing was performed.

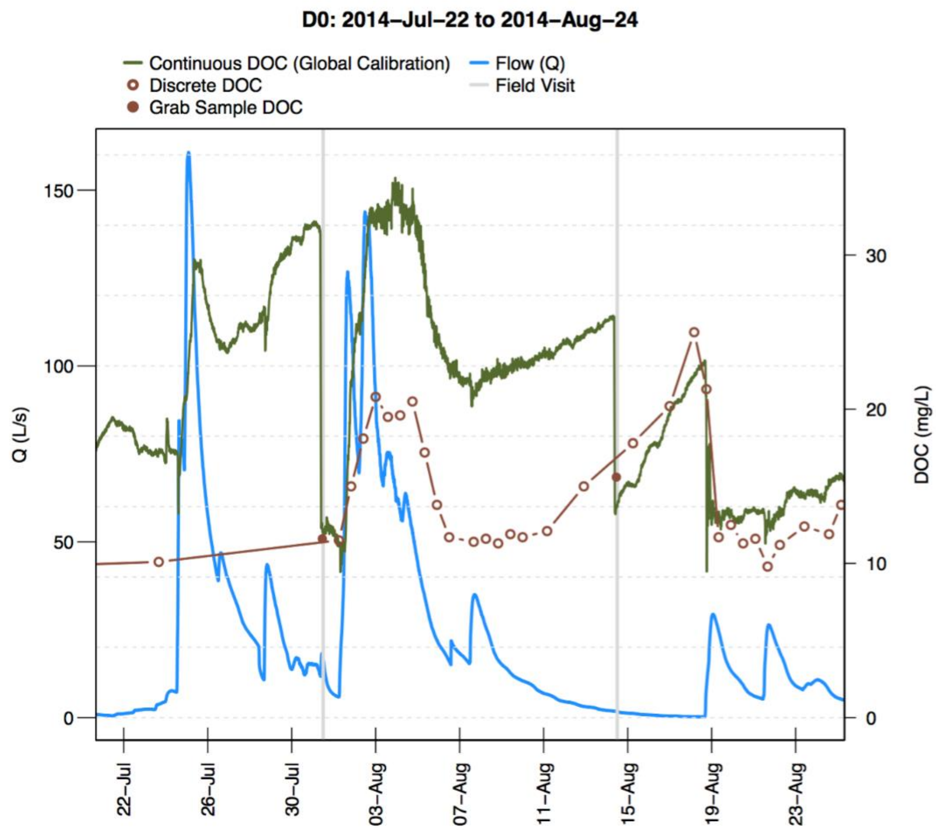


Figure 3.8. Hydrograph (blue line) and DOC chemograph (green line) calculated from the instrument global calibration and discrete, and grab sample concentrations (mg L^{-1}) (2014 July 22 to August 24). Vertical lines correspond to 12:00 pm of the day when servicing was performed.

The unreliable concentration values calculated by the instrument global calibration were unexpected and it was unclear whether the chemometric technique used, namely PLSR, would be able to correct for such fouling. It is also unclear why the level of fouling differed so much between watersheds which are located with less than 500m apart. All fouling results and the effect of HCl cleaning can be found in Appendix A.

PLSR calibration

Because the method relies so heavily on the calibration dataset, an iterative process was devised to obtain the PLSR model that would best fit with the discrete lab analyses. Indeed, it was quickly discovered that during calibration, some points appeared as 'outliers' on the regression lines. These points were compared and plotted with the chemographs calculated and several cases were observed. In some cases, and during events, because of the large changes in concentrations within minutes there was no way to certify that the discrete sample and the absorbance measurements were synchronic. As a result, these points were unreliable to be used in the regression. In some other cases, the concentration values appeared astray from the dynamics expected from the hydrograph.

Two cases quickly appeared depending on the watersheds. In the first case, removing a small number of apparent outliers significantly improved the regression R^2 and the RMSEP and the final number of points removed was less than 15% of the total at the beginning of the iterative process, all this for an acceptably low number of components used (~8 or less). In the second case, removing outliers did not significantly improve the regressions or at the cost of more than 10 components. It was then decided to create regressions over seasonal periods rather than over the whole year. Even then regressions could be derived for a limited number of cases. A summary of all the iterations (trials) performed for DOC, NO_3^--N, TDN, and TSS is given in Table 3.5, showing several iterations had to be performed, removing outliers and re-running PLSR, in order to obtain the best possible prediction of continuous data.

Table 3.5. Summary of partial least squares regression (PLSR) trials for all watersheds (D0, D1, D2, D3) for dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), and total suspended solids (TSS).

WS	Parameter	Trial	No. Observations	No. PLSR Components	R^2	RMSEP (mg L^{-1})
D0	DOC	1	146	9	0.88	1.75
		2	142	10	0.92	1.46
		3	142	9	0.91	1.44
		4	141	5	0.79	1.75
		5	141	10	0.93	1.37
		6	141	6	0.81	1.72
		7	134	8	0.92	1.31
		8	131	6	0.88	1.48
		9	131	7	0.91	1.36
		10	131	8	0.93	1.31
		11	131	11	0.96	1.18
		12	129	1	0.61	2.42
		13	129	6	0.89	1.39
		14	127	2	0.70	2.12
		15	127	6	0.89	1.39
		16	127	7	0.92	1.31
		17	127	9	0.95	1.27
	NO_3^--N	1	104	7	0.86	0.037
		2	103	10	0.94	0.026
		3	100	9	0.93	0.028
		4	97	6	0.86	0.033
		5	97	7	0.90	0.029
		6	97	10	0.94	0.027
	TDN	1	146	7	0.94	0.036
		2	143	7	0.96	0.029
		3	143	10	0.98	0.029
	TSS	1	146	5	0.52	10.5
		2	141	5	0.76	3.33
D1	DOC	1	168	5	0.68	1.66
		2	161	5	0.62	1.32
		3	155	5	0.60	1.27
		4	80	5	0.82	0.87
		5	65	5	0.89	0.60

Table 3.5. Continued.

	NO_3^--N	1	95	5	0.24	0.049
		2	87	5	0.18	0.045
		3	54	7	0.30	0.034
		4	34	2	0.072	0.024
		5	34	5	0.51	0.023
		6	33	5	0.71	0.015
		7	30	4	0.80	0.011
		8	30	6	0.86	0.010
	TDN	1	167	6	0.62	0.042
		2	149	6	0.49	0.035
		3	139	6	0.52	0.033
		4	139	10	0.74	0.030
		5	123	5	0.52	0.034
		6	123	9	0.75	0.028
D2	DOC	1	159	7	0.44	2.17
		2	147	8	0.62	1.62
		3	144	8	0.67	1.44
		4	138	8	0.71	1.34
		5	135	8	0.72	1.28
	NO_3^--N	1	76	7	0.87	0.15
		2	71	5	0.78	0.21
		3	71	13	0.99	0.05
		4	60	6	0.85	0.18
		5	40	4	0.78	0.23
		6	36	8	0.99	0.10
		7	35	4	0.79	0.25
		8	35	6	0.95	0.15
		9	31	7	0.99	0.04
	TDN	1	158	8	0.84	0.11
		2	148	5	0.58	0.17
		3	145	7	0.90	0.13
		4	138	7	0.92	0.14
		5	133	6	0.94	0.07
D3	DOC	1	186	6	0.36	3.01
		2	186	12	0.73	2.37

Table 3.5. Continued.

		3	137	4	0.51	1.93
		4	123	7	0.74	1.35
		5	114	6	0.73	1.33
		6	114	9	0.80	1.35
	NO_3^--N	1	123	4	0.19	0.074
		2	108	4	0.23	0.058
		3	86	4	0.43	0.043
		4	79	4	0.62	0.029
		5	79	6	0.67	0.028
		6	62	4	0.81	0.022
		7	62	7	0.88	0.020
	TDN	1	186	9	0.41	0.125
		2	175	6	0.32	0.099
		3	175	9	0.45	0.096
		4	157	6	0.36	0.073
		5	154	6	0.37	0.068
		6	154	10	0.52	0.063
		7	142	6	0.46	0.053
		8	142	11	0.70	0.046
		9	116	8	0.61	0.032
		10	111	8	0.74	0.025

Using this method for all water quality parameters (i.e., NO_3^--N, NH_4^+-N, PO_4^{3-}-P, DOC, TDN, TKN, and TSS), only DOC, NO_3^--N, and TDN were able to be predicted on a continuous basis with relative certainty for one watershed (D0). Even after several iterations of removing outliers and trying various numbers of components, the continuous and discrete data from the other watersheds (D1, D2, D3) were not able to be adequately correlated for any of the water quality parameters. Watersheds D1 and D2 offered a few weeks of corresponding trends between continuous and discrete data; while most continuous data watershed D3 was not well aligned with discrete sample concentrations. Even though TSS data was expected to expected to correlate well with spectral data, the attempts to obtain a good correlation showed that range of calibration points was too limited (i.e., most calibration data fell between 5 and 15 mg L^{-1}); therefore, PLSR was not able to predict the few higher TSS concentrations that occurred with events (e.g., Figure 3.10). As Figure 3.9 shows there is only one calibration point greater than the dominant concentration range driving the regression, which is not adequate for predicting the sudden spikes in TSS that occur with events throughout the year. Similar results were obtained for the other watersheds (data not shown).

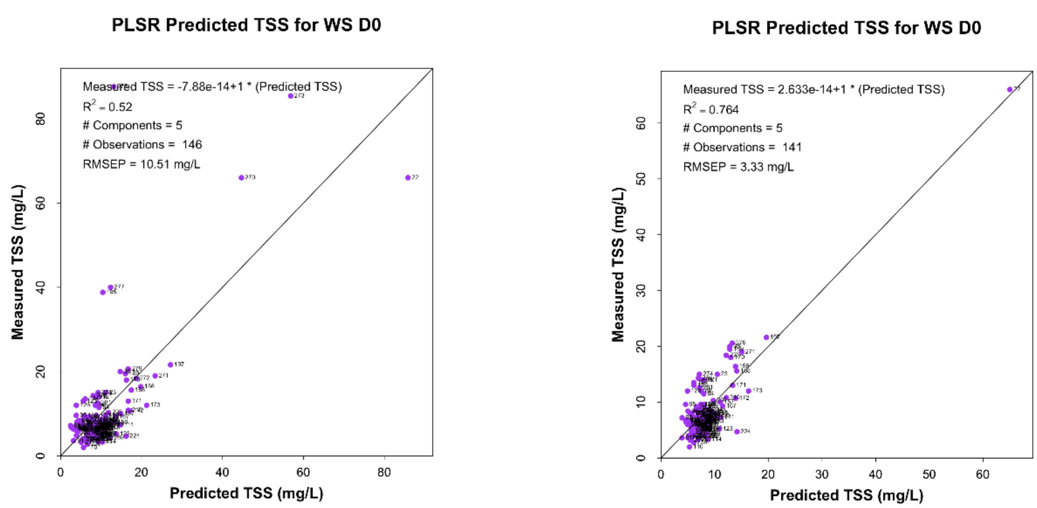


Figure 3.9. Relationships obtained by partial least squares regression (PLSR) between predicted and measured total suspended solids (TSS) data for watershed D0 before and after removing outliers.

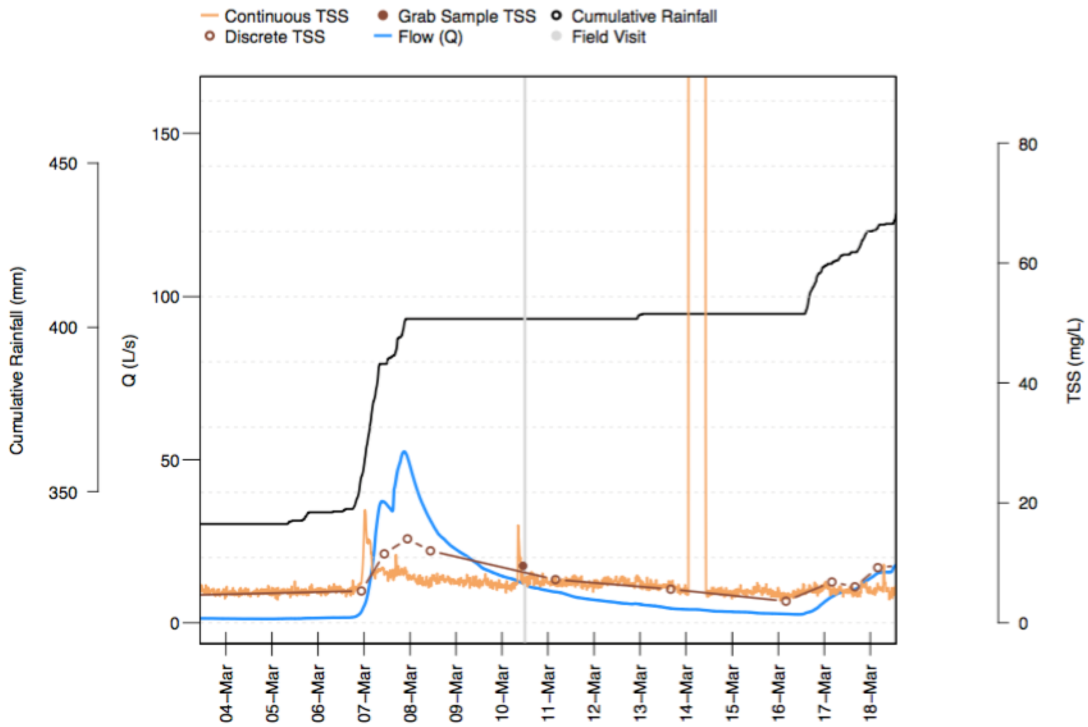


Figure 3.10. Continuous and discrete total suspended solids (TSS) data with hydrograph and cumulative rainfall for watershed D0.

The results for the D0 watershed suggest that the chemometric technique used was able to correct, at least for three parameters, the effect of fouling. The underlying hypothesis for the use of this technique is that there is a co-variability of the ‘color matrix’ of the water with concentrations. Etheridge et al., (2014) and Birgand et al., (2016) have suggested this was the reason for obtaining significant correlation for parameters such as PO_4-P, which are not known to absorb light. The lack of significant correlation found may signify that for this watershed, there might have been no co-variability or, that the concentration range was not large enough to generate significant correlations, as this case would be emphasized by fouling.

The likely explanation for the inability to correlate concentrations with spectra data in the other watersheds (D1, D2, D3) is the greater levels of fouling that occurred on those s::can lenses. Given that higher absorbance values are associated with greater fouling, figures in Appendix A along with Figure 3.11 show that absorbance values before cleaning were consistently greater in D1, D2, and D3 compared with D0 for all four seasons. Absorbance measurements in air and DI water were taken during the routine maintenance visits before cleaning the lenses in order obtain the final level of fouling that had accumulated on the lenses over the two-week period. Figure 3.11 shows that the absorbance at 220 nm was consistently lower in watershed D0 than in all other watersheds. From this observation we can conclude that the higher levels of optical fouling in the other watersheds was the likely reason for the inability to correlate concentrations with spectral data in the other watersheds (D1, D2, D3). The plot sometimes shows two points on one day because there were separate measurements for absorbance in air and in water.

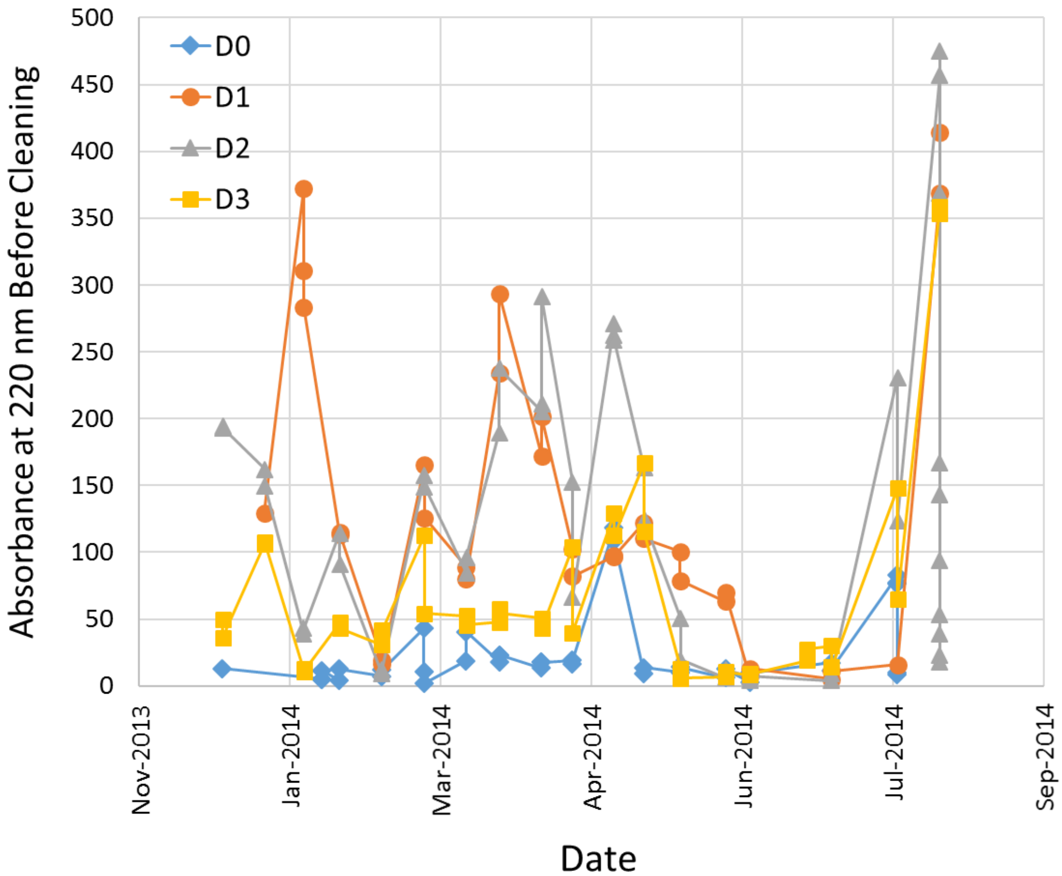


Figure 3.11. Absorbance of water and air at 220 nm for all watersheds (D0, D1, D2, D3) before cleaning during field visit (after two weeks operating without maintenance) in Carteret County, North Carolina.

Example application of the iterative method for DOC for the D0 watershed

A first trial of PLSR was run on the set of clean data. The number of components was chosen from the PLSR output based on the point of inflection of the cross validations (CV's). For example, after running PLSR on the cleaned data set of DOC (146 data points), 9 components (comps) were chosen (Figure 3.12) to predict concentrations based on the PLSR model and measured data. A plot was generated of measured versus predicted values as shown in Figure 3.13. Then, outliers were selected based on visual inspection of the plot of measured versus predicted values (Figure 3.13) and verified by cross-checking these points on the time-series plots of continuous and discrete data.

The specific steps for selecting and removing outliers were as follows. On the plot of measured versus predicted values (Figure 3.13), each point was labeled with the laboratory identification number. Rather than simply removing outliers based on this one plot, a given relationship with a reasonable r-squared value and number of components was used to predict a continuous concentration and plot these values over time. Then, any obvious outliers from the general trend along the 1:1 line of measured versus predicted values were inspected along the trend of the time series data. Looking at the continuous data with the discrete data plotted over time, the outliers were confirmed when particular discrete samples did not align with general trend of both the continuous data and the discrete data based on typical patterns observed for certain flow conditions. Since the measurement times were absent from the plot of measured versus predicted values, the original file of laboratory measurements combined with corresponding absorbance data (i.e., fingerprint data) which included the laboratory identification number and measurement time was used to identify the measurement time of a particular outlier on the plot of measured versus predicted values. The trend of the time series was then inspected around this particular measurement time to confirm whether or not this data point was truly an outlier. The outliers removed from the data set were numbers 119 (4/15/14 5:56), 155 (7/3/14 9:59), 158 (7/5/14 3:59), and 196 (8/18/14 4:00). The outliers that were removed may have been due to a variety of factors such as the instrument (i.e., s::can spectrophotometer) not working properly or unknown errors or contamination associated with sample collection, transport, and analysis.

After removing the confirmed outliers from the data set, PLSR was re-done with the new data set and 9 components were chosen based on the output in Figure 3.14. For DOC, this relationship using 9 components (Figure 3.15) was the final relationship used to predict continuous DOC values for the entire absorbance spectra obtained from November 12 2013 through November 30 2014. A final model was selected based on a balance of the highest r-squared value and lowest root mean square error of prediction (RMSEP). While considering these factors, there was an awareness that a higher r-squared value can be forcibly obtained by choosing a higher number of components; that is, a higher r-squared value does not necessarily indicate a better fit when the model is actually just fitting noise. Selecting a higher number of components results in a noisier time series (i.e., increase in frequency or magnitude of spikes within the continuous data). For example, using 9 components rather than 7 (Figure 3.16) results in a slightly noisier signal of DOC continuous concentration; whereas, too few components (e.g., 2 comps) results in a smoother signal that does not adequately represent the true signal (Figure 3.16).

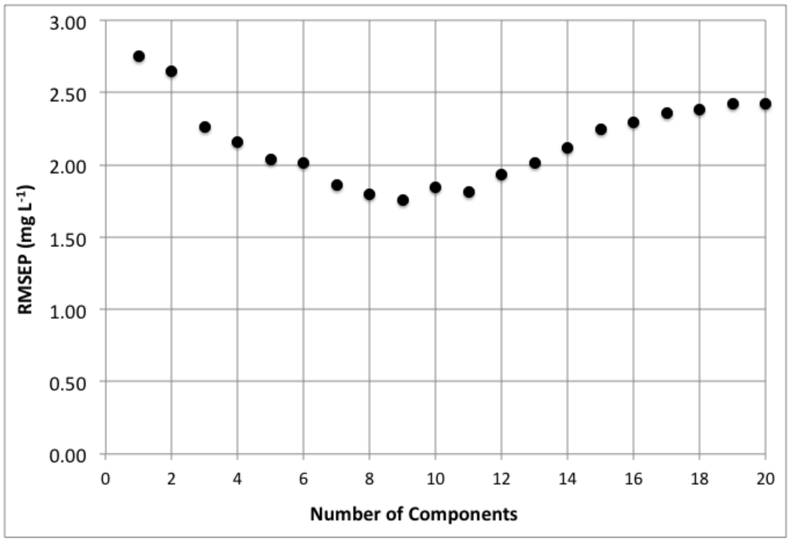


Figure 3.12. Root mean square error of prediction (RMSEP, mg L^{-1}) as a function of the number of components for the first trial of the partial least squares regression model for dissolved organic carbon (DOC) in watershed D0.

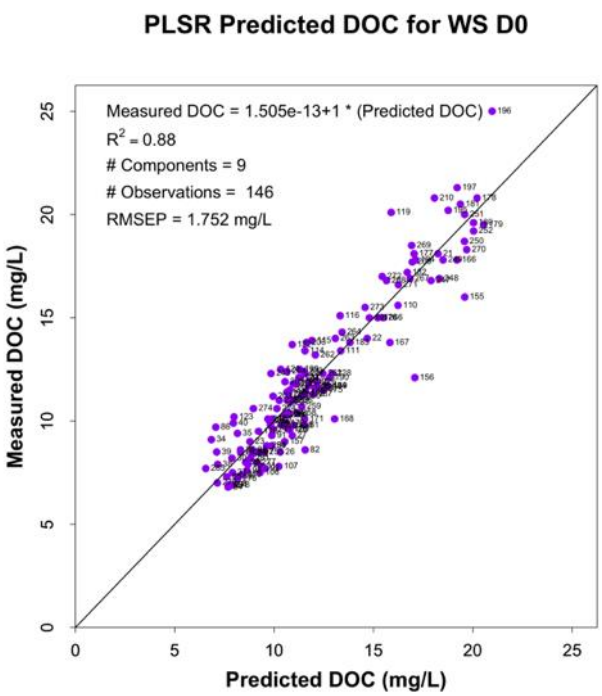


Figure 3.13. Relationship between measured and predicted dissolved organic carbon (DOC) values from first partial least squares regression (PLSR) trial for watershed D0.

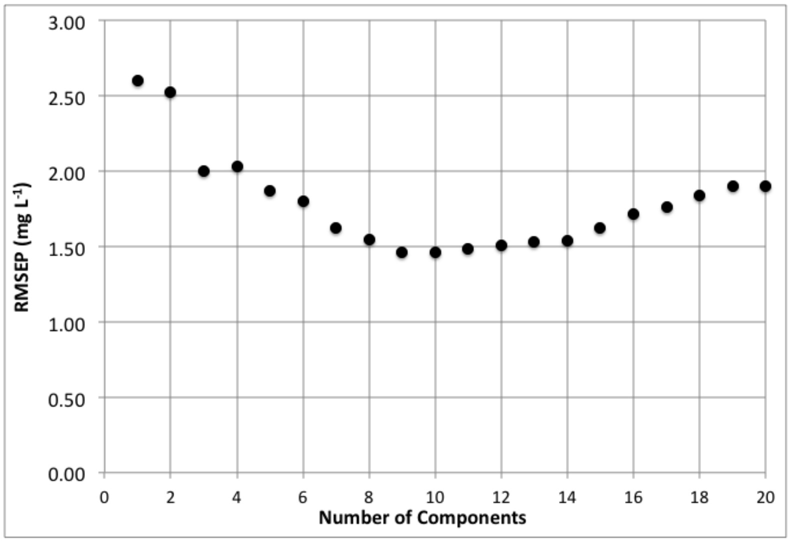


Figure 3.14. Root mean square error of prediction (RMSEP, mg L^{-1}) as a function of the number of components for the second trial of the partial least squares regression model for dissolved organic carbon (DOC) in watershed D0.

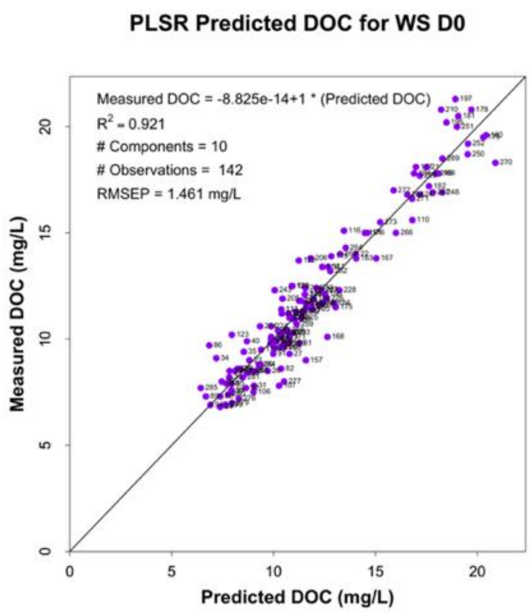
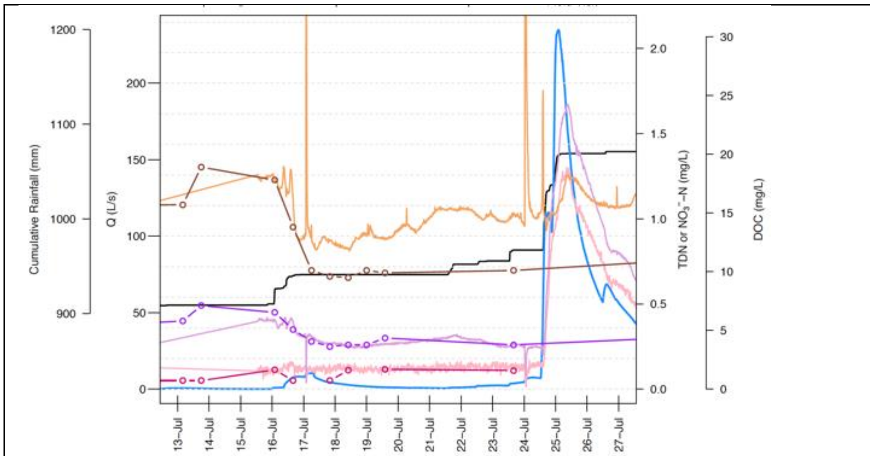
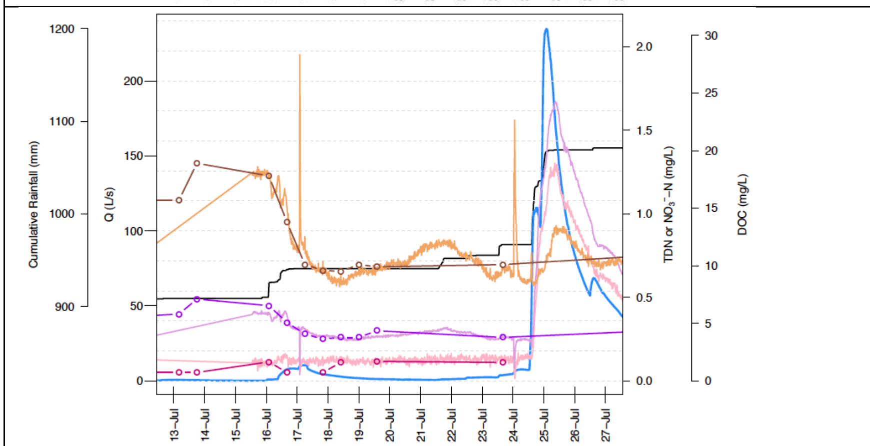
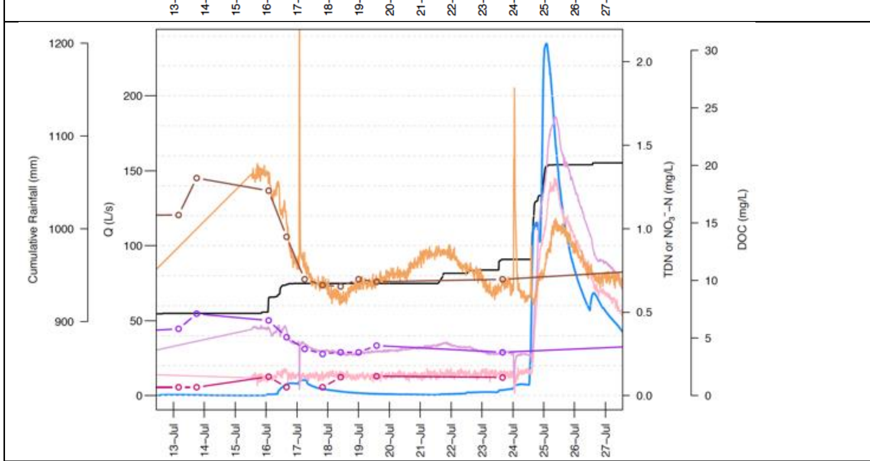


Figure 3.15. Final relationship between measured and predicted values used to predict continuous dissolved organic carbon (DOC) values for watershed D0.

Figure 3.16. Example of predicted continuous dissolved organic carbon (DOC) concentration for variable number of components from the partial least squares regression to predict the continuous concentration data from the measured spectral data and showing variable fit and noise in the chemographs obtained.

<table>
<tr><td></td><td>2 components: less noise compared with more components, but does not fit discrete data as well</td></tr>
<tr><td></td><td>7 components: less noise compared with 9 components</td></tr>
<tr><td></td><td>9 components: more noise compared with 7 components).</td></tr>
<tr><td>Continuous NO$_3^-$–N   Continuous TDN   Continuous DOC   Flow (Q)
Discrete NO$_3^-$–N   Discrete TDN   Discrete DOC   Cumulative Rainfall
Grab Sample NO$_3^-$–N   Grab Sample TDN   Grab Sample DOC   Field Visit</td><td></td></tr>
</table>

Example application of the iterative method for NO_3^--N for the D0 watershed

After running the first PLSR for NO_3^--N, 7 components were chosen (Figure B.20 in Appendix B). From the plot of measured versus predicted values (Figure B.21 in Appendix B) and the time-series of continuous and discrete data, only one outlier was removed: number 233 (9/21/14 3:59), as the continuous and discrete data were not congruent at this point. After rerunning PLSR with the outlier removed, 10 components were chosen from the new output (Figure B.23 in Appendix B), which was used to produce the final relationship (Figure B.28 in Appendix B) used to predict continuous NO_3^--N values for watershed D0.

Example application of the iterative method for TDN for the D0 watershed

After running the first PLSR for TDN, 7 components were chosen (Figure B.30 in Appendix B). From the plot of measured versus predicted values (Figure B.31 in Appendix B) and the time-series of continuous and discrete data, three outliers were removed: numbers 233 (9/21/14 3:59), 240 (9/26/14 14:00), and 110 (4/7/14 13:58), as the continuous and discrete data were not congruent at these points. After rerunning PLSR with the outliers removed, 7 components were chosen from the new output (Figure B.33 in Appendix B), which was used to produce the final relationship (Figure B.34 in Appendix B) used to predict continuous TDN values for watershed D0.

Local calibration: Large improvement over the global calibration

Without the PLS chemometrics technique, the concentration values calculated from the global calibration were essentially unreliable and therefore useless. The PLSR models were able to correct for the fouling as no break can be seen in the calculated chemographs (Figure 3.17 and Figure 3.18) at the time of optics cleaning, and to satisfactorily fit the lab data in most cases (details above).

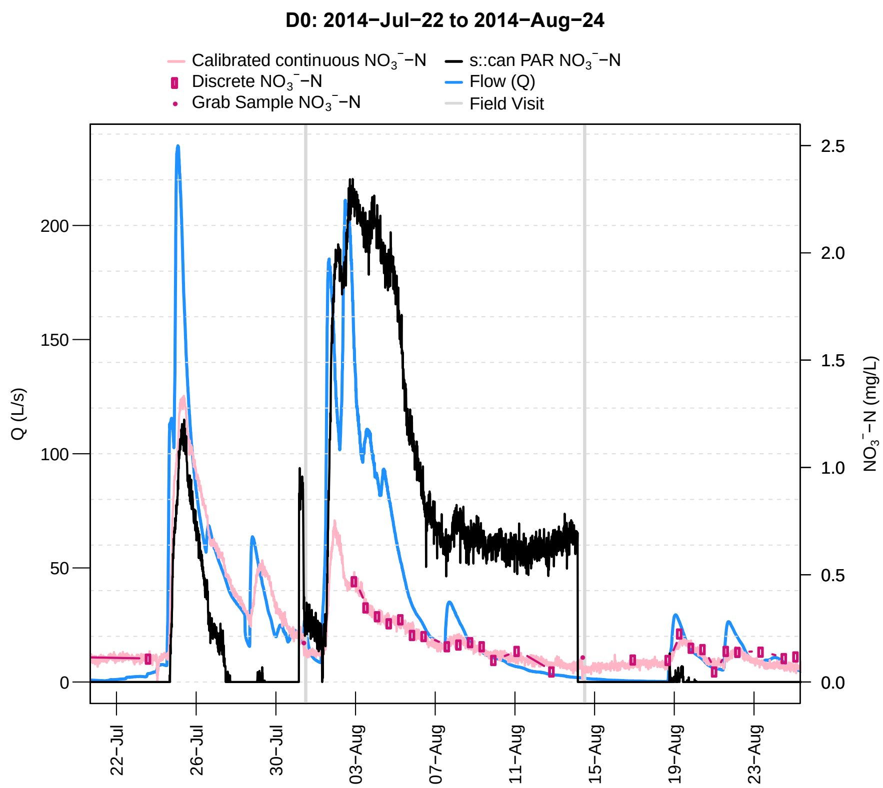


Figure 3.17. Hydrograph (blue line) and nitrate (NO_3^--N) chemographs calculated from the instrument global calibration (black line) and local calibration (pink line), and discrete, and grab sample concentrations (mg L^{-1}) (2014 July 22 to August 24). Vertical lines correspond to 12:00 pm of the day when servicing was performed.

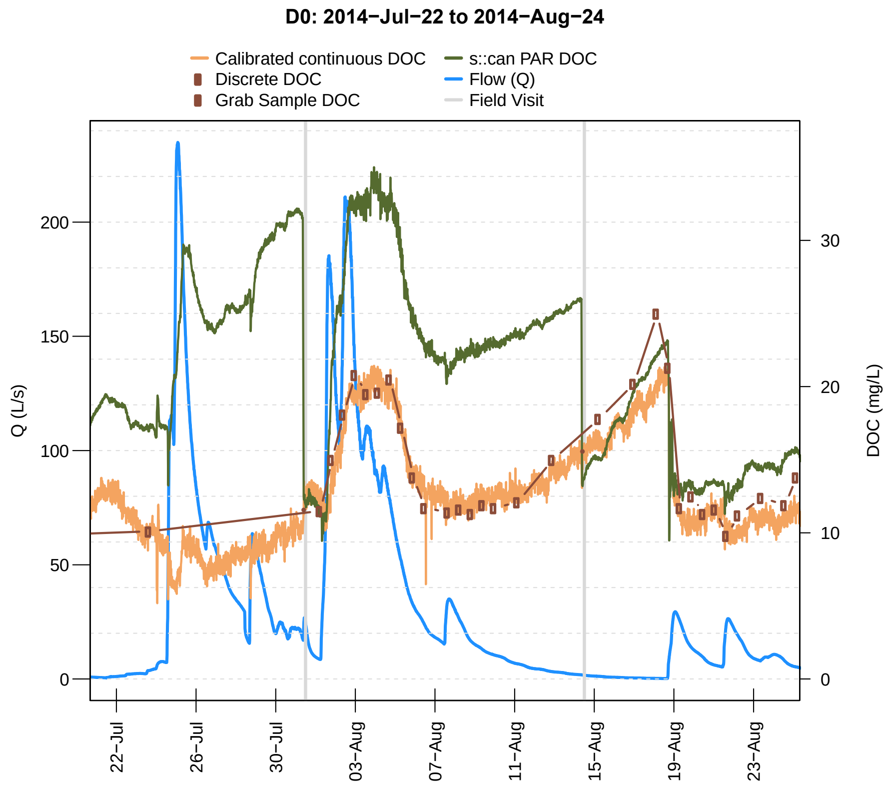


Figure 3.18. Hydrograph (blue line) and DOC chemographs calculated from the instrument global calibration (green line) and local calibration (brown line), and discrete, and grab sample concentrations (mg L^{-1}) for the D0 watershed (2014 July 22 to August 24). Vertical lines correspond to 12:00 pm of the day when servicing was performed.

Limits of the method with extensive fouling

For the three other watersheds for which both discrete and continuous data were collected, the continuous data could not be well correlated with the discrete data. Several trials were made in an effort to obtain well correlated continuous data, but the other three watersheds would not yield desirable results. From the cleaned dataset for watershed D1, DOC was further reduced to 65 data points, TDN to 123, and NO_3^--N to 30 data points after additional iterations of removing outliers. Still, the continuous data was not well correlated with the discrete samples (Figure 3.19). From the cleaned dataset for watershed D2, DOC was further reduced to 135 data points, TDN to 133, and NO_3^--N to 31 data points. NO_3^--N and TDN only aligned with the discrete samples during the prolonged wet period in early August 2014; however, continuous DOC in watershed D2 was never well correlated with the discrete samples (Figure 3.20). For watershed D3, even after several trials of removing outliers and reducing the number of DOC data points to 114, TDN to 111, and NO_3^--N to 62 data points, none of these continuous concentrations were well aligned with the discrete samples (Figure 3.21).

As stated previously, the inability to correlate these absorbance spectra with concentration data was likely due to the greater degree of lens fouling that occurred in these watersheds. The outflow from all of these artificially drained watersheds was not consistent. Rather than a relatively consistent outflow from these watersheds or even a consistent pattern of flow (as in a tidal marsh), there were extended periods of little or no flow as well as periods of intense rainfall which caused the water table to remain elevated for an extended period of time. This unique variability in canal stage may have contributed to the elevated fouling that occurred here. During dry periods, there may have been stagnant water in the ditches in which turbidity levels were increasing. The s::can may have taken several measurements of this stagnant turbid water, which would have contributed to the lens fouling. Although there were still times when watershed D0 was stagnant, watershed D0 did have more consistent outflow than the other watersheds.

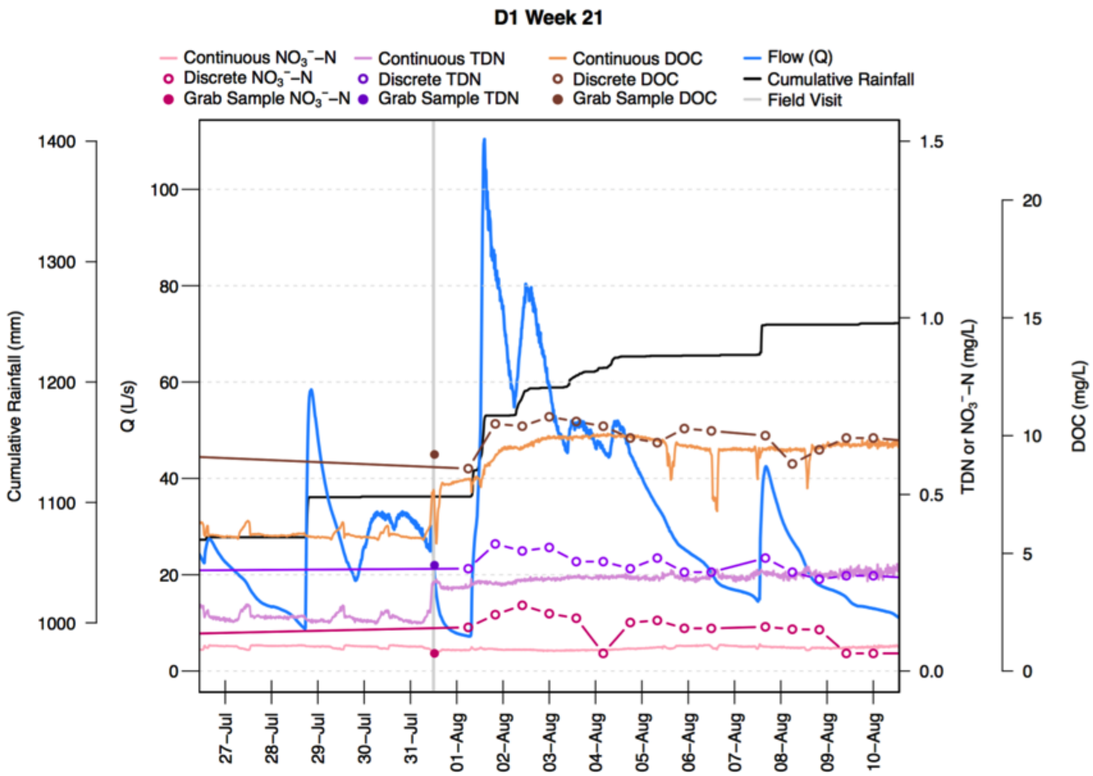


Figure 3.19. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D1 watershed (2014 July 27 to Aug 10).

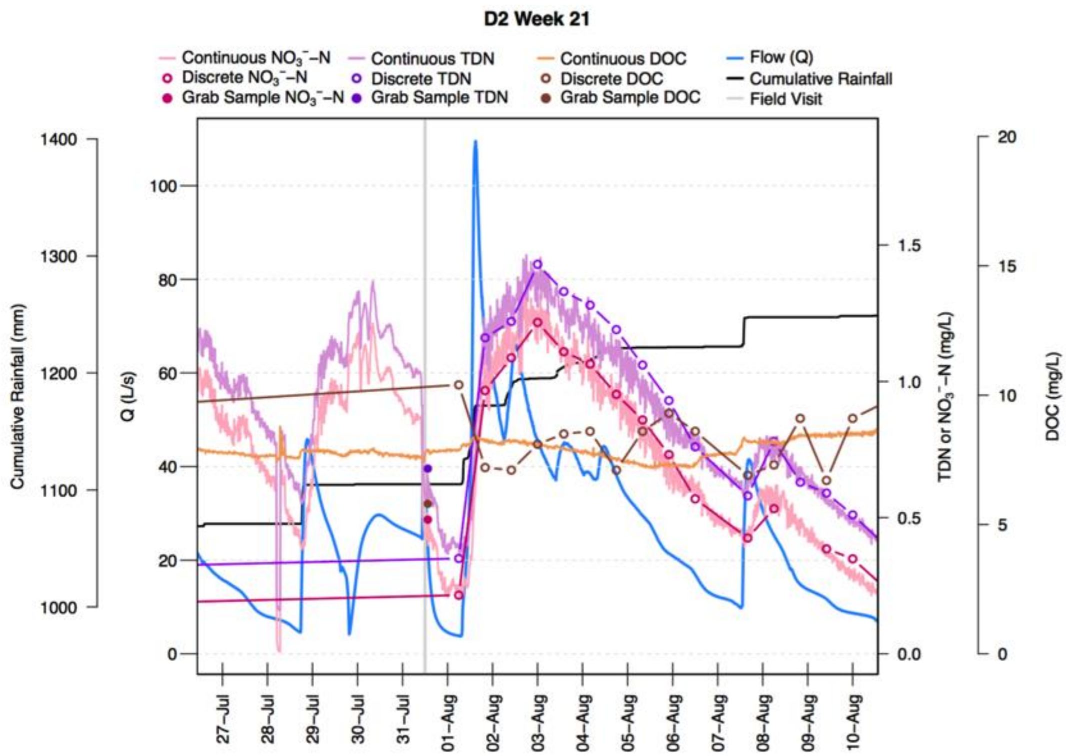


Figure 3.20. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D2 watershed (2014 July 27 to Aug 10).

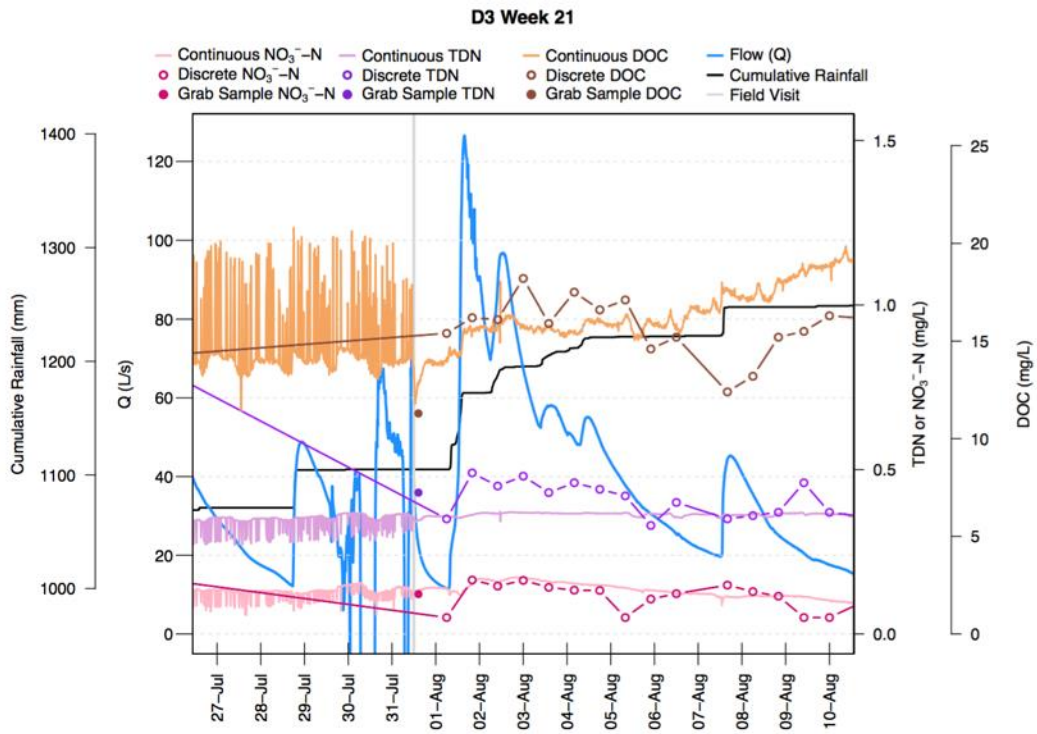


Figure 3.21. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D3 watershed (2014 July 27 to Aug 10).

Insights gained from continuous water quality monitoring

The continuous concentrations (i.e., 15-minute data) predicted from the absorbance values were able to capture a more detailed picture of concentration trends compared with discrete sample analysis alone, particularly during events when changes occur rapidly. The following results and discussion focus on describing the trends of DOC, TDN, and NO_3^--N observed when continuous data aligned with discrete sample concentrations, focusing on the control watershed (D0), particularly during flow events, and the probable biogeochemical processes associated with these trends. These biogeochemical processes are influenced by hydrology and related to the drainage patterns of these artificially drained coastal plain watersheds. In the coastal plain watersheds the banks of the canals are nutrient-deficient because this area is not in continuous contact with the water table (Figure 3.22). There is less organic matter and more mineralization in the ‘near-stream’ region, i.e., near the ditches of coastal plain watersheds where the water table draws down near the drainage outlet and reversely tends to be higher at the furthest point from the ditches. These drainage patterns directly affect the nutrient dynamics; hence, the particular patterns observed in these coastal plain watersheds, with DOC dilutions and NO_3^--N increases during events. The observed dilution effect of DOC and ON is supported by previous research from two other artificially drained coastal plain watersheds in North Carolina; the buildup of DOC (up to more than 30 mg/L) and ON was attributed to upward diffusion from highly organic sediment, which was then flushed and diluted during events (Appelboom, 2004; Birgand, 2000). The NO_3^--N concentration effect “during summer was attributed to the lack of NO_3^--N storage in the relatively small water volume” during summer; whereas, during winter, they hypothesize that the higher water table causing the higher base flow also provided a greater storage volume for NO_3^--N which was then leached from the upper soil horizon (Appelboom, 2004; Birgand, 2000).

This monitoring period was a relatively wet year with 1613 mm cumulative rainfall from Nov 12 2013 to Nov 30 2014, compared with 1517 mm average measured at this site since 1988 (Amatya and Skaggs, 2011). The year was characterized by consistent, normal flow conditions throughout the winter and early spring, followed by a period of little or no flow from late April through most of July, and then a prolonged wet period from Jul 23 to Aug 23 2014. There were a series of large events during the prolonged wet period which caused the water table to remain near the surface for an extended period of time. During this prolonged wet period (~30 days), a total of ~394 mm of rainfall occurred, with 102 mm of rainfall occurring in 17.5 hr (July 24 to 25 2014) and 67 mm of rainfall in 7.5 hr (Aug 1 2014). The largest event of the year (111 mm in 27 hr) occurred Sept 8 2014 following about 12 days of no flow. The water quality dynamics were heavily driven by these hydrological conditions and the patterns discussed below will focus on the typical nutrient patterns observed versus some exceptions observed after particularly dry antecedent conditions and during the prolonged wet period when the elevated water table caused an opposite effect on DOC dynamics.

Typology of DOC and nitrate dynamics and likely processes inferred

Among all the events observed between November 2013 and 2014, two main types of responses of concentration to flow were observed. They are illustrated in Figure 3.22 below.

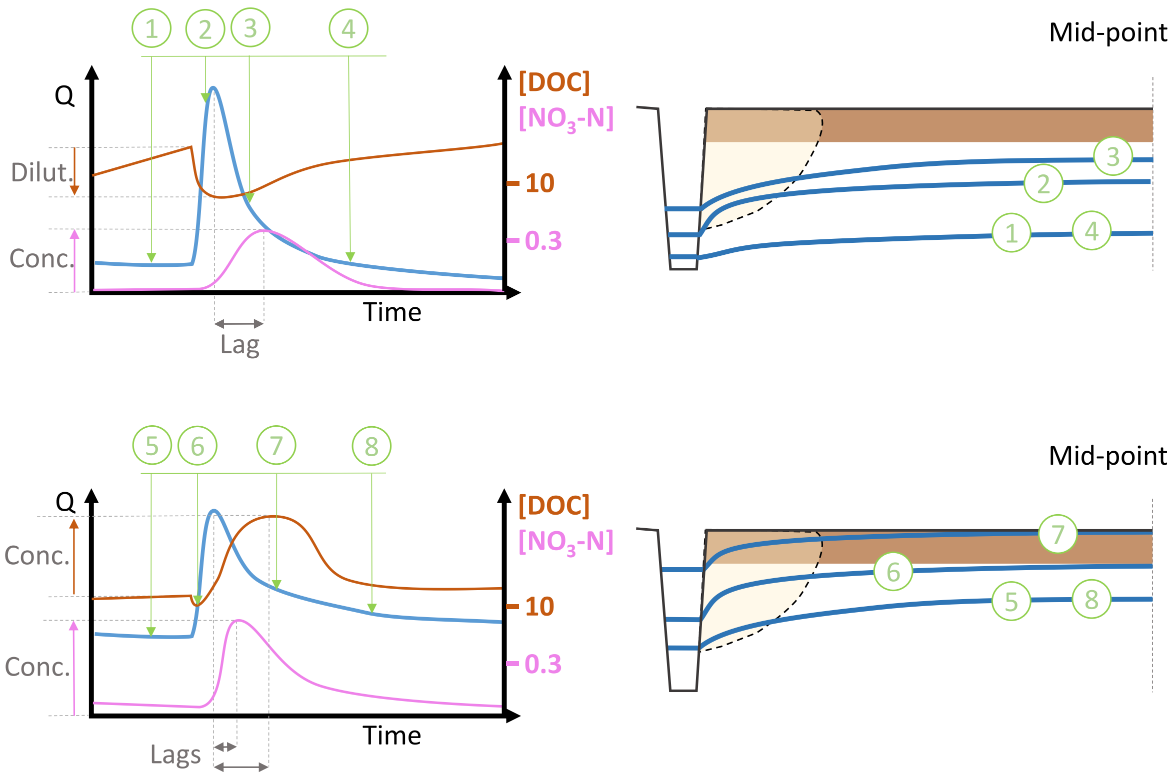


Figure 3.22. Left column: DOC (brown line) and nitrate (pink line) concentration and flow (blue line) dynamics as a function of time showing dilution and concentration effects, during rather low flow/low water table antecedent conditions (top row) and rather high flow/high water table antecedent conditions (bottom row). Right column: hypothetical water table profiles corresponding to marked times numbered from 1 to 8 are represented in dark blue (not to scale; organic surface horizon represented in brown and near-ditch soil profile represented in beige).

a. Low flow and low water table antecedent conditions – in these conditions, and prior to a rainfall event, DOC concentrations tended to increase as a function of time and were most often above 10 mg/L (item number 1 in Figure 3.22 and e.g., Figure 3.23; all other illustrations available in Appendix C). At these times, nitrate concentrations were at or below the detection limit. This can be interpreted as the enrichment in DOC of a relatively small volume (draining or not) of water due to the diagenetic processes in the sediment (Birgand, 2000). During low flow, conditions would be conducive to denitrification in the ditches, and could suffice to explain the absence of nitrate.

At the onset of the rise of the hydrograph, DOC concentrations tended to decrease exhibiting what is often referred to as a ‘dilution’ effect, while nitrate concentration slowly increased, exhibiting the opposite ‘concentration’ effect, although with a lag. DOC concentration troughs appeared in synchrony with or slightly ahead of the flow peaks, while the nitrate concentration peaks (0.3 to 1.3 mg/L) lagged behind the flow peak (Figure 3.23).

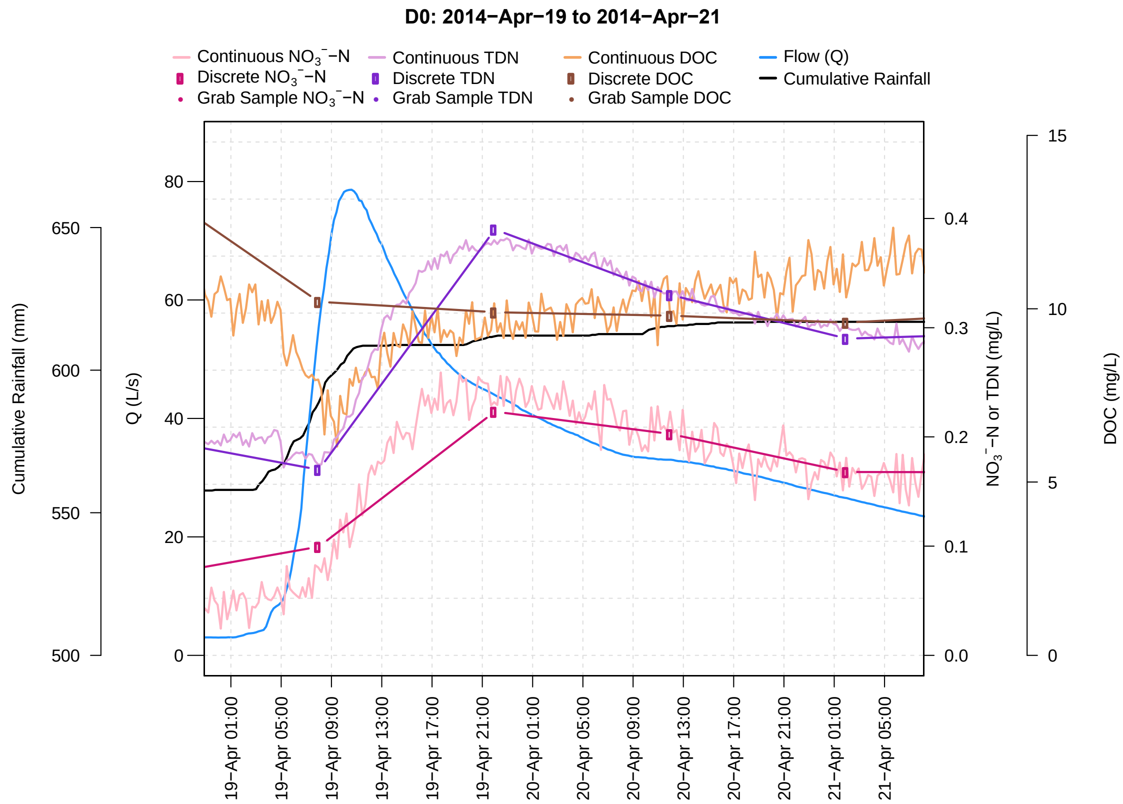


Figure 3.23. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Apr 19 to 21).

Because of the flat topography and roughness of the soil profile, also because this was observed for small and large events with the same antecedent conditions, surface runoff can be safely ruled out. The processes generating the rising limb and flow peaks appeared to leach areas of the soil profile which were relatively poor in DOC and nitrate. In upland watersheds, DOC concentrations during events seem to almost always follow a 'concentration' effect (e.g., Boyer et al., 1997; Morel et al., 2009; Raymond and Saiers, 2010; Laudon et al., 2011; Lambert et al., 2014; Thomas et al., 2016). This has been attributed to the flushing of the organic rich riparian soil (e.g., Boyer et al., 1997), although the contribution of the DOC from the hillslope top soil has recently been shown (Lambert et al., 2016). A possible explanation for the unique dilution effect of the DOC concentrations observed in these flat artificially drained watersheds may be associated with the unique hydrological functioning of these systems. Drainage hydraulics and numerical solutions of the Richard's equation tell us that the shape of the water table, directly following rainfall is not elliptical, but tends to be deformed at the near stream zone, where the hydraulic gradient is steeper. The consequences of this is that there is a disproportionally large portion of the flow volume that leaches through the near-ditch soil profile (Paris, 2004; deformed water table illustrated as item number 2 in Figure 3.22). This zone of the soil, because of the water table drawn down near the ditch, tends to be relatively drier than the rest of the soil profile, and undergoes more mineralization. This zone being drier and being leached, in relative terms, with higher volumes than the rest of the soil profile, is expected to contain less leachable material, including DOC and NO_3-N. This is our explanation for the 'dilution' effect of DOC concentration, unique to these systems. The nitrate concentration peak lag and the increase of DOC concentrations after the flow peak, most likely correspond to water which infiltrated vertically in the soil, away from the near ditch area, where it would be enriched in leachable nitrate in the soil, and then moved laterally until it reached the ditches (item number 3 in Figure 3.22). The recession of the nitrate peak likely corresponds to the drawdown of the water table to where it started (item 4 in Figure 3.22). As the water table draws down, the volume of the soil leached diminishes and drains deeper less organic parts of the soil likely containing less nitrogen. Additionally, conditions in the deeper part of the soil profile undergo anaerobic conditions that favor denitrification, all of which likely participate in the recession of the nitrate chemograph. The dilution effect of DOC and concentration effects of nitrate during events had been previously observed in coastal plain watersheds 100 times the size (Birgand, 2000; Appelboom, 2004)

b. High flow and high water table antecedent conditions – in these conditions, and prior to a rainfall event, DOC concentrations may be lower and not clearly increasing compared to low flow conditions as the sediment diagenetic processes play a relative smaller role (item number 5 in Figure 3.22). Nitrate concentrations may be above detection limit as a legacy of previous wet conditions. At the onset of now a large event with an already elevated water table, a first DOC dilution effect of relatively short duration was generally observed, most likely because of the water table shape deformation in the near-stream zone leaching a large volume of water through a relatively nutrient depleted soil profile (item number 6 in Figure 3.22). However, this dilution effect generally appeared clearly ahead of the flow peak and lasted much shorter, before DOC concentrations increased again, exhibiting then a large 'concentration' effect, where concentrations nearly doubled (e.g., Figure 3.24). Similar to the dry conditions, nitrate concentrations peak lagged after the flow peak, but before the now DOC concentration peak, which was more a plateau than a peak. The large increase in DOC concentration can only be related to a sudden massive additional source of DOC where drainage water can be enriched. The water table data (Figure 3.25) show that for the event illustrated in Figure 3.24 during August 2-3 2014, the water table reached the surface and remained there for an extended time (~3-4 days), granting access to the top organic rich horizon of the soil and allowing the drainage water to be enriched with highly labile organic matter. In fact, for this particular event, the DOC concentrations remained very high around 20 mg/L until the water table started to go below 30 cm under the soil surface, regardless of the flow rate measured at the outlet. This suggests that the DOC concentration peak was generated as the water table reached the organic horizon of the soil (item number 7 in Figure 3.22), able to leach massive amounts of DOC (concentrations around 20 mg/L) regardless of the flow rates draining through this horizon. The nitrate concentration peak occurred earlier than the DOC peak and concentration receded while the DOC concentrations remained high. This suggests that the nitrate stock leached from the soil profile and particularly from the organic horizon likely held a more limited amount of nitrate, and/or not regenerated at nearly the pace at which DOC seemed to be available.

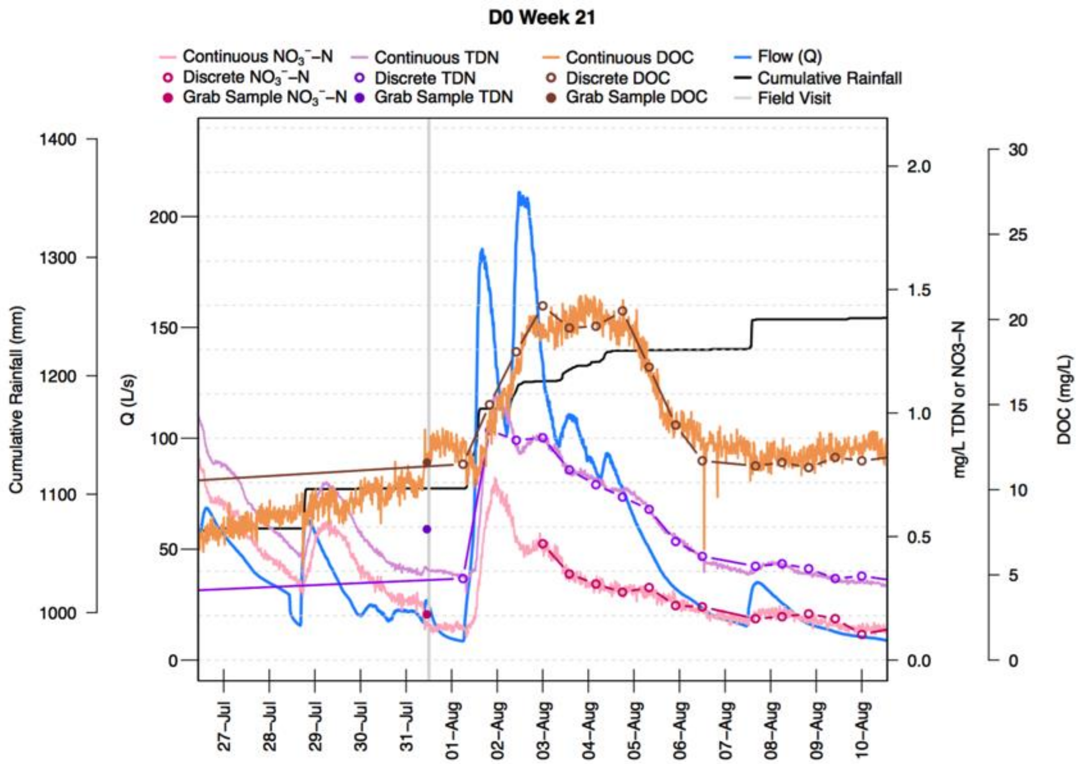


Figure 3.24. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 July 27 to August 10).

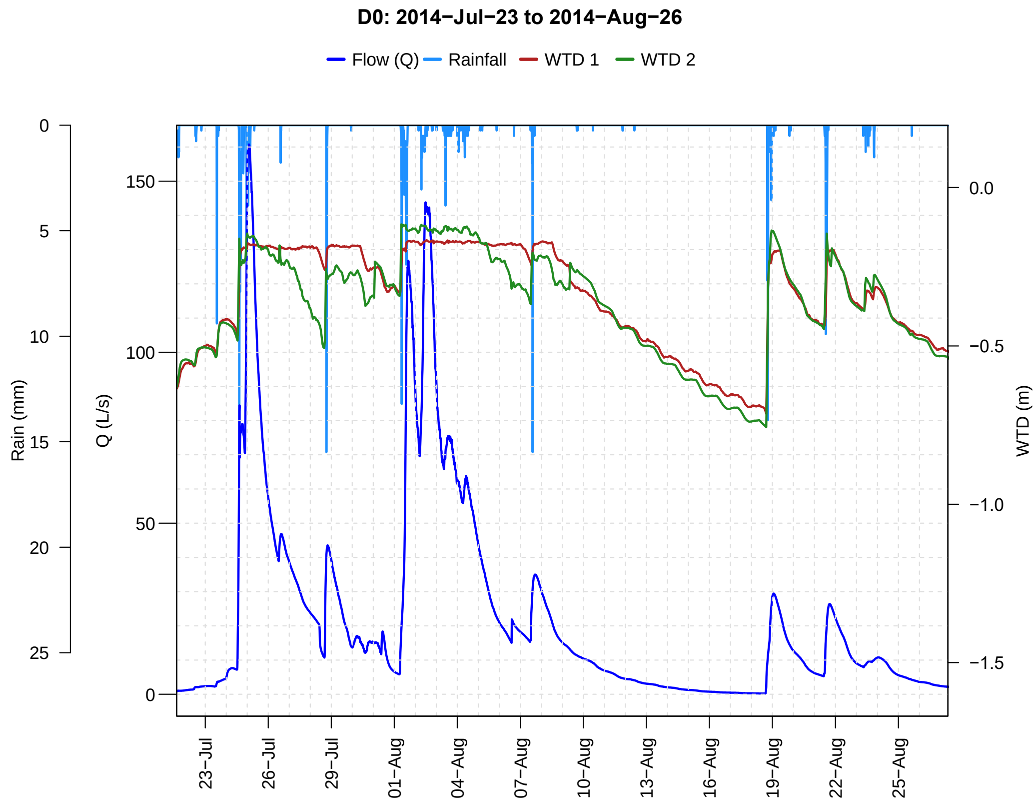


Figure 3.25. Hydrology including flow (L s^{-1}), rainfall (mm), and water table depth (m) in two locations (WTD 1 and 2) in watershed D0 during July 23 to August 26.

This study is possibly the first one able to show the direct impact of the near stream zone and of the top organic horizon to generate DOC exports from low gradient watersheds. It actually confirms a previous finding that emphasized the role of the riparian zone in DOC export: in an upland watershed, where the shape of the landscape and water table is conducive to maintaining an organically rich riparian zone, i.e., relatively high background DOC concentration that is diluted by flow events (Boyer et al., 1997; Morel et al., 2009; Raymond and Saiers, 2010; Laudon et al., 2011); while, in an artificially drained, flat watershed, our hypothesis is that the near stream zone tends to be a relatively organically poor zone due to this area being well-drained and remaining dry for the majority of time throughout the year and so we typically observe trends opposite to those of upland watersheds. The potential role of the top organically enriched horizon of upland soils to generate DOC exports in upland watersheds, has always been difficult to prove as the signal is generally overwhelmed by that of the riparian zone, although recent studies have been able to show the impact of the hillslope (e.g., Lambert et al., 2014; Thomas et al., 2016). Our study shows that in flat watersheds of the lower coastal plain, the top organic horizon plays a major role in the export of DOC, associated with large rainfall events able to bring the water table to the soil surface.

3.5 Conclusion

Continuous water quality probes have the potential to create a true revolution in the understanding of biogeochemical processes in watersheds as they are uniquely poised to capture ‘hot moments’ when water and solute transport are disproportionally high (sensu McClain et al., 2003; Vidon et al., 2010). Among continuous sensors, *in situ* ultraviolet-visual spectrophotometers are among the most promising although they seem to have an ‘Achilles’ heel’, i.e., the propensity of optics to foul due to biofilm or precipitate coating in water.

Despite our best effort to physically minimize fouling by shortening the time of exposure of the optics to water, significant to severe fouling was still observed after two weeks in the field. The concentrations calculated by the instrument using the manufacturer's 'Global Calibration' were unreliable and essentially worthless without a local calibration. The Partial Least Square Regression technique used to locally calibrate the absorbance spectra with concentrations was able to generate acceptable results for nitrate, DOC and TDN, but only for the watershed for which least fouling was observed. This came at the thanks to two-week maintenance and thorough cleaning of the optics, and rigorous, iterative local calibration process.

To our knowledge, this may be the first study that reports that fouling is a major issue and that even chemometrics cannot correct for. The exact reasons for extreme fouling are not exactly known but the highly reduced conditions observed in the ditches (visible iron bacteria biofilm coating all surfaces all year long) are most likely the reason for this. Installing optical probes in these environments may thus lead to the same level of fouling and risk of yielding unusable data.

For the one watershed that offered reliable continuous data, the continuous concentrations captured a more detailed picture of concentration trends compared with less frequent discrete sample analysis alone, particularly during events when changes occur rapidly. The uniqueness of hydraulic functioning of artificially drained flat lands provides a unique opportunity to enrich our understanding of nutrient export in water. In particular, the ‘dilution’ and ‘concentration’ effects observed for DOC and nitrate concentrations, confirm the roles of the near stream zone of the soil and landscape, and, of the role of the organic horizon located further away from the natural drainage outlet to generate DOC and nitrate loads. Our observations, although opposite of those in upland watersheds for DOC for low water table conditions, suggests in a unique way that the organic horizon of upland watersheds may play an important role in the transport of DOC and nitrate in watersheds.

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CHAPTER 4: Modeling hydrology in upland forested watersheds in the southeastern United States using APEX

4.1 Introduction

A watershed scale study was conducted in the southeast United States to evaluate the environmental effects of large-scale forest bioenergy crop production system. The goal was to utilize these results to optimize intercropping systems in a manner that protects the important ecosystem services provided by forests while contributing to the development of a sustainable and economically-viable biomass industry in the southeastern United States. Along with evaluating measured hydrology and water quality data, one of the objectives was to test an existing watershed scale model to evaluate environmental sustainability of intercropping switchgrass with loblolly pine.

This chapter specifically focuses on the modeling objectives of the study. A hydrology and water quality study was conducted on four upland watersheds in Greene County, Alabama to evaluate the sustainability of intercropping switchgrass with loblolly pine trees for timber and biofuel production. A paired watershed approach was used with a conventional pine control and three treatments: switchgrass intercropping with thinned pine, switchgrass intercropping with replanted pine, and switchgrass monoculture. Hydrology and water quality data were collected for five years including a two-year pretreatment period, a one-year treatment period (site preparation), and a two year established period. The data collected were used to evaluate the ability of the Agricultural Policy/Environmental eXtender (APEX) model to simulate the hydrology and sediment export of four watersheds.

The APEX model can be used to assess the hydrology of a variety of land management practices at the small watershed scale. The model simulates the hydrology and nutrient and sediment loading from agricultural, silvicultural and natural land uses typical of rural landscapes. Field management capabilities include tillage, fertilization, and planting methods for a wide variety of crops in addition to various management practices to reduce erosion and nutrient loss. Each watershed is subdivided into smaller drainage areas, assumed to each be homogeneous in soil, land use, management, and weather. The Environmental Policy Integrated Climate (EPIC) model was used as the basis for the field simulations of APEX. In addition to the EPIC functions of weather simulation, hydrology, erosion-sedimentation, nutrient cycling, pesticide fate, crop growth, soil temperature, tillage, economics, and plant environment control, APEX can route water, sediment, nutrients, and pesticides over land and through channels to the watershed outlet. Loads of sediment, nitrogen, phosphorous, and pesticides can be estimated for each subarea and at the watershed outlet. The complete theoretical documentation of the model is available in Williams et al. (2012). (Williams et al., 2012).

APEX is a highly detailed and flexible model capable of simulating complex physical, chemical and biological processes resulting from hydrological, soil, plant, weather, and management characteristics (Williams, 1990). Water and water borne constituents from fields across a varied landscape are routed to the watershed outlet. This allows for comparison to data measured at the outlet. It offers several hydrological outputs (e.g., water yield, evapotranspiration [ET], soil water content, percolation, surface runoff, vertical and lateral subsurface flow, return subsurface flow) as well as simulated crop characteristics (e.g., crop biomass, leaf area index, rooting depth, crop height) for up to five crops. The model has been designed for upland watersheds, similar to the experimental sites in Alabama and Mississippi. Calibration and validation results from several studies have shown the usefulness of APEX for plot, field, and small watershed scales (Gassman et al., 2006; Mudgal et al., 2010; Saleh et al., 2004; Tuppad et al., 2009; Wang et al., 2007; Wang et al., 2008; Wang et al., 2009; Williams et al., 2006; Yin et al., 2009).

The multi-subarea capability allows for the consideration of heterogeneities within a watershed such as variations in land cover, soil type, and management practices. This multi-subarea feature is an improvement from the EPIC model and has allowed for simulations of smaller-scales (i.e., field and landscape), which is ideal for the experimental watersheds in Alabama. Another advantage of APEX is that it can interface with ArcGIS, which allows for ease of subarea delineation using a digital elevation model (DEM) and overlaying watershed boundaries, stream network, and soil map. The ArcGIS interface can also be used to obtain necessary information for editing input files such as area, slope, and stream lengths, unique to each subarea.

APEX allows for a number of weather inputs including temperature, precipitation, wind speed, relative humidity, and radiation to calculate ET (with five available options for calculating ET). The default calculation of potential ET uses the Penman-Monteith equation. Detailed input of layered soil data (i.e., hydrologic soil group, field capacity, saturated conductivity, lateral hydraulic conductivity) enables a more accurate representation of the stratified soil that exists throughout the watershed. The detailed operation schedule inputs include land use number, the time of operation (daily), identification numbers specific to the operation (e.g., plant, offset rip, disk, harvest), piece of equipment used and the crop type, the time from planting to harvest, among other factors.

The crop growth model in APEX is derived from the ALMANAC model (Kiniry, 1992). The model calculates increases in crop biomass as a function of intercepted radiation and radiation use efficiency. Intercepted radiation depends on leaf area index which is a function of heat units, crop stress, and crop development stage. Both pine and switchgrass are included as possible crop types with associated physical parameters already built into the model including optimal and minimal temperatures for plant growth, fraction of growing season when leaf area declines, maximum crop height, maximum rooting depth, and crop category number (i.e., perennial). Each of these physical parameters may be adjusted if necessary. Additionally, APEX has been modified for forestry applications by including rainfall interception by canopy, litter, subsurface flow, nutrient movement, and routing enrichment ratios (Saleh et al., 2004).

APEX has been used to predict the hydrology and water quality impacts of converting row crops to switchgrass in Indiana (Feng et al, 2015) and the high plains of Texas (Chen et al., 2016). Input parameters for switchgrass were derived from field data using the ALMANAC model (Kiniry et al., 2005) or the SWAT model (Trybula et al., 2015) which is based on

ALMANAC. Results of the simulation studies showed that converting row crops to switchgrass would decrease water yield, erosion, and nitrogen and phosphorus loading in the case of corn conversion (Feng et al, 2015) and would reduce surface runoff in the case of cotton conversion (Chen et al., 2016). While beneficial environmental impacts can occur when row crops are converted to switchgrass, the environmental impacts of converting managed forest to switchgrass or switchgrass intercropped with pine trees are not certain since the quantity and quality of water draining from forests is not much different than that draining from natural lands. If APEX can accurately simulate the hydrology and water quality of converting conventional forest to switchgrass or intercropped switchgrass, then it can be a useful tool for evaluating the sustainability of this potential land use change. The objectives of this modeling study were to evaluate the effectiveness of APEX in simulating stream outflow and sediment yield for an intercropping scenario by (1) evaluating sensitive parameters for calibrating hydrology in these upland watersheds; (2) identifying the weaknesses and strengths of the model and (3) evaluating the effect of the errors, i.e., what is the nature of the error and how is it affecting prediction.

4.2 Methods

Study site and watershed setup in ArcGIS

The four watersheds modeled in this study were located in Greene County, Alabama, United States. The watershed descriptions are given in the previous chapter and are summarized in Table 4.1. These watersheds were divided into subareas based on a digital elevation model

(DEM), stream network, soil type, and land use using ArcMap. An automatic subarea delineation was generated using ArcAPEX using the DEM and stream network as a first approximation. The boundaries were then manually adjusted to account for particular land features (i.e., roads and windrows) identified in satellite images (Figure 4.2 to Figure 4.5). The various subareas allowed for a more heterogeneous representation of the overall watershed given that each subarea is individually homogenous in climate, soil, land use, and topography. The existing stream network was manually extended into each subarea in order that all subareas would be hydrologically linked to the outlet. Each watershed had a stream management zone (SMZ), which was an undisturbed buffer zone of brush and deciduous trees on either side of the main channel. Additionally, each watershed contained at least one subarea that remained as mature pine (i.e., subarea 3 in watershed GR1; subareas 2 and 12 in GR2; subarea 3 in GR3; and subareas 3 and 11 in GR4).

Table 4.1. Watershed area and treatments in Greene County, Alabama, USA.

Watershed	**Area (ha)**	**Average Elevation (m)**	**# APEX Subareas**	**Land Cover (Treatment)**
GR1	11.3	81.9	6	Young pine (control)
GR2	25.1	83.8	16	Intercropped, thinned pine
GR3	24.4	85.5	20	Intercropped, replanted pine
GR4	16.5	86.5	14	Switchgrass only

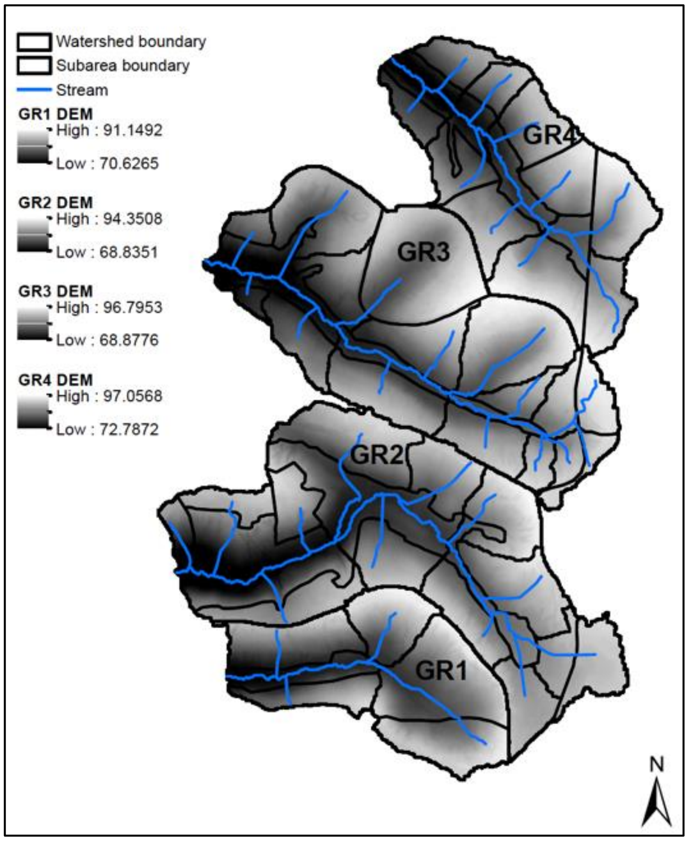

Figure 4.1. Digital elevation model (DEM), manually delineated stream network, and delineated subareas for the four watersheds (GR1, GR2, GR3, GR4) modeled in Greene County, Alabama.

Figure 4.2. Aerial image of watershed GR1 (young pine control) with manually delineated stream network (cyan) and subarea boundaries (red), labeled 1 through 6.

Figure 4.3. Aerial image of watershed GR2 (thinned, intercropped) with manually delineated stream network (cyan) and subarea boundaries (red), labeled 1 through 16.

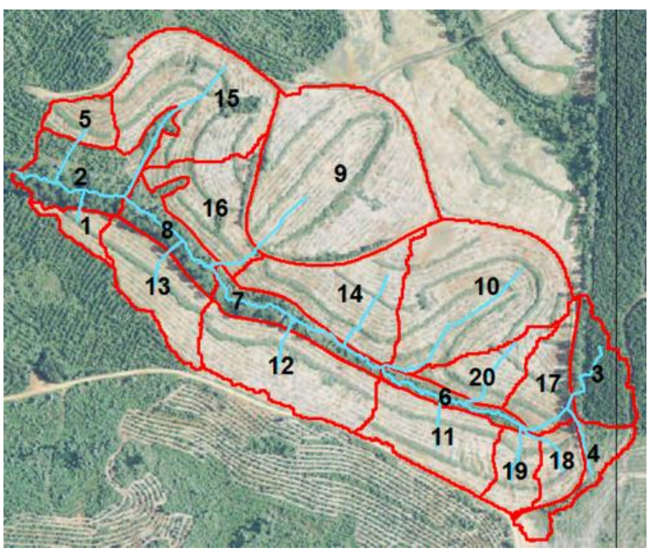

Figure 4.4. Aerial image of watershed GR3 (intercropped, replanted) with manually delineated stream network (cyan) and subarea boundaries (red), labeled 1 through 20.

Figure 4.5. Aerial image of watershed GR4 (switchgrass only) with manually delineated stream network (cyan) and subarea boundaries (red), labeled 1 through 14.

Subarea setup

The initial subarea input files to run the model were generated using ArcAPEX and the automatic subarea delineation. The text files were then manually edited to calibrate the model. The subarea file was adjusted to properly represent the APEX routing mechanism. For the routing mechanism, a negative area causes information in the subarea to be added to another subarea before entering the downstream subarea. The subarea file for each watershed was edited, beginning with editing channel lengths (CHL) and reach channel lengths (RCHL), by manually checking these lengths in ArcGIS. For downstream subareas, the CHL has to be greater than the RCHL. For these subareas where ArcAPEX did not calculate these lengths correctly, the measured RCHL (using measure tool in ArcGIS) and a slightly larger value for CHL were manually input.

Control File inputs

The control file contains information for the number of simulation years, the beginning of the simulation (i.e., 2005 for this simulation), the desired time interval of output (i.e., daily for this simulation), and other input parameters. The default Penman-Monteith was used for the potential ET equation. The default CN estimate of Q was used for runoff estimation. The floodplain saturated hydraulic conductivity (FPSC) was set at 30 mm h^{-1} for all watersheds and this was not adjusted during calibration. The maximum groundwater storage (mm, GWSO) was set as 0. The groundwater residence time in days (RFTO) was set as 10 days. Return Flow/(Return Flow + Deep Percolation) (RFPO) was set in the control file and in the soil files at the uppermost limit of 0.99.

Daily weather input

The weather input is the main driver in accurately simulating the hydrology. Daily weather data sufficient to use the Penman-Monteith equation to calculate potential ET were collected on the site near watershed GR4. Measured weather parameters were: average incoming solar radiation (MJ m^{-2}), air temperature (°C), precipitation (mm), relative humidity (%), and average wind speed (m s^{-1}). The raw weather data was obtained at a 15-minute interval and transformed into a daily timestep before supplying it to the model. For the necessary warmup period for APEX simulation, 2005 to 2010, supplemental daily weather data was obtained from Starkville, Mississippi which was the nearest weather station that provided all necessary weather parameters including solar radiation. There were some periods of missing weather data. For these dates, the model filled in the missing data.

Operation schedules

The various operation schedules of the four watersheds were simulated within APEX. In the operation schedule the following inputs are specified: the time of operation, the actual operation (e.g., plant, harvest, clearcut, fertilize), the crop (e.g., pine, range, switchgrass), and the land use number. Land use number and the hydrologic soil group are used to determine the curve number and therefore greatly impact surface runoff. The land use numbers used in the simulation ranged from 27 to 29 for pine; 24 for range; and 23 for switchgrass. For the planting operation, the potential heat units (PHU) and plant population (plants or final tiller number m^{-2}) were also be specified. The PHU greatly influence crop growth as these are the total number of growing degree days required for the plant to grow from emergence to maturity. Due to a necessary five-year warm up period, operations were input starting in 2005 in order to begin calibrations in 2010. These operations during the warm-up period included planting a crop and some other obligatory annual operation, which for our case was driving a truck over the land.

Some of the actual operations were modified in the simulation in order to simplify the simulation and obtain more realistic crop growth and hydrology. In addition to pine and switchgrass, range was also grown in all watersheds except GR1 to act as a filler before the planting of pine and switchgrass or to represent understory growth. Only pine was grown in watershed GR1 (young pine, control).

The following operations were used in GR1: planting pine, driving a truck, clearcut, and offset rip; in GR2: planting range, driving a truck, offset rip, planting pine, thinning pine, applying herbicide on the range, disking and planting switchgrass, and harvesting switchgrass; in GR3: planting range, planting pine, driving a truck, clearcut pine, kill pine, harvest range, kill range, offset rip, disking and planting switchgrass, and harvesting switchgrass; for GR4: disking and planting switchgrass, driving a truck, planting pine, clearcut pine, kill pine, harvest switchgrass, planting range, and harvesting range. For watershed GR4 two separate operation schedules were used for the calibration and validation periods. In order simulate proper switchgrass growth during the validation period (2012-2014), the switchgrass had to be planted during the warmup period (from the beginning of the simulation in 2005). During the calibration period (2010-2012) for watershed GR4 only pine and a range were simulated. All other input files for GR4 remained the same for both calibration and validation periods.

Table 4.2. Actual operation schedule for each watershed simulated in Greene County, Alabama.

	Date	**Operation**
GR1	Mar 2008	Previous stand harvested
	Nov 2008	Site preparation (offset rip)
	Feb 2009	Planted pine (1077 trees ha^{-1})
	Sep 2012	Herbicide sprayed
GR2	Mar 2008	Previous stand harvested

Table 4.2. Continued.

	Nov 2008	Site preparation (offset rip)
	Feb 2009	Planted pine (1077 trees ha^{-1})
	Apr 2012	Herbicide sprayed
	May 2012	Disking and switchgrass planting
	May 2013	Disking and switchgrass planting
	Mar 2014	Fertilization
	June 2014	Herbicide sprayed
	Oct 2014	Switchgrass harvest
GR3	Mar 2006	Planted pine (1077 trees ha^{-1})
	Sep 2012	Herbicide sprayed
	Oct 2012	Sheared trees, piled in windrows
	Nov 2012	Site preparation (offset rip)
	Feb 2013	Planted pine (1077 trees ha^{-1})
	May 2013	Switchgrass sown
	Mar 2014	Fertilization
	June 2014	Herbicide sprayed
	Oct 2014	Switchgrass harvest
GR4	Feb 2007	Planted pine (1077 trees ha^{-1})
	Mar 2012	Sheared trees, piled in windrows
	Apr 2012	Herbicide sprayed
	May 2012	Disking and switchgrass planting
	May 2013	Disking and switchgrass planting
	Mar 2014	Fertilization
	June 2014	Herbicide sprayed
	Oct 2014	Switchgrass harvest

Soil inputs

Two different soil files were used for each watershed, one for the SMZ and one for all other subareas. The soil files were set up with three soil layers at 0.15, 0.30, and 4 m depths, with various characteristics for each layer. Table 4.3 provides the soil characteristics that were adjusted for the various watersheds including soil hydrologic group (HSG), saturated hydraulic conductivity (SATC), lateral conductivity (HCL), and sand (SAN) and silt (SIL) content. The soil used in the treatment watersheds was also applied to the few mature pine subareas within each watershed. A different soil file was used to represent the SMZ soil. The sand, silt, and the organic carbon (WOC) contents in the top soil layer were further adjusted after hydrology calibration for calibrating sediment output.

Table 4.3. Soil characteristics (soil hydrologic group [HSG], saturated hydraulic conductivity [SATC], lateral conductivity [HCL], sand [SAN], silt [SIL] content) for different subareas (treatment or stream management zone [SMZ]) within watersheds (GR1, GR2, GR3, GR4).

Watershed	**Subarea type**	**HSG**	**Depth to bottom of layer** (m)	**SAN** (%)	**SIL** (%)	**SATC** (mm h^{-1})	**HCL** (mm h^{-1})
GR1	Treatment	3	0.15	78	15	15	3
			0.30	55	17	0.001	10
			4	48	2	0.00001	10
	SMZ	3	0.15	75	20	1	10
			0.30	55	17	0.0001	10
			4	48	2	0.00001	10
GR2	Treatment	3	0.15	78	15	50	10
			0.30	55	17	0.001	10
			4	48	2	0.00001	10
	SMZ	3	0.15	75	20	1	10
			0.30	55	17	0.0001	10
			4	48	2	0.00001	10
GR3	Treatment	3	0.15	68	20	10	9
			0.30	55	28	2	4
			4	48	7	1	1
	SMZ	2	0.15	68	20	2	10
			0.30	55	28	2	8
			4	48	7	1	1
GR4	Treatment	3	0.15	68	20	20	8
			0.30	55	17	4	6
			4	48	7	1	1
	SMZ	2	0.15	68	20	2	10
			0.30	55	28	2	8
			4	48	7	1	1

PARM file adjustments

Most parameters in the PARM file did not have an effect on water yield except for the subsurface flow factor (PARM 90). This parameter needed to be increased from the original value of 2 to values ranging from 70 to 100, since a significant amount of water was suspected of bypassing the flumes via groundwater seepage. Increasing PARM 90 allocates more flow to subsurface flow and quick return flow. Other PARM values that were adjusted and had some influence on water yield are listed in Table 4.4.

Table 4.4. Parameters influencing hydrology that were adjusted in the APEX PARM file and final values used for each watershed.

PARM(n)	**Description**	**GR1**	**GR2**	**GR3**	**GR4**
20	Runoff curve number initial abstraction	0.30	0.20	0.40	0.20
25	Exponential coefficient used to account for rainfall intensity on curve number	1.7	0.0	1.5	0.0
40	Groundwater storage threshold				
42	SCS curve number index coefficient	1.6	1.5	1.5	2.5
90	Subsurface flow factor	100	85	70	100

Crop file adjustments

In the switchgrass watershed (GR4), there was land cover change between the calibration and validation periods from pine to switchgrass. Separate operation schedules in which the crop type is specified had to be used in order to adequately simulate the switchgrass growth. Crop parameters including radiation use efficiency or biomass-energy ratio (WA in CROP.DAT) and the fraction of growing season when LAI begins to decline (DLAI in CROP.DAT) had to be adjusted. Similar to crop parameter adjustments made by Trybula et al. (2015), WA was reduced to 12.0 from the default value 45.0; DLAI was increased to 0.60 from the default value of 0.40 for switchgrass.

Model performance assessment

The model parameters were calibrated separately for all four watersheds (GR1 through GR4) with hydrological data from Mar 4 2010 to Feb 29 2012 and validated with data from the Mar 1 2012 to Dec 1 2014. The model performance was evaluated based on graphical comparisons of predicted and measured cumulative daily streamflow, as well as Nash Sutcliffe efficiency (NSE), percent bias (PBIAS), the ratio of the root mean square error to the standard deviation of measured data (RSR), and R^2 with regards to simulated and measured daily, monthly, and annual water yield from the watershed outlet. The graphical comparisons and monthly NSE were primarily considered during calibration. The model performance was assessed based on evaluation techniques and performance ratings recommended by Moriasi et al. (2007) (Table 4.5).

Table 4.5. Performance rating recommendations for statistics (Nash-Sutcliffe efficiency [NSE] and percent bias [PBIAS]) for a monthly time step of streamflow (modified from Moriasi et al., 2007).

Model Performance Rating	**NSE**	**PBIAS (%)**
Very good	0.75 < NSE < 1.00	PBIAS < ±10
Good	0.65 < NSE < 0.75	±10 < PBIAS < ±15
Satisfactory	0.50 < NSE < 0.65	±15 < PBIAS < ±25
Unsatisfactory	NSE < 0.50	PBIAS > ±25

4.3 Results and Discussion

Young Pine Control Watershed

Calibrating the model to match the daily flow values was difficult and the best results yielded a unsatisfactory NSE of 0.47 and a very good PBIAS of 0.5% during calibration (Figure 4.6). Daily NSE were lower as expected given that the Curve Number method of runoff estimation was not originally developed for calculating a daily water balance. Errors in daily flow values were due to under prediction of low flows; however, higher flow predictions were more accurate (Figure 4.7, Figures H.5 to H.16 in Appendix H). Predicted monthly flows were better than daily values with a very good NSE of 0.83 during calibration. Larger errors in predicted monthly flows occurred at the beginning of the period and toward the end of the period. During the validation period, simulated daily flow improved with a good daily NSE of 0.65 and a very good PBIAS of -8.5%. As with the calibration period, the errors were due to under prediction of low flows. Statistics for monthly flows (very good NSE=0.82 and very good PBIAS=-8.6%) were improved for the validation period as well, but still there were larger errors occurring from June 2013 onward. The cause of these larger errors is unclear given that there were no operations on the control watershed. The NSE values reported for this control watershed were low compared to three undisturbed forested watersheds in Texas, where Saleh et al. (2004) reported very good NSE values of 0.84, 0.85, and 0.88 for daily flow simulated with APEX.

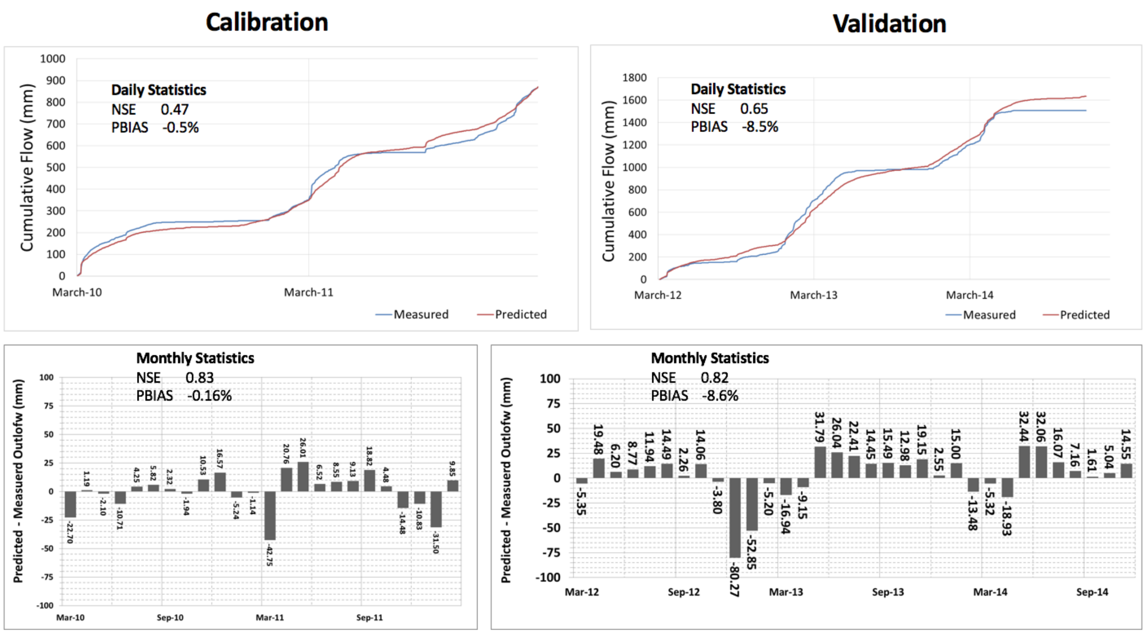

Figure 4.6. Predicted and measured cumulative daily stream outflow (mm) and net differences between measured and predicted monthly outflow during calibration and validation periods for watershed GR1 (young pine control) in Greene County, Alabama. Daily and monthly Nash-Sutcliff efficiency (NSE) coefficients and percent bias (PBIAS) for each period are also shown.

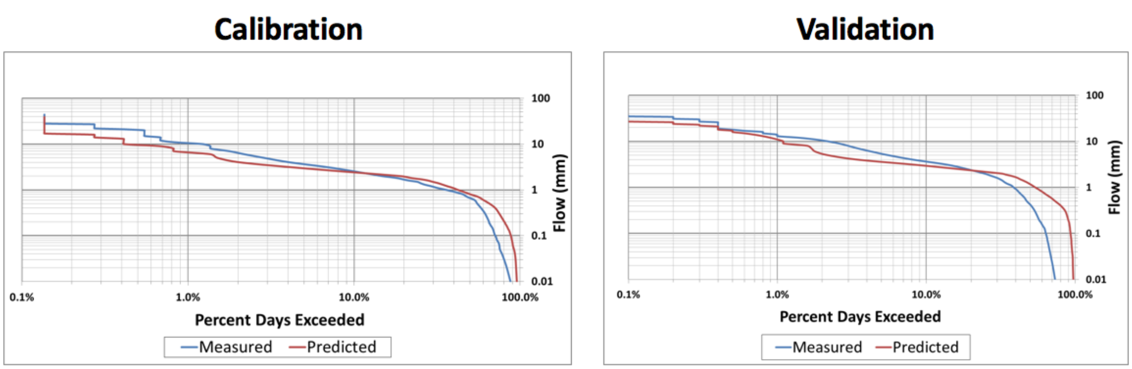

Figure 4.7. Flow exceedance curves for predicted and measured daily stream outflow during calibration and validation periods for watershed GR1 (young pine control) in Greene County, Alabama.

Intercropped-Thinned Watershed

Calibrating the model to match the daily flow values was difficult and the best results yielded a good NSE of 0.72 and a very good PBIAS of -0.1% (Figure 4.8). Errors in daily flow values were due to under prediction of low flows; however, higher flow predictions were more accurate (Figure 4.9, Figures H.17 to H.23 in Appendix H). Predicted monthly flows were better than daily values with a very good NSE of 0.74. The NSE for daily flows was reduced to a satisfactory 0.58 and the PBIAS was improved to a very good -3.1% during the validation period. As with the calibration period, the errors were due to under prediction of low flows. Statistics for monthly flows (very good NSE=0.92 and very good PBIAS=-1.3%) were also improved for the validation period. The largest error occurred in January 2013, but there were no particular operations that would have contributed to the timing of larger errors.

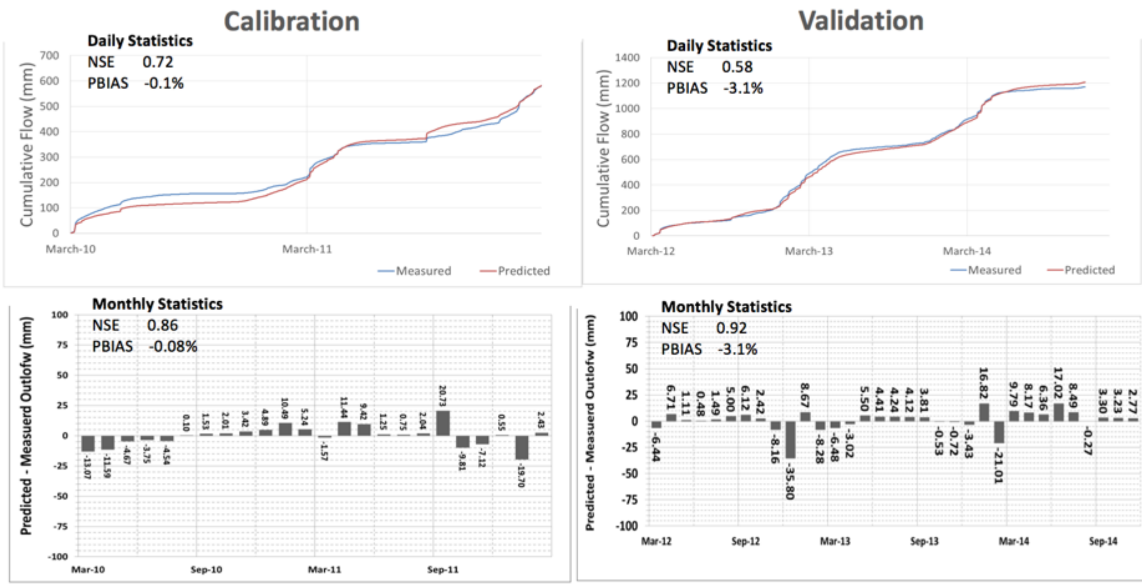

Figure 4.8. Predicted and measured cumulative daily stream outflow (mm) and net differences between measured and predicted monthly outflow during calibration and validation periods for watershed GR2 (intercropped, thinned) in Greene County, Alabama. Daily and monthly Nash-Sutcliff efficiency (NSE) coefficients and percent bias (PBIAS) for each period are also shown.

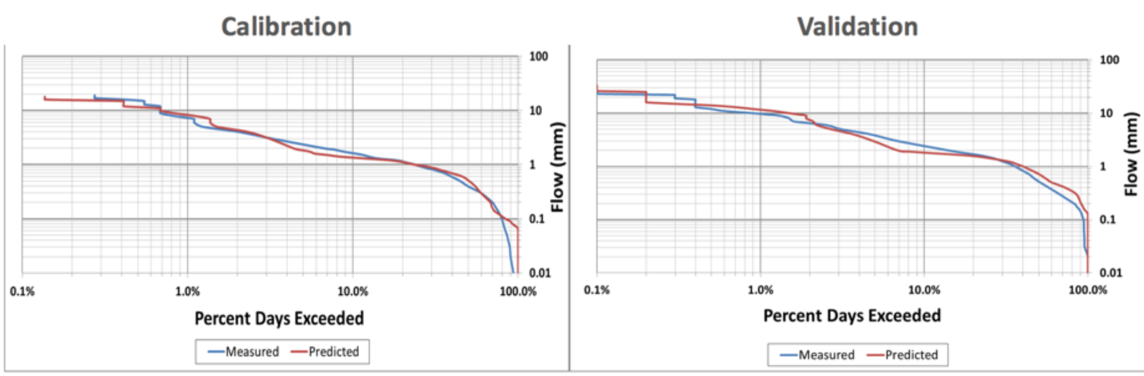

Figure 4.9. Flow exceedance curves for predicted and measured daily stream outflow during calibration and validation periods for watershed GR2 (intercropped, thinned) in Greene County, Alabama.

Intercropped-Replanted Watershed

Calibrating the model to match the daily flow values was difficult and the best results yielded an unsatisfactory NSE of 0.39 but a very good PBIAS of 6.0% (Figure 4.10). Errors in daily flow values were due to under prediction of low flows; however, higher flow predictions were more accurate (Figure 4.11, Figures H.24 to H.31 in Appendix H). Predicted monthly flows were better than daily values with a good NSE of 0.74. Larger errors in predicted monthly flows occurred at the beginning of the period and toward the end of the period. The NSE for daily flows was improved to a satisfactory 0.51 and a very good PBIAS of -1.5% during the validation period. As with the calibration period, the errors were due to under prediction of low flows. Statistics for monthly flows (very good NSE=0.92 and very good PBIAS=-1.3% were also improved for the validation period with larger errors occurring from August 2012 until March 2013 and for March and April 2014. Some operations may have impacted these results such as the offset rip that occurred in November 2012 and the tree planting in February 2013. Fertilizer was applied March 2014, but likely did not impact flow. For three forested watersheds in Texas that underwent similar operations of clearing, shearing, windrowing, and burning, Saleh et al. (2004) reported good to very good daily NSE values of 0.74, 0.85, and 0.85 for daily storm runoff. For three forested watersheds that underwent clearing, roller chopping, and burning, they reported good to very good daily NSE values of 0.74, 0.75, and 0.87 (Saleh et al., 2004). For the Tonk Creek and Wasp Creek watersheds, Tuppad et al. (2009) reported monthly NSE values of 0.55 and 0.63 for calibration and validation, respectively, for monthly stream flow.

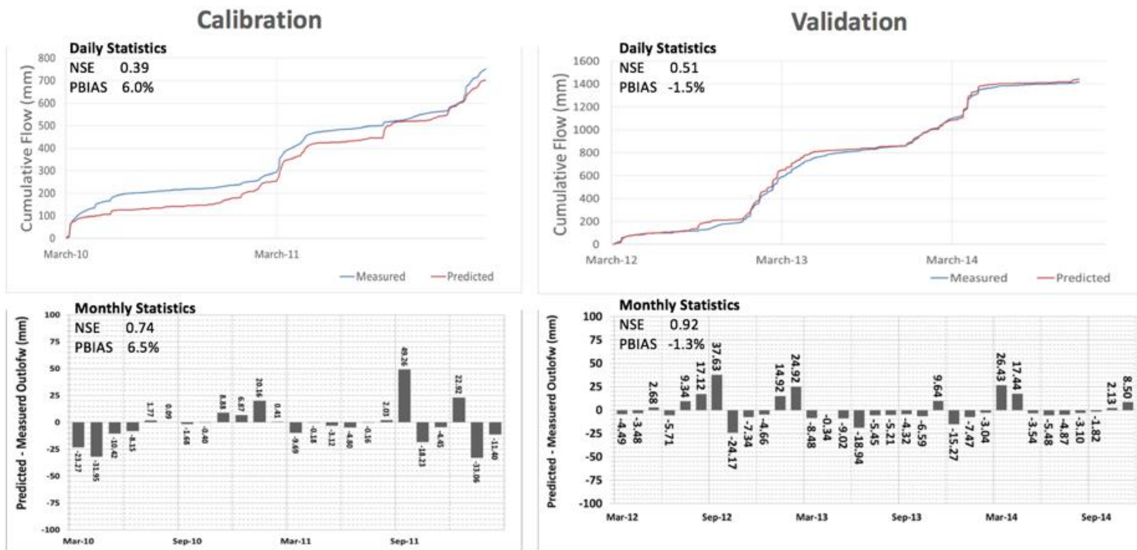

Figure 4.10. Predicted and measured cumulative daily stream outflow (mm) and net differences between measured and predicted monthly outflow during calibration and validation periods for watershed GR3 (intercropped, replanted) in Greene County, Alabama. Daily and monthly Nash-Sutcliff efficiency (NSE) coefficients and percent bias (PBIAS) for each period are also shown.

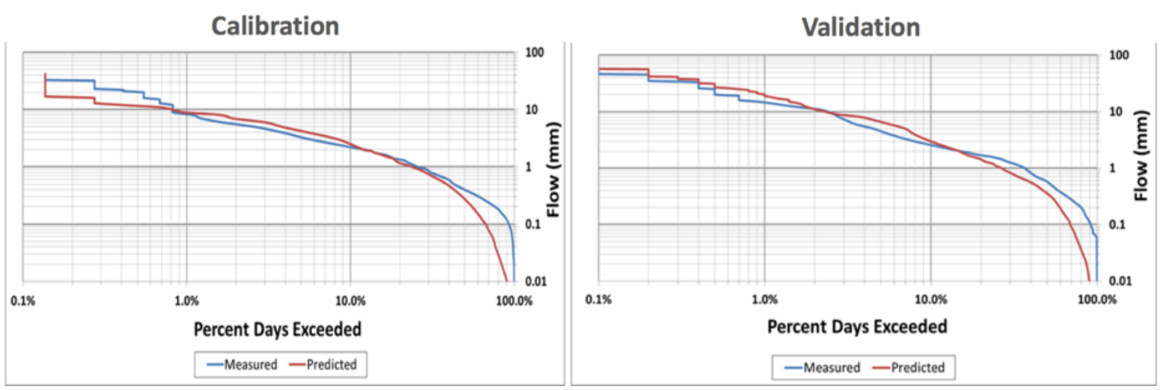

Figure 4.11. Flow exceedance curves for predicted and measured daily stream outflow during calibration and validation periods for watershed GR3 (intercropped, replanted) in Greene County, Alabama.

Switchgrass Watershed

Calibrating the model to match the daily flow values proved to be the most difficult for the switchgrass watershed and the best results yielded a satisfactory NSE of 0.52 and a very good PBIAS of -6.9% (Figure 4.10). Errors in daily flow values were due to under prediction of low flows; however, higher flow predictions were more accurate (Figure 4.13, Figures H.32 to H.40 in Appendix H). Predicted monthly flows during calibration were better than daily values with a very good NSE of 0.92 and very good PBIAS of -6.6%. The NSE for daily flows was reduced to an unsatisfactory 0.39 and an unsatisfactory PBIAS of -35% during the validation period. Although there were errors still due to under prediction of low flows, it is likely that the change in land cover during the validation period greatly influenced the larger error during this period. Statistics for monthly flows (good NSE=0.69 and unsatisfactory PBIAS=-34%) were also improved for the validation period with larger errors occurring from February to June 2013 and February to June 2014.

The simulated operation schedules were somewhat modified from the actual operation schedule in order to achieve a more accurate representation of crop growth. Although the switchgrass growth was being reasonably simulated for GR4 based on LAI and biomass predictions, the predicted flow was still consistently over predicted by APEX during the validation period. Given that the vegetation between the calibration and validation periods for GR4 was so different (pine vs. switchgrass), parameters affecting switchgrass growth may not have been taken into account during the calibration period. Switchgrass was not planted until the validation period; therefore, a separate operation schedule was used for the validation period, in which switchgrass was the first crop planted during the warm-up period (with pine and range still included). For the operations schedule during the calibration period, range was planted first, followed by pine (switchgrass was excluded).

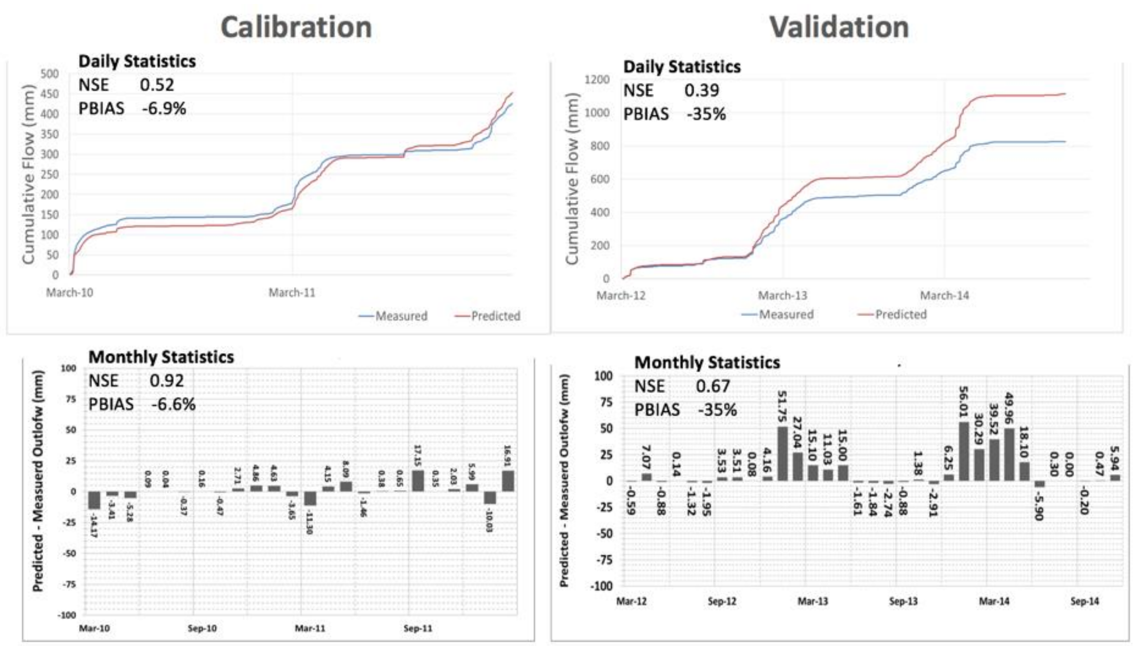

Figure 4.12. Predicted and measured cumulative daily stream outflow (mm) and net differences between measured and predicted monthly outflow during calibration and validation periods for watershed GR4 (switchgrass) in Greene County, Alabama. Daily and monthly Nash-Sutcliff efficiency (NSE) coefficients and percent bias (PBIAS) for each period are also shown.

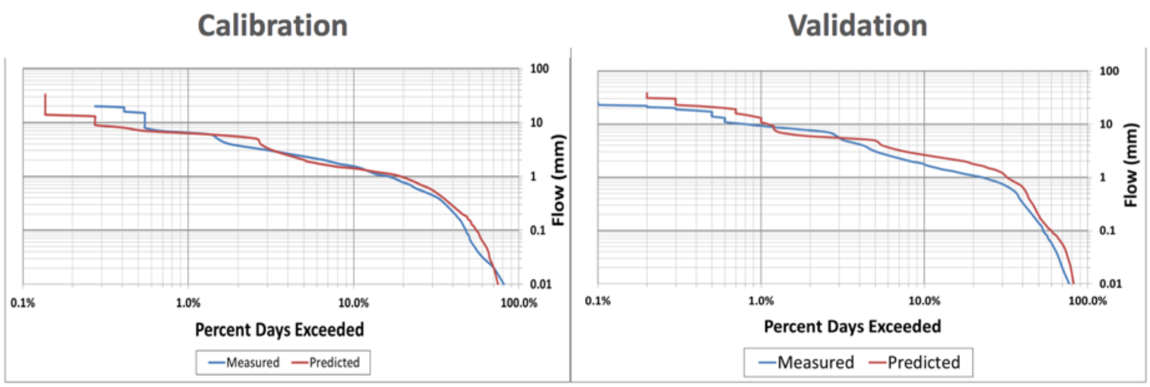

Figure 4.13. Flow exceedance curves for predicted and measured daily stream outflow during calibration and validation periods for watershed GR4 (switchgrass) in Greene County, Alabama.

Sensitive parameters

When calibrating hydrology in these upland watersheds, the subsurface flow factor (PARM 90) in the parameter file was one of the most sensitive parameters. By increasing this value to between 70 and 100 from the traditional value of 2 more flow was allocated to groundwater loss to more accurately represent the flow paths of these watersheds. PARM 20, 25, and 42 also had an impact on water yield. Other research has also shown the NRCS Curve Number index coefficient (PARM 42) to have an influence on water yield (Wang et al., 2006; Mbonimpa et al., 2015; Mudgal et al., 2010; Yin et al., 2009). The groundwater storage threshold (PARM 40) did not have an effect on water yield for the calibration of the watersheds reported in this article, but was found to have an influence in other studies (Wang et al., 2012). Wang et al. (2012) also found the following parameters to also have an influence on water yield: crop canopy-PET factor (PARM 1), the floodplain saturated conductivity (FPSC), maximum groundwater storage, and groundwater residence time, but these parameters were not calibrated for the watersheds in this study. These parameters may be adjusted in further calibrations of these watersheds. The most sensitive soil parameters were the soil hydrologic group (HSG), saturated hydraulic conductivity (SATC), lateral conductivity (HCL), sand (SAN) and silt (SIL) content. For sediment calibration, SAN, SIL, and organic carbon (WOC) contents in the top soil layer were sensitive (results given in Appendix H [Figure H.41; Table H.2]). Final input values of several parameters and equations used in this simulation are given in Appendix H (Table H.1).

Within the operation schedule, the land use number and potential heat units (PHU) for the crop were sensitive parameters, as reported by others (Wang et al., 2006; Wang et al., 2012; Yin et al., 2009). Specifically for switchgrass, crop characteristics (in the Crop File) including the radiation use efficiency (WA) and the fraction of the growing season when LAI starts to decline (DLAI) were sensitive parameters. Wang et al. (2012) reported the radiation use efficiency as a sensitive parameter for crop yield, but not water yield. Within the Soil file, the hydrologic soil group, saturated hydraulic conductivity, and lateral hydraulic conductivity had a slight influence on water yield, although bulk density did not. Similarly, Mudgal et al. (2010) also found saturated hydraulic conductivity affected water yield, but not bulk density. The return flow/(return flow + deep percolation) (RFPK in the Control File or RFP0 in the Soil File) was found to be influential on water yield, as also reported by Wang et al. (2006) and Wang et al. (2012).

Strengths and limitations of the model

Overall, APEX is able to simulate hydrology from upland forested watersheds well, with monthly NSE ranging from 0.74 to 0.92 during calibration and from 0.69 (GR4, switchgrass) to 0.92 during the validation period (Table 4.7). The model generally overestimated annual flow with percent differences in annual stream flow ranging from -11% to +40% (GR1), -5% to +26% (GR2), -13% to +10% (GR3), and -7.5% to +57% (GR4) (Table 4.6). The current simulations of outflow follow the general trends of measured flow; however, the model currently overestimates peak flow while underestimating base flow. This may be due to the timing of water loss to deep seepage and could possibly be adjusted by modifying inputs such as return flow/(return flow + deep percolation), although initial trials have failed to correct this. Another possible explanation for this may be an ET parameter causing base flow to be too low, namely the calculation of EVZ, the total potential soil water evaporation from the soil (plant evaporation calculated separately). The model also requires a "warm-up" period of at least five years prior to the beginning of measurements. Because of this, weather data from a more distant location was required as input during this period, although this may not have a significant impact on the calibration and validation periods.

Table 4.6. Measured and predicted cumulative streamflow (mm) and the respective percent differences from each watershed (GR1, GR3, GR3, GR4) in Greene County, Alabama.

	Year	**1**	**2**	**3**	**4**	**5**
		3/4/2010 - 2/29/2011	3/1/2011 - 2/29/2012	3/1/2012 - 2/29/2013	3/1/2013 - 2/29/2014	3/1/2014 - 12/1/2014
GR1	Measured	347	521	709	581	226
	Predicted	344	525	631	699	317
	Percent Difference	-0.9%	0.9%	11.0%	20.3%	40.0%
GR2	Measured	219	362	494	493	192
	Predicted	209	372	468	507	241
	Percent Difference	-4.5%	2.9%	-5.4%	2.7%	26.0%
GR3	Measured	291	460	596	588	246
	Predicted	253	449	653	540	255
	Percent Difference	-13.0%	-2.4%	9.5%	-8.2%	3.8%
GR4	Measured	177	249	368	339	127
	Predicted	164	290	446	471	199
	Percent Difference	-7.5%	16.6%	21.4%	39.1%	57%

Table 4.7. Summary of statistical values (Nash-Sutcliffe efficiency [NSE] and R^2) for simulated flow in four watersheds in Greene (GR) County, Alabama (GR1, GR2, GR3, GR4).

			GR1	**GR2**	**GR3**	**GR4**
Daily	*Calibration*	NSE	0.47	0.72	0.39	0.52
		PBIAS	-0.5%	-0.1%	6.8%	-6.9%
		RSR	0.73	0.53	0.78	0.70
		R^2	0.48	0.73	0.46	0.58
	Validation	NSE	0.65	0.58	0.51	0.39
		PBIAS	-8.5%	-3.1%	-1.5%	-34.9%
		RSR	0.59	0.65	0.70	0.78
		R^2	0.66	0.64	0.67	0.71
Monthly	*Calibration*	NSE	0.83	0.86	0.74	0.92
		PBIAS	-0.16%	-0.08%	6.47%	-6.6%
		RSR	0.41	0.37	0.51	0.29
		R^2	0.85	0.86	0.75	0.92
	Validation	NSE	0.82	0.92	0.92	0.69
		PBIAS	-8.6%	-3.05%	-1.26%	-34.0%

Table 4.7. Continued.

		RSR	0.43	0.29	0.28	0.56
		R^2	0.86	0.92	0.94	0.94
Annual	*Calibration*	NSE	0.99	0.99	0.93	0.67
		PBIAS	-0.16%	-0.08%	6.47%	-6.6%
		RSR	0.04	0.15	0.27	0.58
	Validation	NSE	0.78	0.95	0.93	0.21
		PBIAS	-8.6%	-3.11%	-1.27%	-34.0%
		RSR	0.47	0.39	0.26	0.89

The vegetation grown during the warm-up period and the order in which crops are planted in the operations schedule does impact the growth of other crops and how ET is calculated, particularly when intercropping is involved. Whatever crop is grown first typically becomes the dominant crop (when multiple crops are grown or intercropping occurs). Multiple simulations were generated to show the differences in ET caused by the order of planting multiple crops in an operation schedule. For example, Figure 4.14 shows ET and the heights of each crop (i.e., pine, range, and switchgrass) over the entire simulation period for one subarea in watershed GR3. One simulation was run in which the range (RNGE) was planted first (i.e., the first year of simulation) and a separate simulation was produced for which the only change made to the operation schedule was the order of which crop was planted first (i.e., pine was planted during the first year of simulation). This one change had a substantial impact on the ET calculation since the crop that is planted first becomes the dominant crop from which ET is calculated and the model only calculates one value of ET on a daily basis (or chosen time step) even for a multiple crop (i.e., intercropped) scenario. In this example, there are three crops simulated: pine, range, and switchgrass. The order in which they are first planted (either during warm-up period or later) influences the order in which they appear as either the first, second, or third crop. Additionally, killing operations (which follow clearcut) will impact which crop is first. For example, if the pine was originally the first crop, ET will be calculated from pine, but when it is clearcut ("killed"), then the next dominant crop (e.g., range or switchgrass) will become the first crop and ET will now be calculated from that crop.

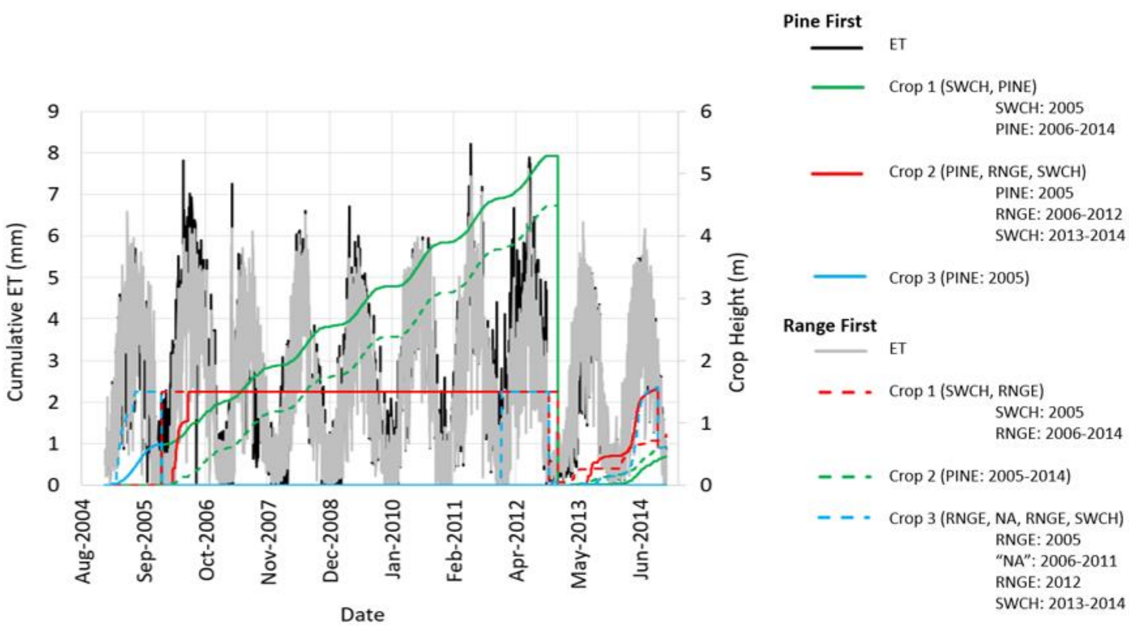

Figure 4.14. Example (watershed GR3; subarea 1) of different evapotranspiration (ET) simulated by two different operations schedules: (1) Pine was planted first and (2) range (RNGE) was planted first. The operation schedule in which range was planted first was the final operation schedule used for simulation.

As with any model, there are challenges to calibrating the model by "trial and error." As shown in this study and many others, there are many parameters that can influence water yield. Discerning which parameters have a greater influence than others is challenging as the value of one parameter may influence how another parameter influences output; therefore, the order in which values are changed may influence the final optimum value of a parameter. APEX is a particularly complex model with may parameters. Automatic calibration has been performed on APEX using the software Parameter Estimation (PEST) and Combined PEST and Trial-Error (CPTE), which have shown to improve calibration and validation of water yield simulated by APEX (Doherty, 2010; Mbonimpa et al., 2015). The CPTE is advantageous over PEST in that it allows for manual parameter adjustment to account for local conditions which may be missed by a purely automated parameter estimation (Mbonimpa et al., 2015).

Uncertainty in measured data

The measured flow data was obtained using two instruments which collected data at 2 and 3 min intervals. Due to the noisiness and drift of the raw data, it was manually corrected using AQUARIUS software, in which obvious outliers were removed, data gaps were filled, and drift was corrected by adjusting data to align with manual measurements. While the software did enable adequate data correction, there was room for human error or bias in both the data correction techniques and the manual measurements. Although great care was taken to collect hydrology data using two different automated instruments and biweekly manual measurements, and then correct the raw data, it is known that uncertainty can still exist in measured streamflow and water quality data in small watersheds (Harmel et al., 2006).

4.4 Conclusions

Overall, APEX was able to simulate hydrology from upland forested watersheds well, with monthly NSE ranging from 0.74 to 0.92 during calibration and from 0.69 (GR4, switchgrass) to 0.92 during the validation period. Simulations of outflow follow the general trends of measured flow; however, the model overestimated peak flow while underestimating base flow. Both intercropped sites performed better than the control (young pine) and the switchgrass only sites. Differences between measured and predicted annual stream flow were generally between ±10% for the intercropped sites, but higher for the control (young pine) and switchgrass sites, particularly during the last validation year (2014). Sensitive parameters for simulating hydrology included operation schedule inputs, particularly the order of crop planting within the operation schedule, the subsurface flow factor (PARM 90), radiation use efficiency and the fraction of the growing season when LAI begins to decline for switchgrass, hydrologic soil group, and saturated and lateral hydraulic conductivities. The order of crop planting within the operation schedules proved to be particularly important as this determines which crop becomes the dominant crop from which a single value of daily ET is calculated.

4.5 References

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APPENDICES

APPENDIX A: Absorbance spectra before and after cleaning s::can spectrophotometer lenses (seasonal examples in all watersheds [D0, D1, D2, D3])

A.1 Winter (2014 Jan 27)

Watershed D0

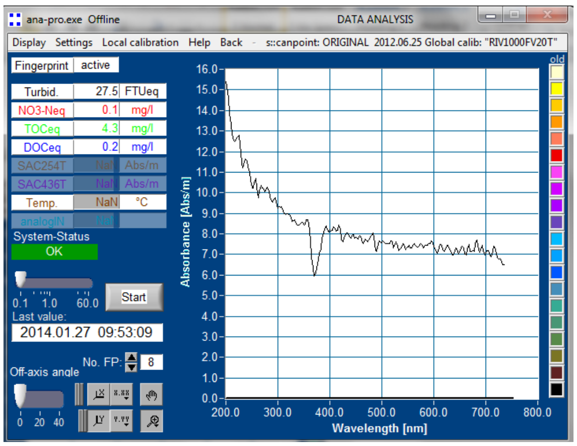

Figure A.1. Screenshot of absorbance spectra as a function of wavelength for watershed D0 before cleaning optics after operating two-weeks in the field without maintenance during the winter (2014 Jan 27).

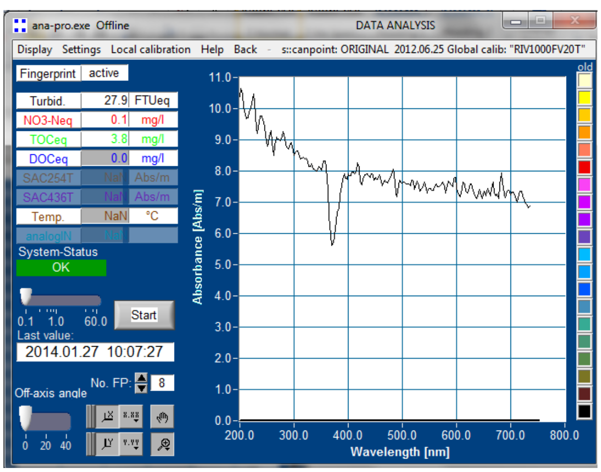

Figure A.2. Screenshot of absorbance spectra as a function of wavelength for watershed D0 after cleaning optics after operating two-weeks in the field without maintenance during the winter (2014 Jan 27).

Watershed D1

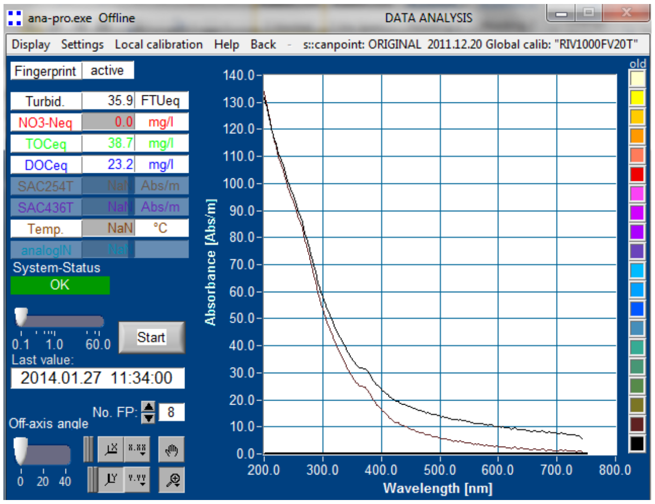

Figure A.3. Screenshot of absorbance spectra as a function of wavelength for watershed D1 before cleaning optics after operating two-weeks in the field without maintenance during the winter (2014 Jan 27).

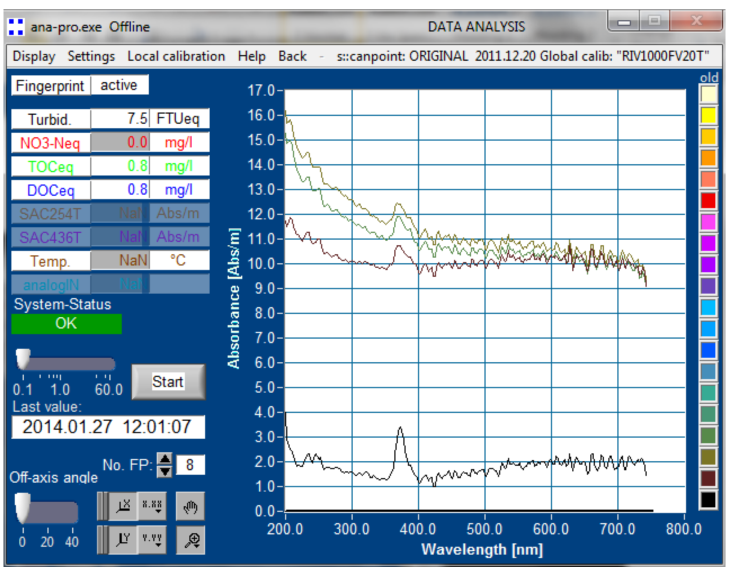

Figure A.4. Screenshot of absorbance spectra as a function of wavelength for watershed D1 after cleaning optics after operating two-weeks in the field without maintenance during the winter (2014 Jan 27).

Watershed D2

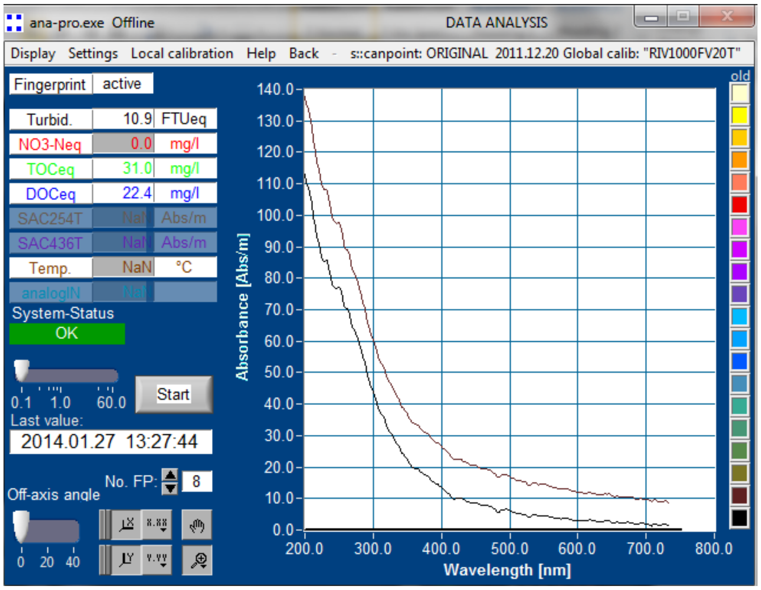

Figure A.5. Screenshot of absorbance spectra as a function of wavelength for watershed D2 before cleaning optics after operating two-weeks in the field without maintenance during the winter (2014 Jan 27).

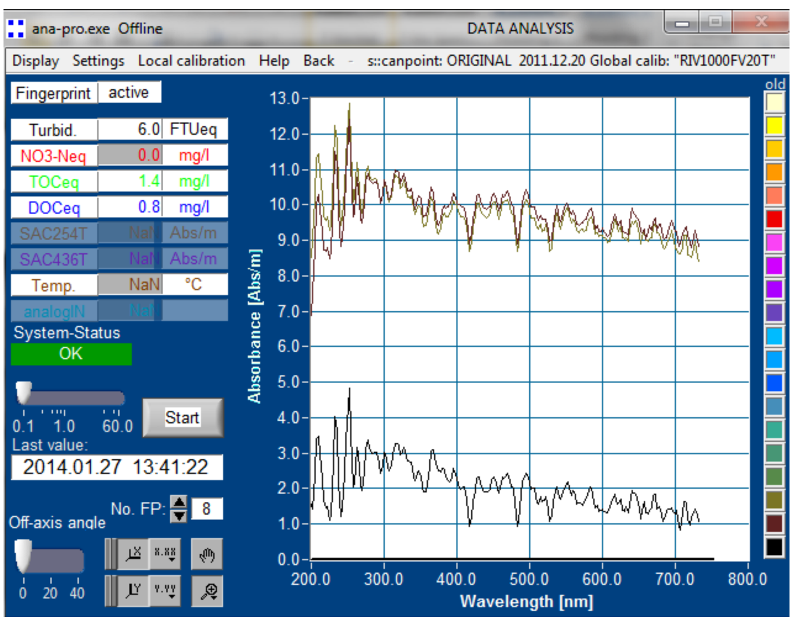

Figure A.6. Screenshot of absorbance spectra as a function of wavelength for watershed D2 after cleaning optics during field servicing visit during the winter (2014 Jan 27).

Watershed D3

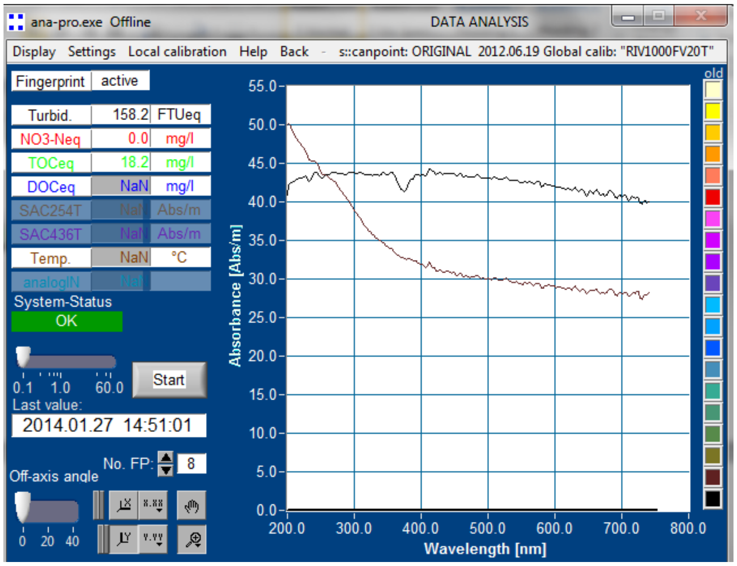

Figure A.7. Screenshot of absorbance spectra as a function of wavelength for watershed D3 before cleaning optics after operating two-weeks in the field without maintenance during the winter (2014 Jan 27).

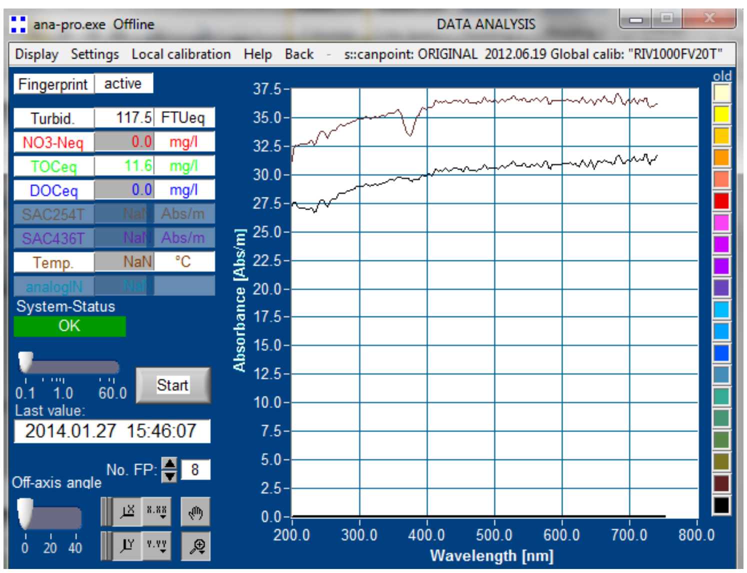

Figure A.8. Screenshot of absorbance spectra as a function of wavelength for watershed D3 after cleaning optics during field servicing visit during the winter (2014 Jan 27).

A.2 Spring (2014 Mar 21)

Watershed D0

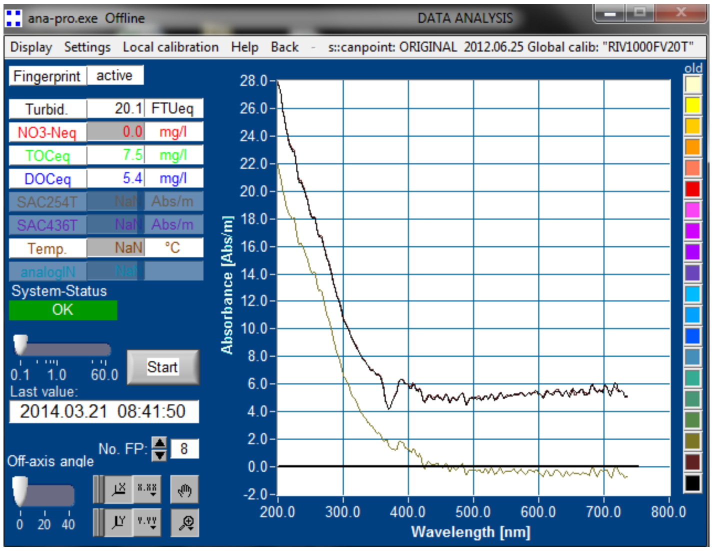

Figure A.9. Screenshot of absorbance spectra as a function of wavelength for watershed D0 before cleaning optics after operating two-weeks in the field without maintenance during the spring (2014 Mar 21).

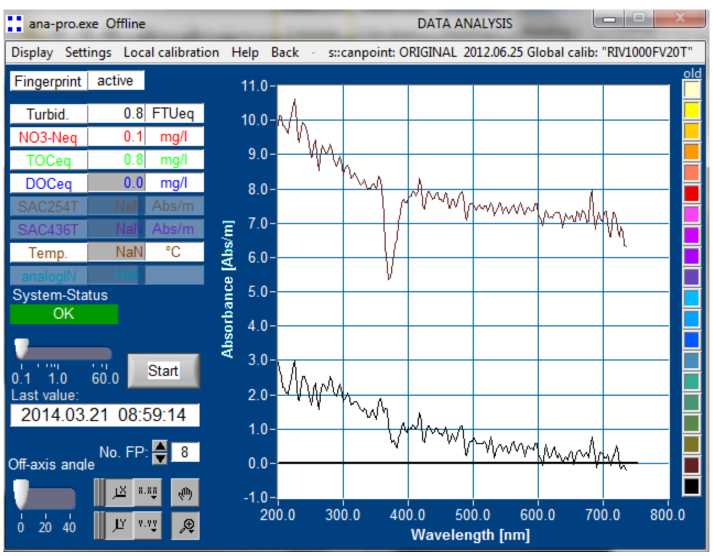

Figure A.10. Screenshot of absorbance spectra as a function of wavelength for watershed D0 after cleaning optics during field servicing visit during the spring (2014 Mar 21).

Watershed D1

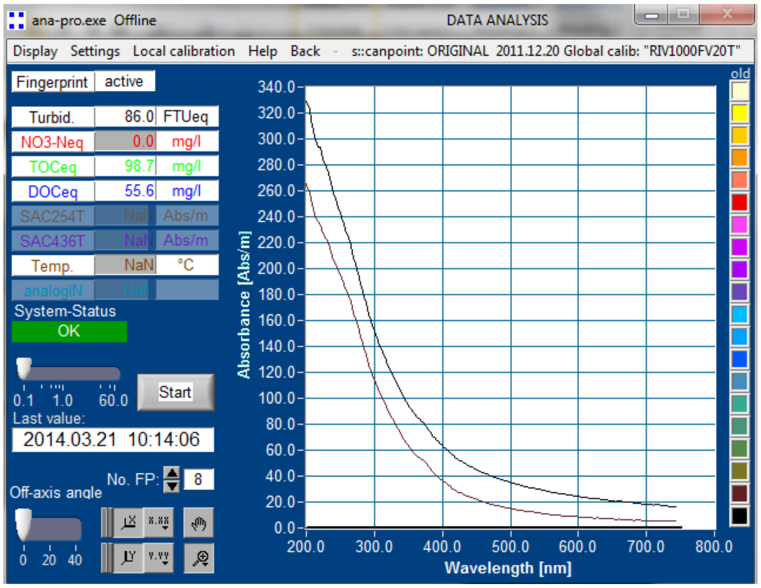

Figure A.11. Screenshot of absorbance spectra as a function of wavelength for watershed D1 before cleaning optics after operating two-weeks in the field without maintenance during the spring (2014 Mar 21).

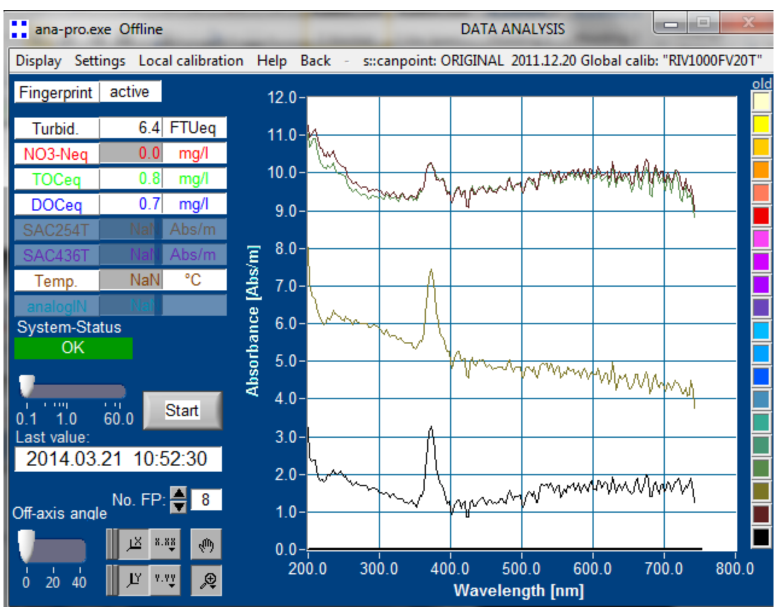

Figure A.12. Screenshot of absorbance spectra as a function of wavelength for watershed D1 after cleaning optics during field servicing visit during the spring (2014 Mar 21).

Watershed D2

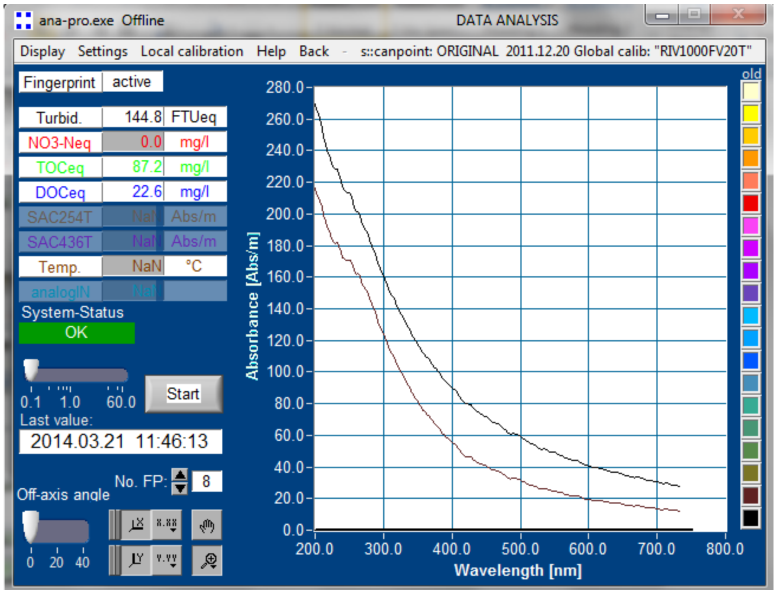

Figure A.13. Screenshot of absorbance spectra as a function of wavelength for watershed D2 after operating two-weeks in the field without maintenance and before cleaning optics during the spring (2014 Mar 21).

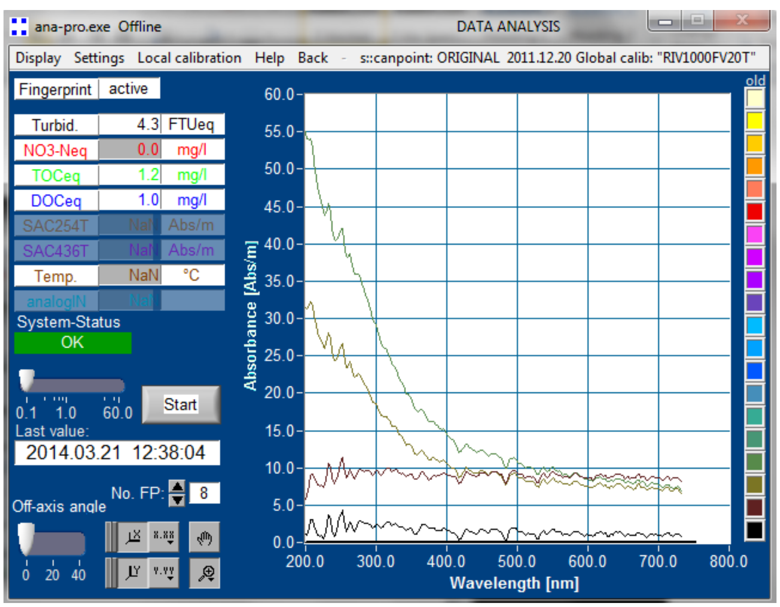

Figure A.14. Screenshot of absorbance spectra as a function of wavelength for watershed D2 after cleaning optics during field servicing visit during the spring (2014 Mar 21).

Watershed D3

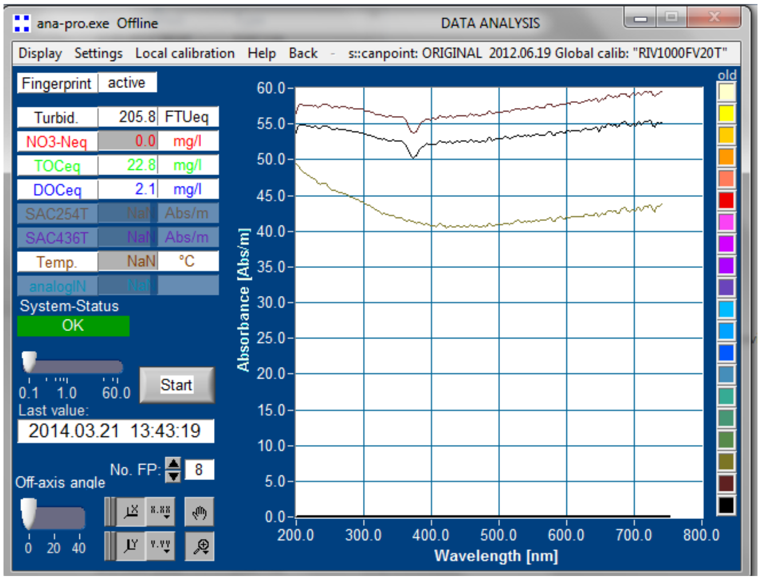

Figure A.15. Screenshot of absorbance spectra as a function of wavelength for watershed D3 after operating two-weeks in the field without maintenance and before cleaning optics during the spring (2014 Mar 21).

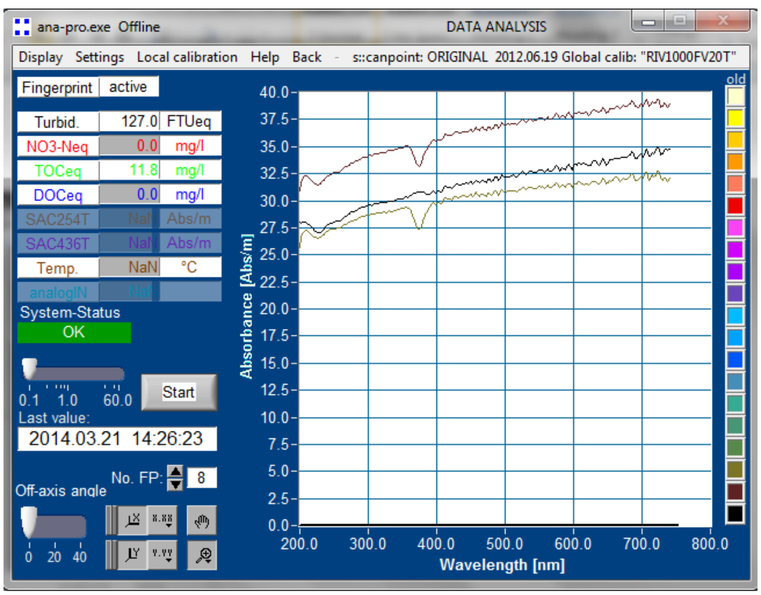

Figure A.16. Screenshot of absorbance spectra as a function of wavelength for watershed D3 after cleaning optics during field servicing visit during the spring (2014 Mar 21).

A.3 Summer (2014 Aug 14)

Watershed D0

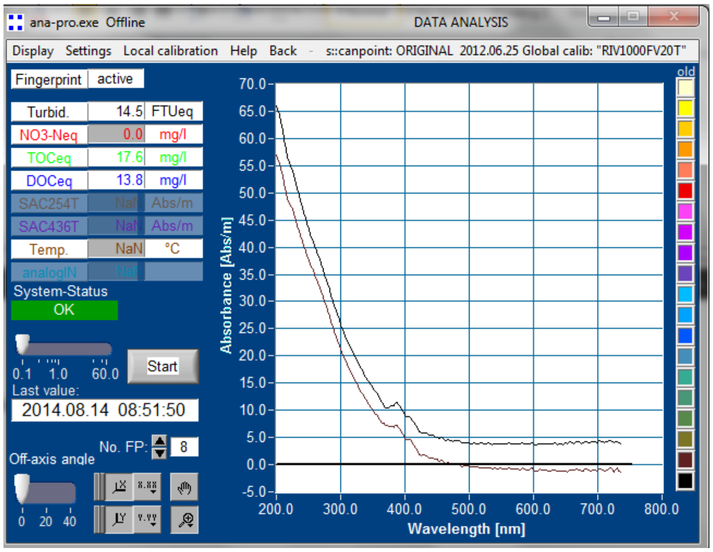

Figure A.17. Screenshot of absorbance spectra as a function of wavelength for watershed D0 after operating two-weeks in the field without maintenance and before cleaning optics during the summer (2014 Aug 14).

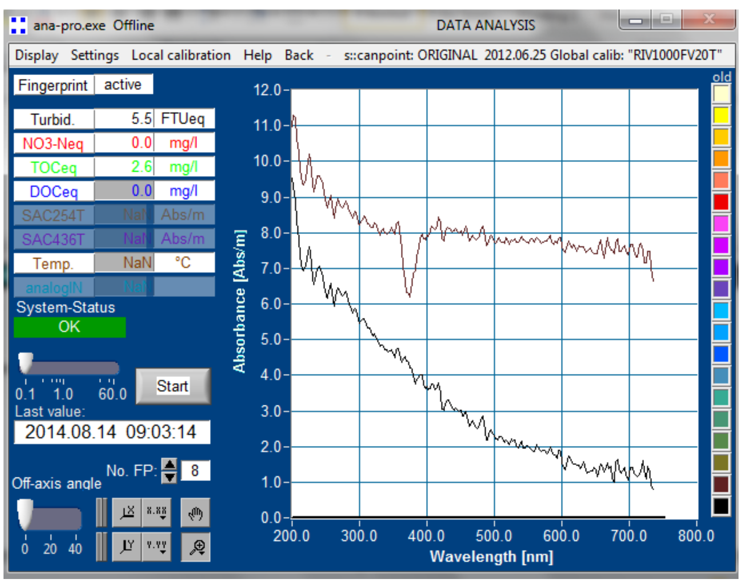

Figure A.18. Screenshot of absorbance spectra as a function of wavelength for watershed D0 after cleaning optics during field servicing visit during the summer (2014 Aug 14).

Watershed D1

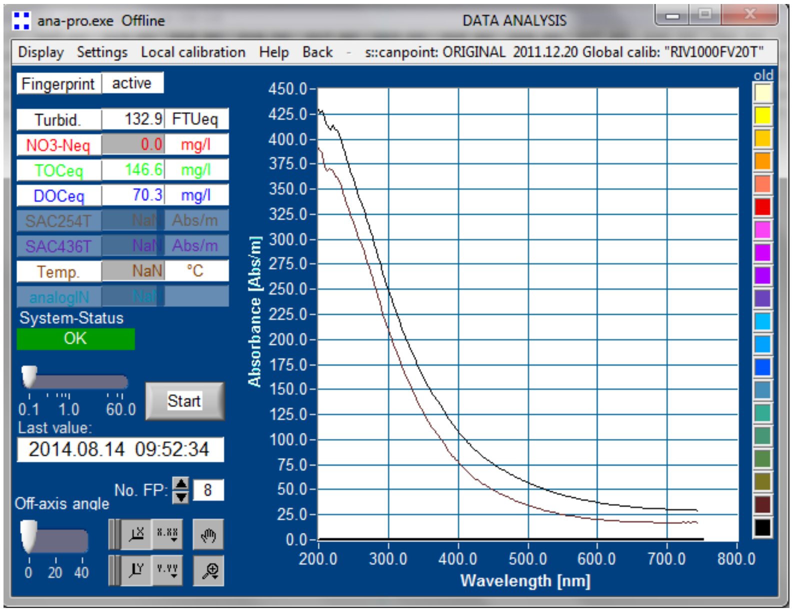

Figure A.19. Screenshot of absorbance spectra as a function of wavelength for watershed D1 after operating two-weeks in the field without maintenance and before cleaning optics during the summer (2014 Aug 14).

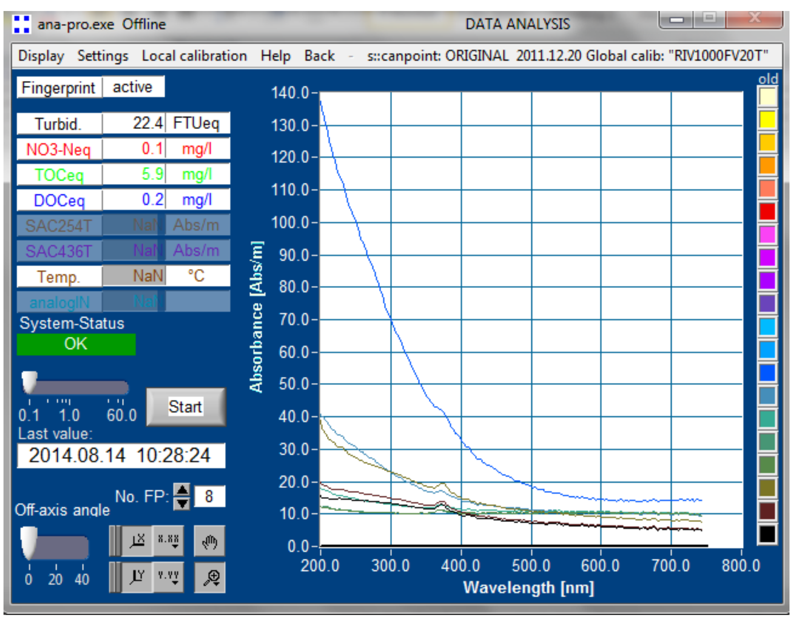

Figure A.20. Screenshot of absorbance spectra as a function of wavelength for watershed D1 after cleaning optics during field servicing visit during the summer (2014 Aug 14).

Watershed D2

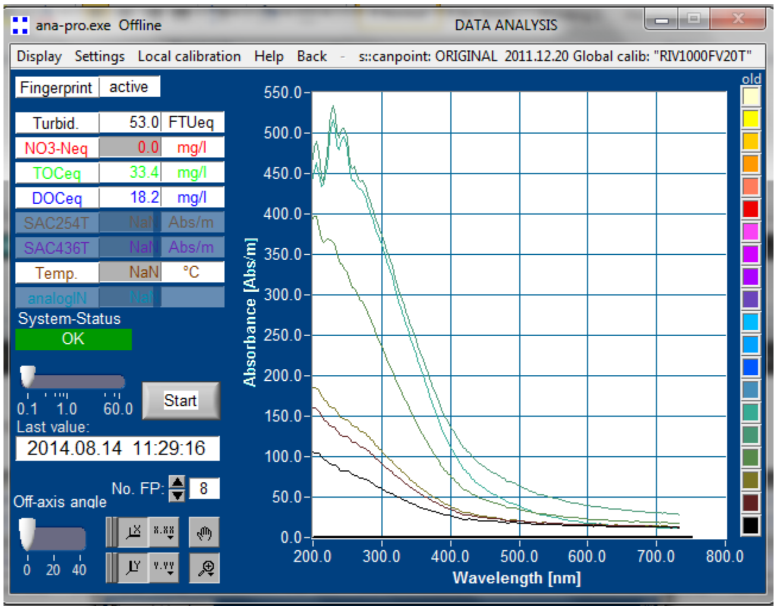

Figure A.21. Screenshot of absorbance spectra as a function of wavelength for watershed D2 after operating two-weeks in the field without maintenance and before cleaning optics during the summer (2014 Aug 14).

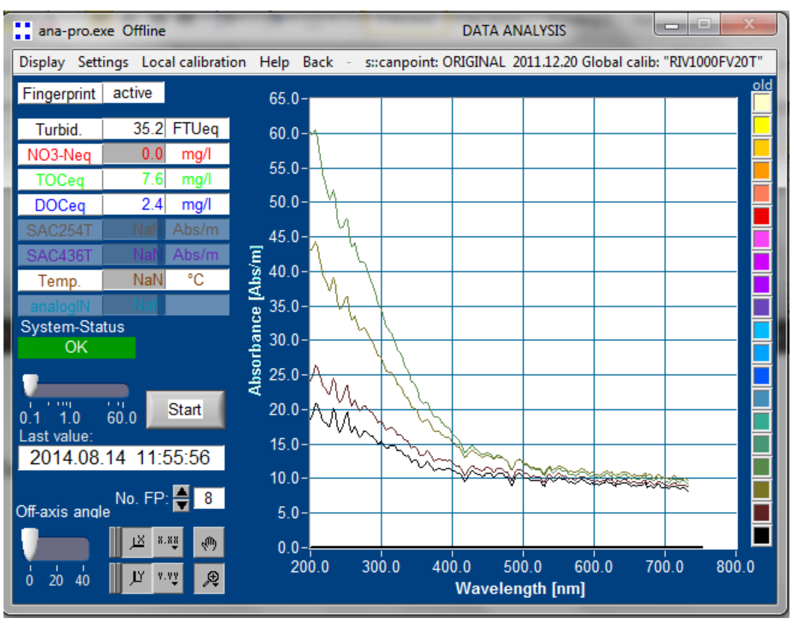

Figure A.22. Screenshot of absorbance spectra as a function of wavelength for watershed D2 after cleaning optics during field servicing visit during the summer (2014 Aug 14).

Watershed D3

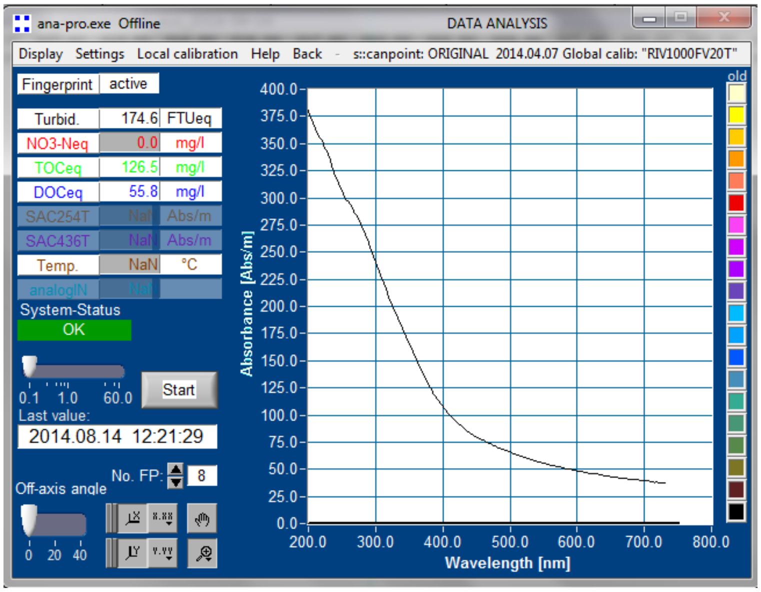

Figure A.23. Screenshot of absorbance spectra as a function of wavelength for watershed D3 after operating two-weeks in the field without maintenance and before cleaning optics during the summer (2014 Aug 14).

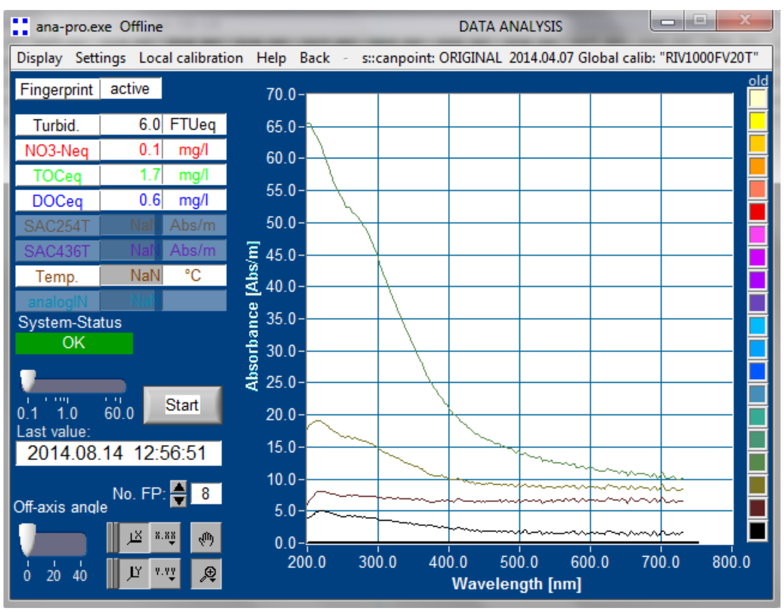

Figure A.24. Screenshot of absorbance spectra as a function of wavelength for watershed D3 after cleaning optics during field servicing visit during the summer (2014 Aug 14).

A.4 Fall (2014 Oct 21)

Watershed D0

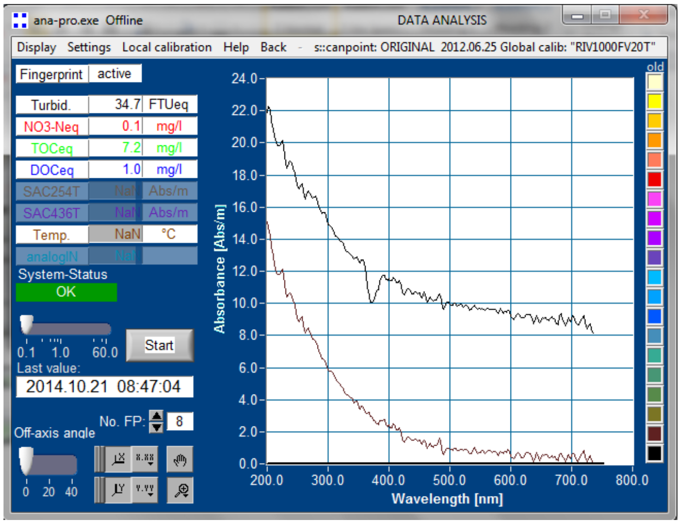

Figure A.25. Screenshot of absorbance spectra as a function of wavelength for watershed D0 after operating two-weeks in the field without maintenance and before cleaning optics during the fall (2014 Oct 21).

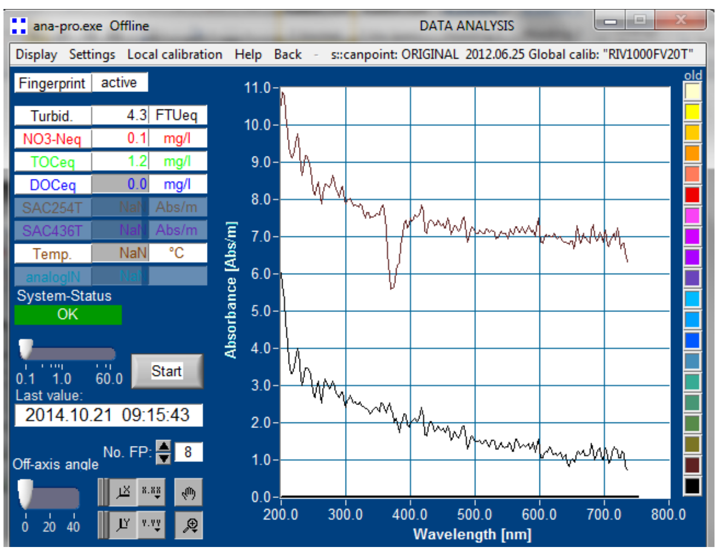

Figure A.26. Screenshot of absorbance spectra as a function of wavelength for watershed D0 after cleaning optics during field servicing visit during the fall (2014 Oct 21).

Watershed D1

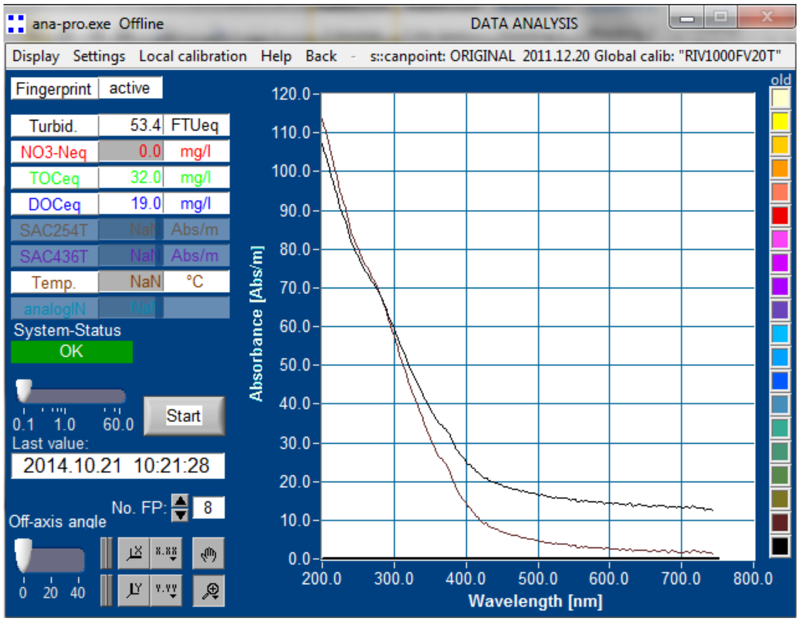

Figure A.27. Screenshot of absorbance spectra as a function of wavelength for watershed D1 after operating two-weeks in the field without maintenance and before cleaning optics during the fall (2014 Oct 21).

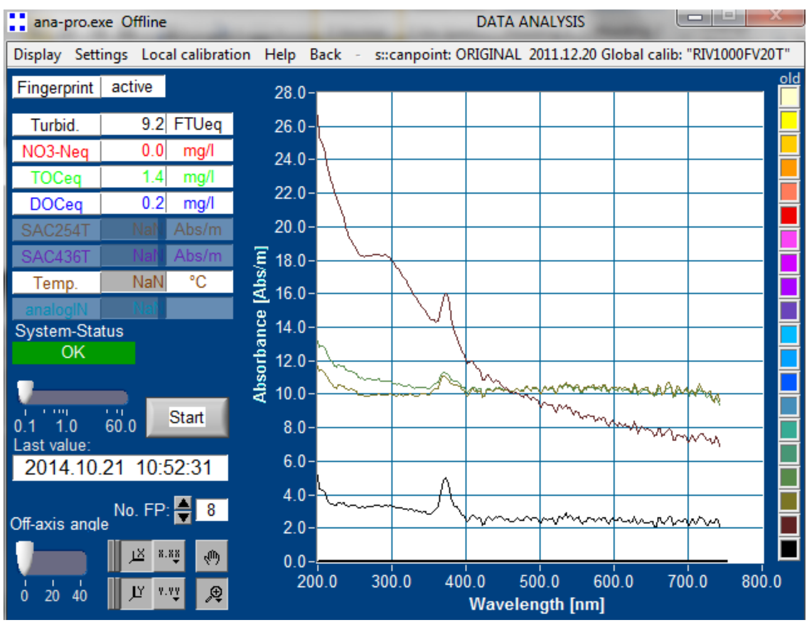

Figure A.28. Screenshot of absorbance spectra as a function of wavelength for watershed D1 after cleaning optics during field servicing visit during the fall (2014 Oct 21).

Watershed D2

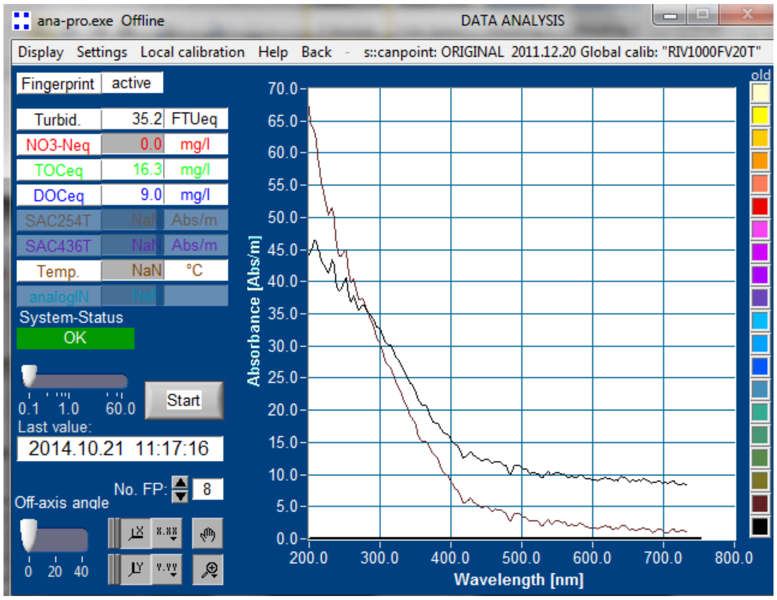

Figure A.29. Screenshot of absorbance spectra as a function of wavelength for watershed D2 after operating two-weeks in the field without maintenance and before cleaning optics during the fall (2014 Oct 21).

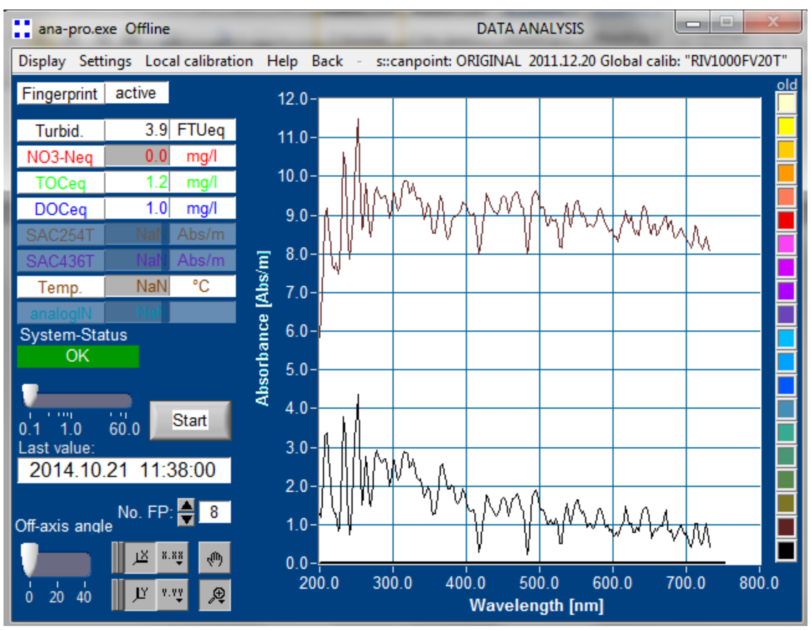

Figure A.30. Screenshot of absorbance spectra as a function of wavelength for watershed D2 after cleaning optics during field servicing visit during the fall (2014 Oct 21).

Watershed D3

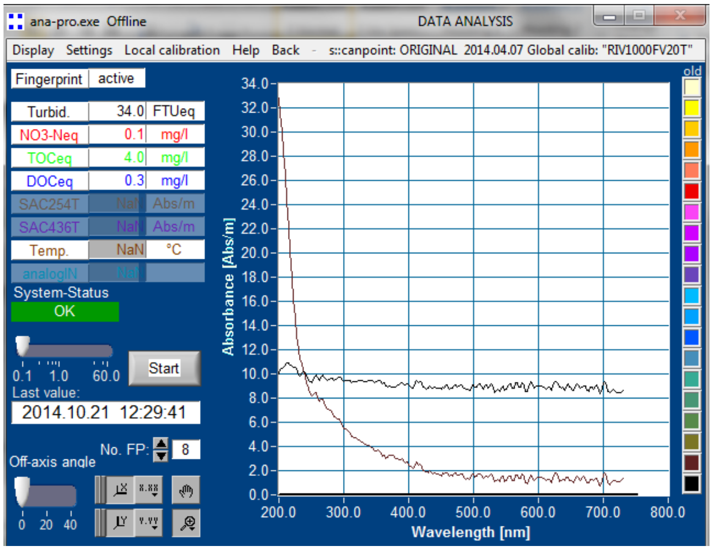

Figure A.31. Screenshot of absorbance spectra as a function of wavelength for watershed D3 after operating two-weeks in the field without maintenance and before cleaning optics during the fall (2014 Oct 21).

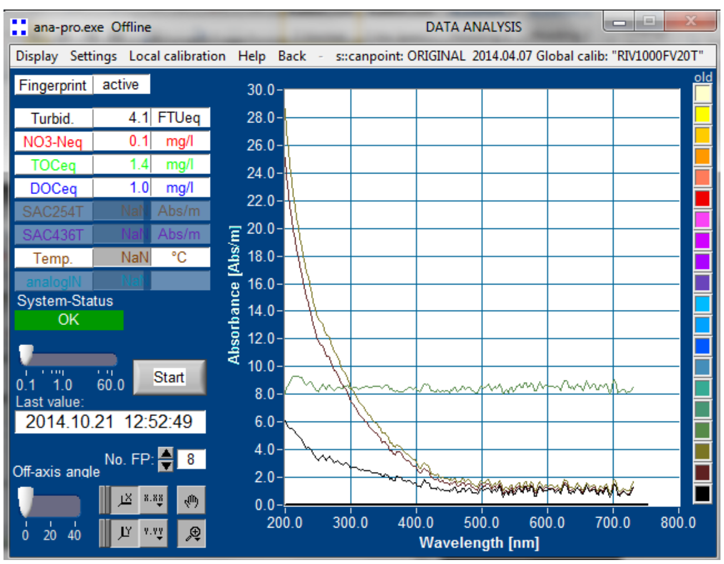

Figure A.32. Screenshot of absorbance spectra as a function of wavelength for watershed D3 after cleaning optics during field servicing visit during the fall (2014 Oct 21).

APPENDIX B: Partial Least Squares Regression (PLSR) Trials

B.1 Watershed D0

Dissolved organic carbon (DOC)

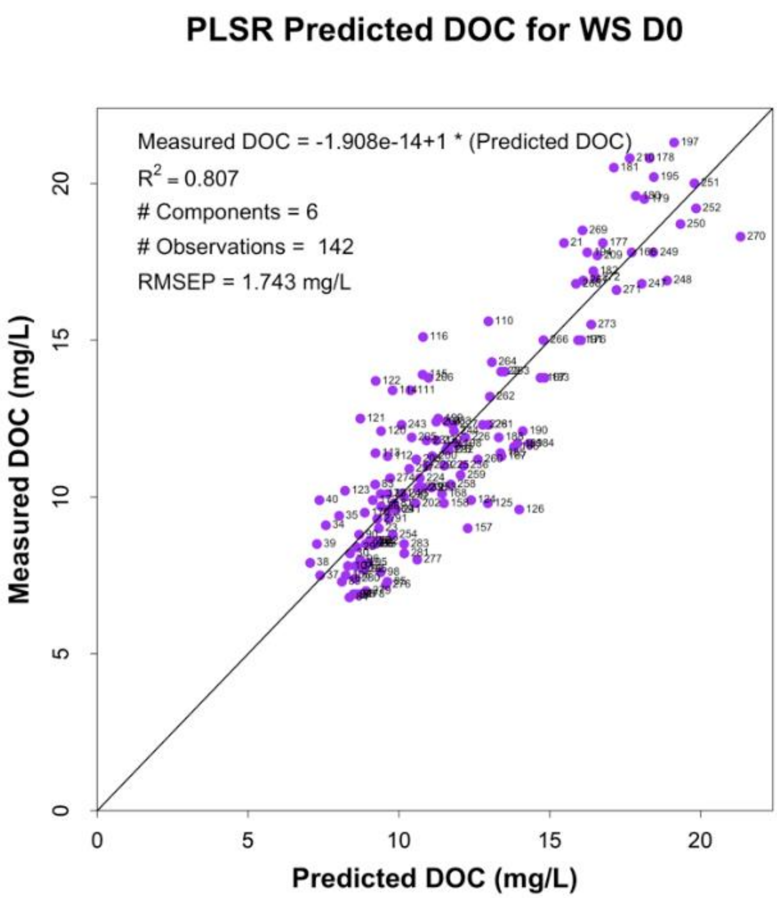

Figure B.1 Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 6 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (142 measured samples).

```
Data:    X dimension: 146 206
         Y dimension: 146 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
CV           3.914    2.754    2.646    2.261    2.160    2.036    2.009    1.858    1.793    1.752     1.845     1.813     1.929     2.014     2.114
adjCV        3.914    2.751    2.657    2.253    2.154    2.029    2.001    1.851    1.782    1.734     1.811     1.789     1.884     1.958     2.049
       15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        2.242     2.294     2.361     2.378     2.426     2.420
adjCV     2.168     2.205     2.264     2.278     2.323     2.316

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
X                       89.92    99.58    99.74    99.95    99.97    99.98    99.99    99.99    99.99     99.99     99.99    100.00    100.00    100.00
as.vector(samp.conc)    51.94    53.79    69.42    72.48    76.13    77.89    81.96    84.91    88.03     89.76     90.61     92.15     93.52     94.38
                      15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     95.11     96.21     96.88     97.31     97.64     97.95
```

Figure B.2. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D0, used to select the number of components.

```
Data:    X dimension: 142 206
         Y dimension: 142 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
CV           3.737    2.600    2.522    2.001    2.027    1.867    1.797    1.625    1.547    1.462     1.461     1.487     1.505     1.530     1.536
adjCV        3.737    2.595    2.521    1.995    2.017    1.858    1.791    1.618    1.540    1.445     1.441     1.469     1.472     1.493     1.497
       15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.623     1.712     1.759     1.838     1.901     1.896
adjCV     1.577     1.651     1.694     1.766     1.825     1.817

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
X                       89.57    99.58    99.72    99.95    99.97    99.98    99.99    99.99    99.99     99.99     99.99    100.00    100.00    100.00
as.vector(samp.conc)    54.03    55.93    73.10    75.41    78.92    80.72    85.02    87.72    90.73     92.13     92.76     94.07     94.88     95.59
                      15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     96.21     97.04     97.43     97.81     98.07     98.34
```

Figure B.3. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the second iteration for dissolved organic carbon (DOC) in watershed D0, used to select the number of components.

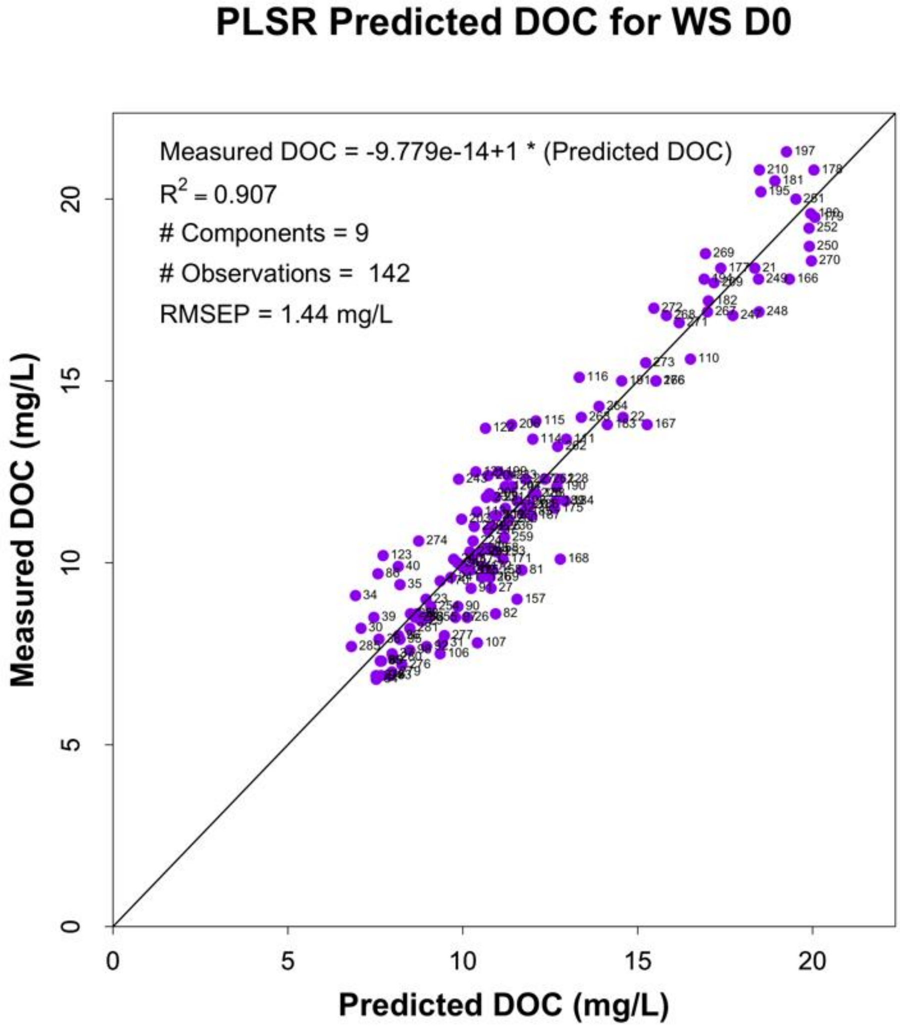

Figure B.4. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 9 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (142 measured samples).

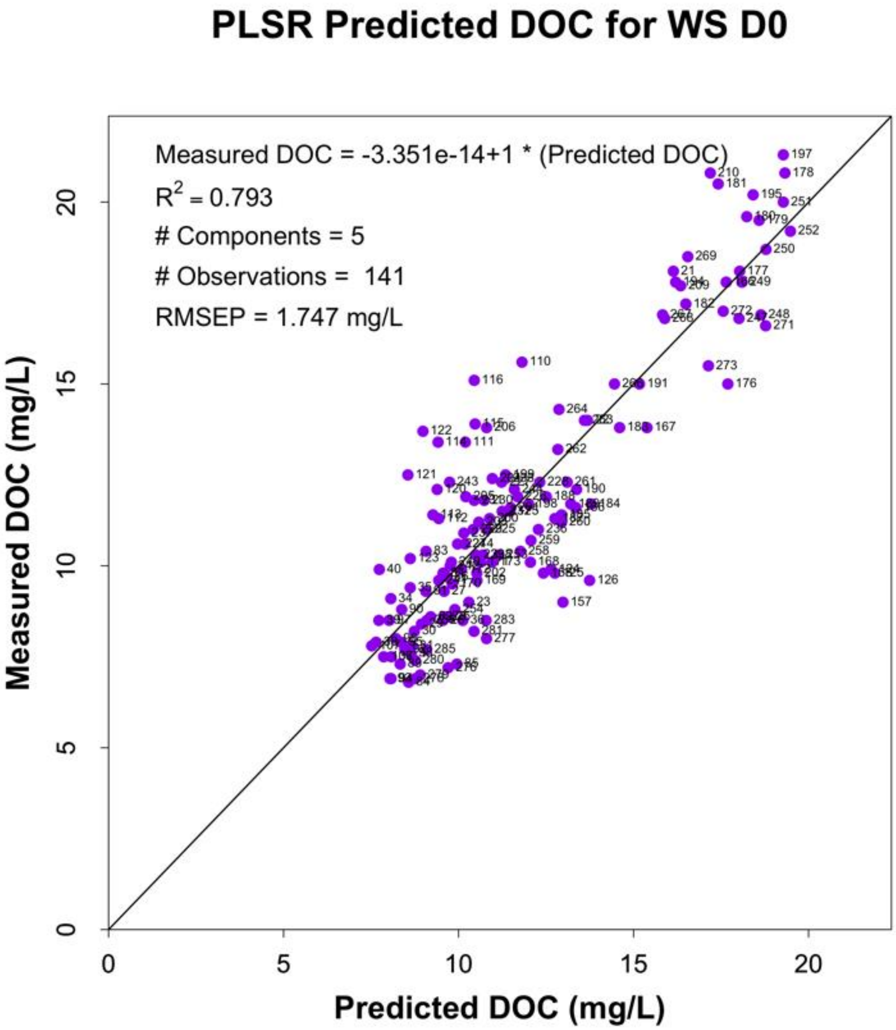

Figure B.5. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 5 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (141 measured samples).

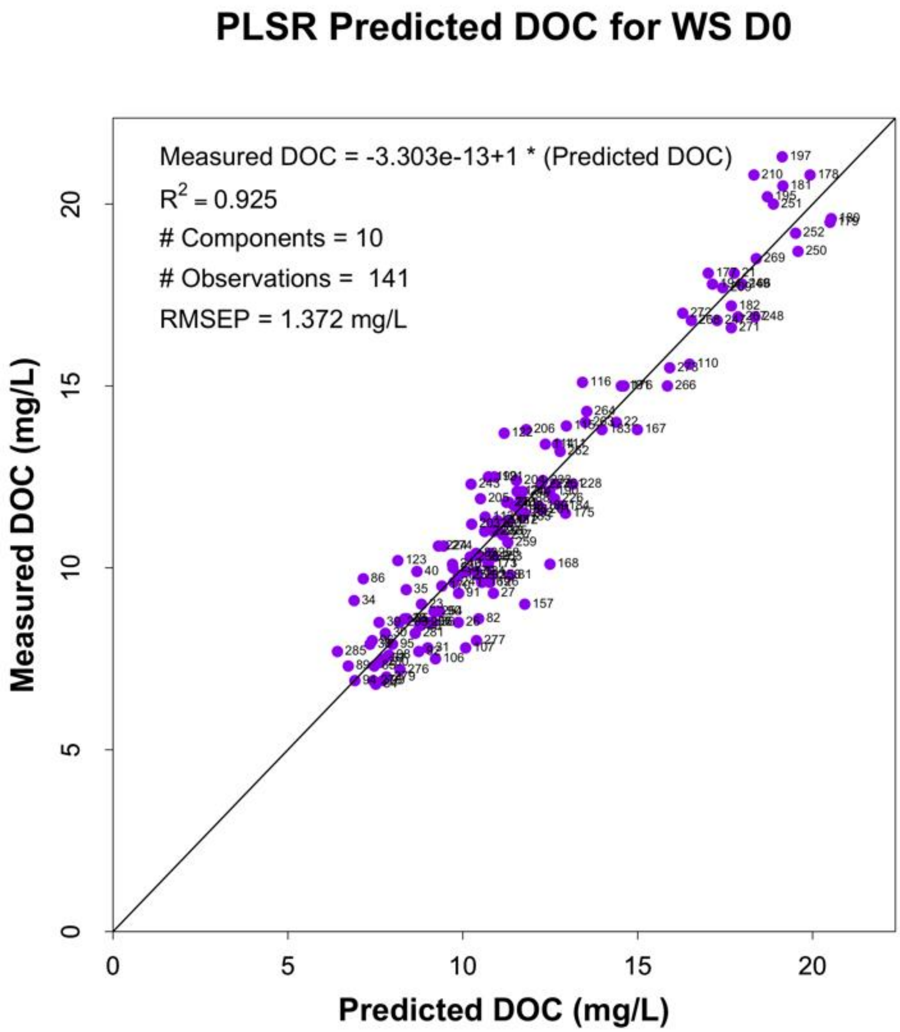

Figure B.6. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 10 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (141 measured samples).

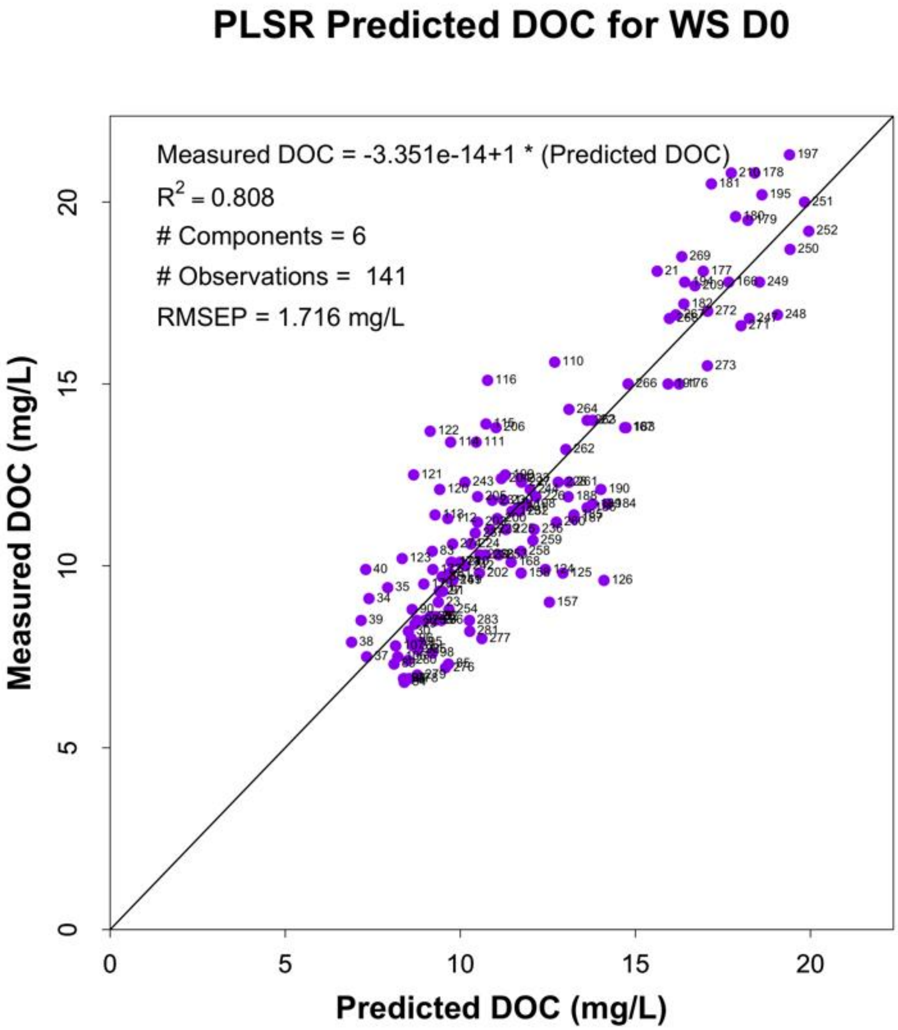

Figure B.7. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 6 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (141 measured samples).

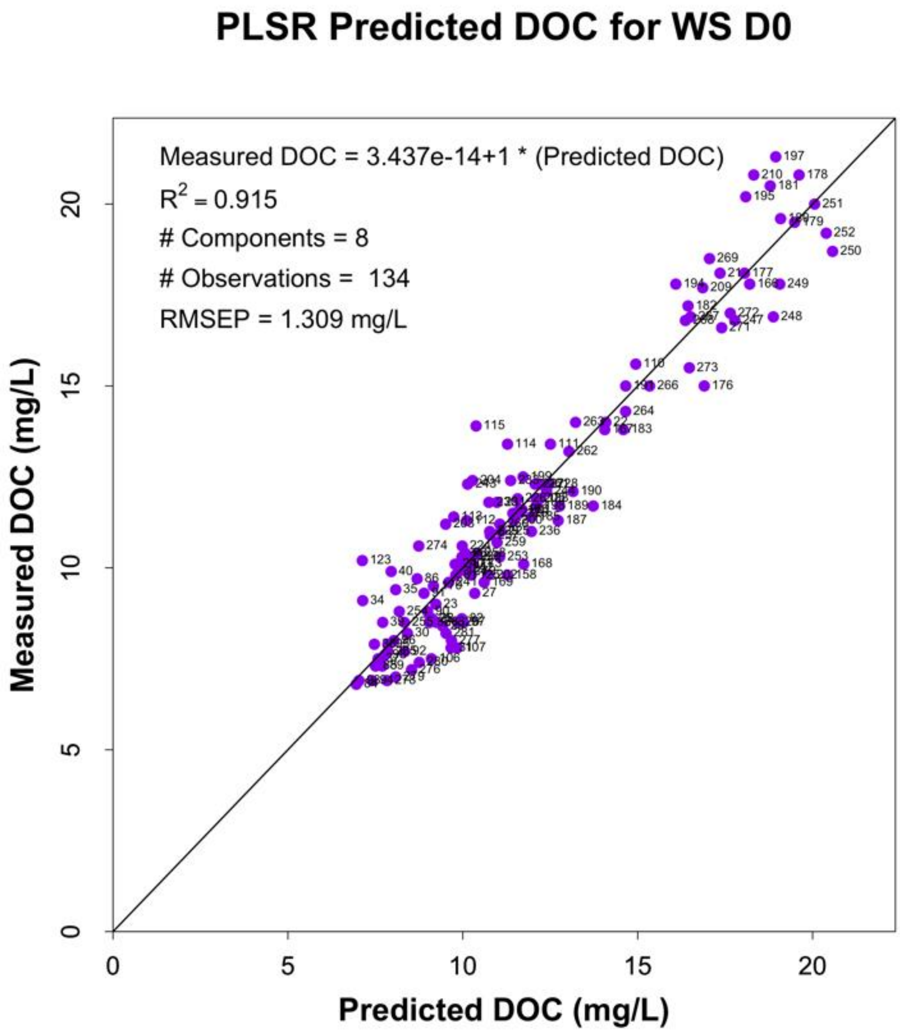

Figure B.8. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 8 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (134 measured samples).

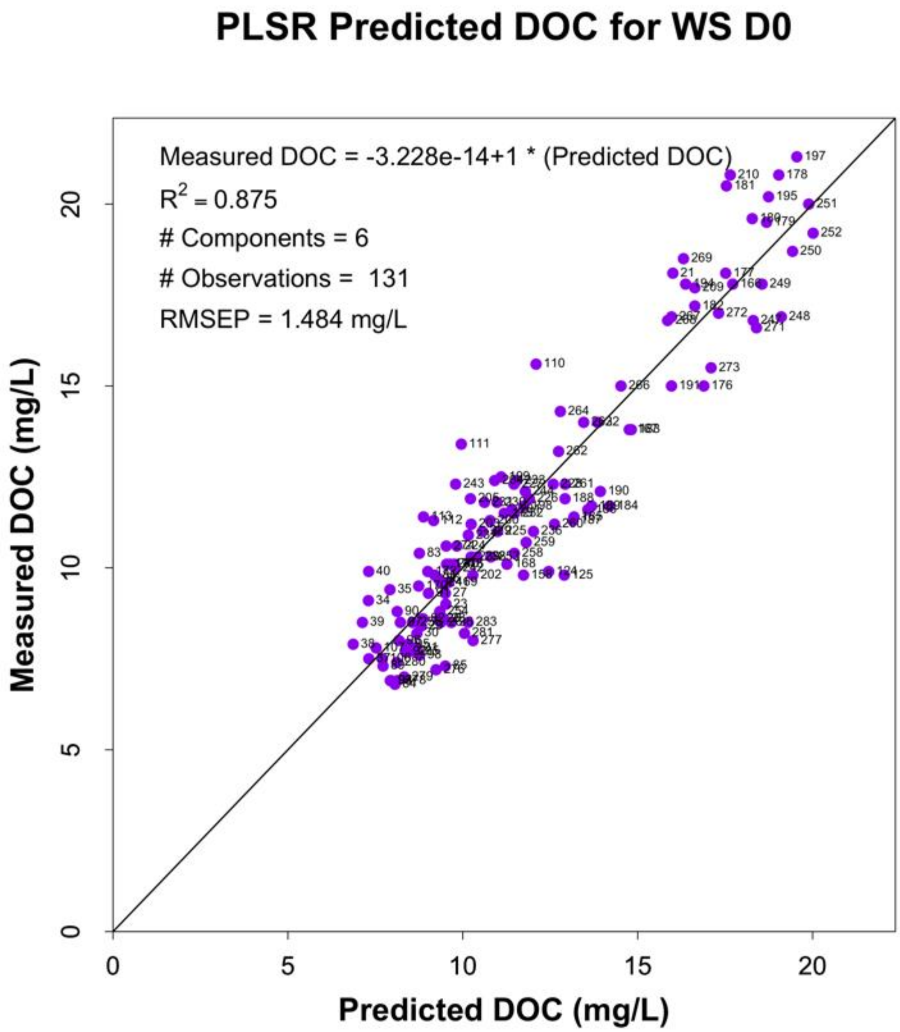

Figure B.9. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 6 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (131 measured samples).

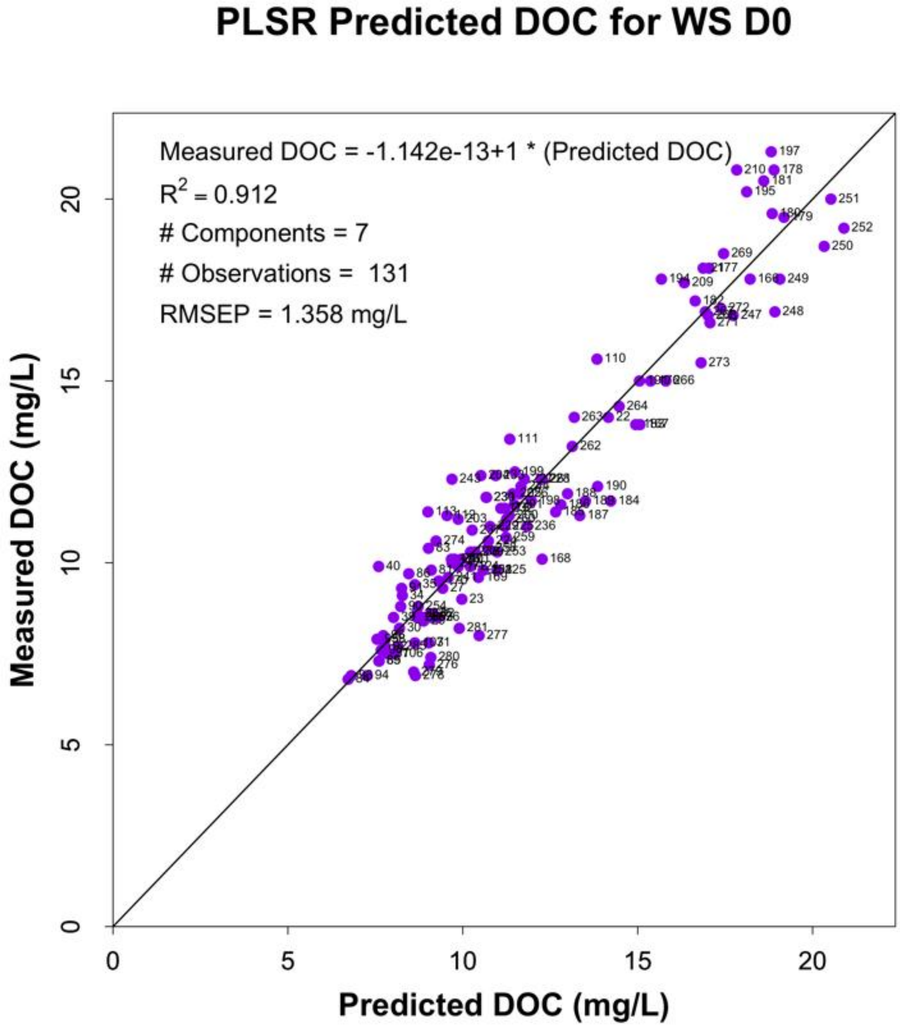

Figure B.10. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 7 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (131 measured samples).

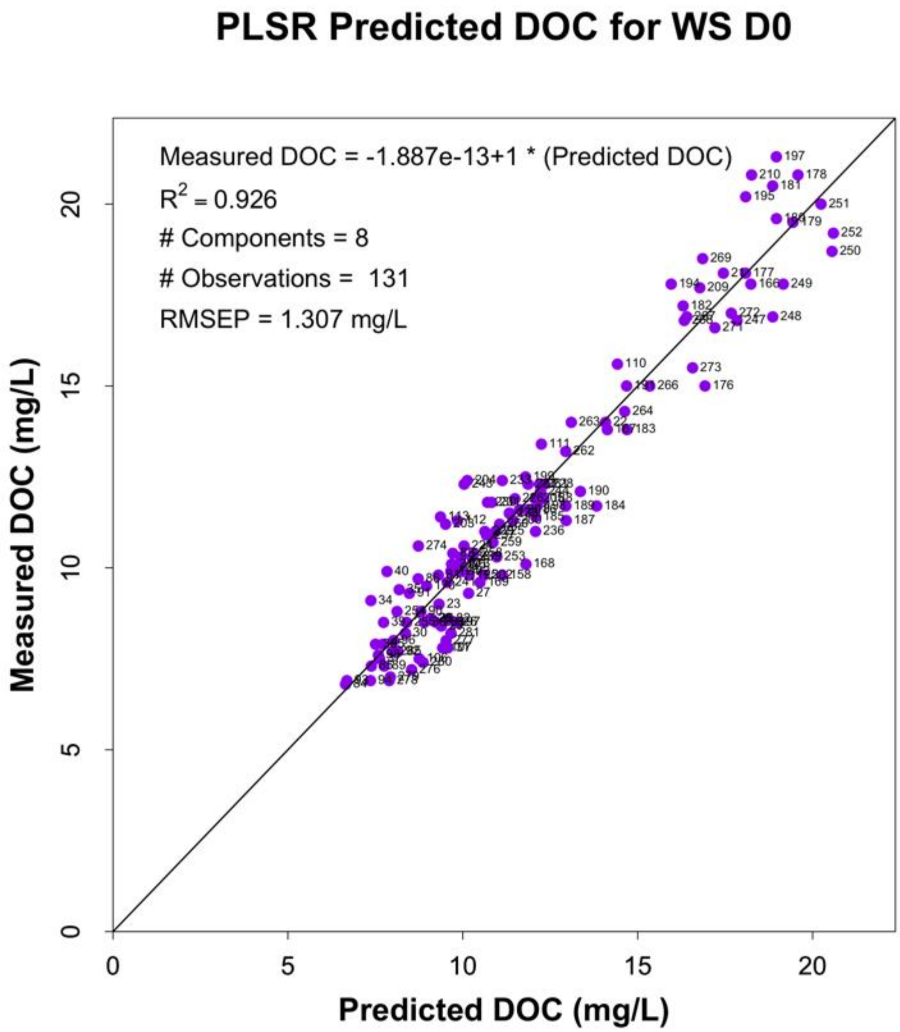

Figure B.11. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 8 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (131 measured samples).

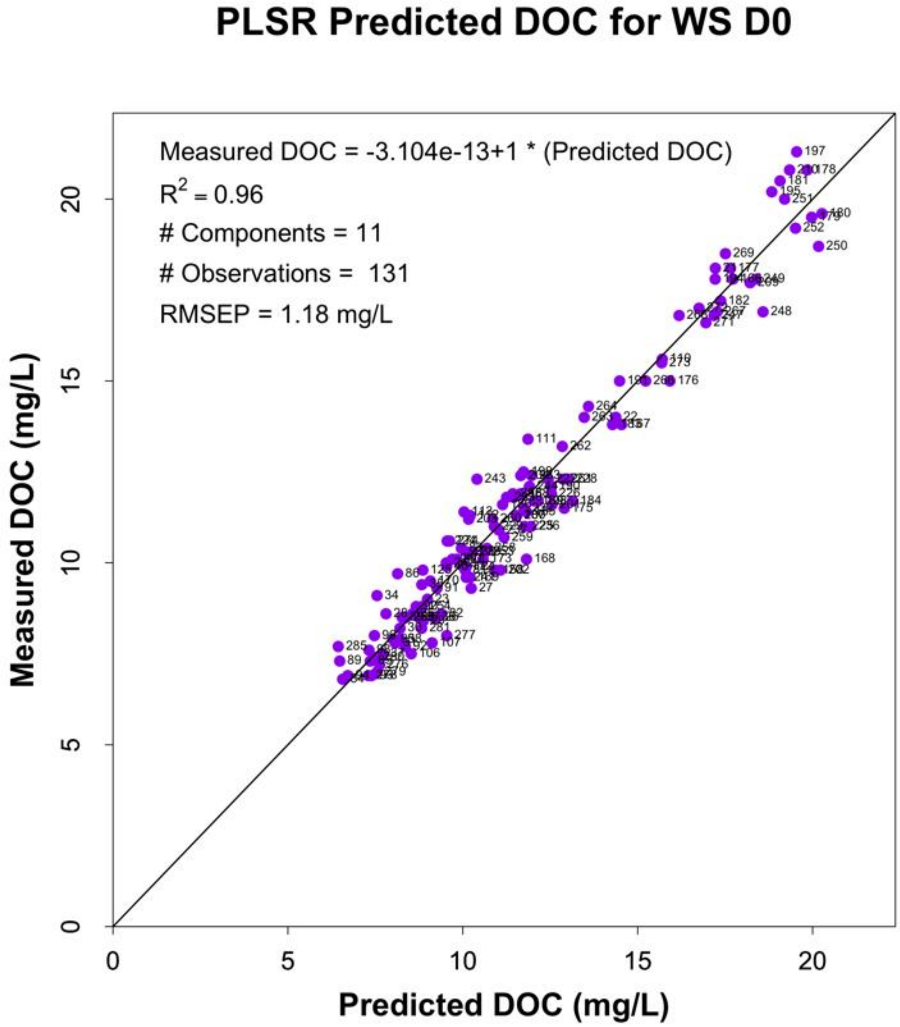

Figure B.12. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 11 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (131 measured samples).

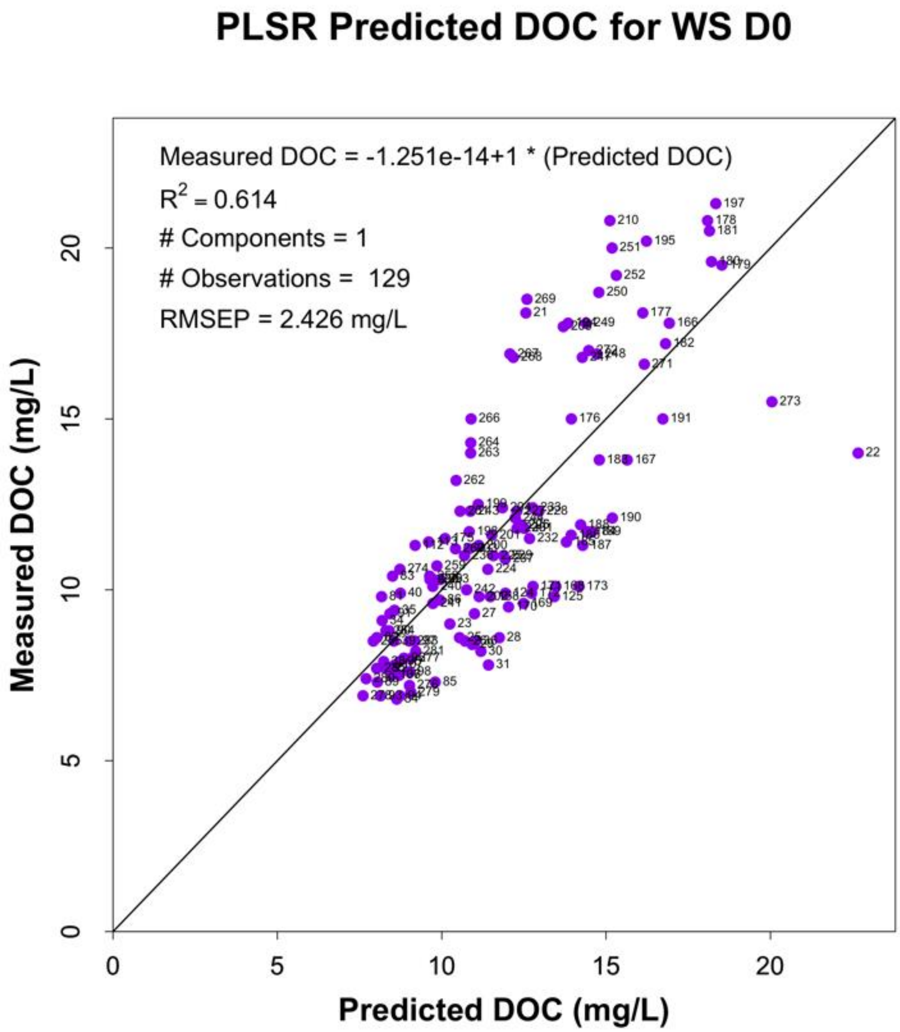

Figure B.13. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 1 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (129 measured samples).

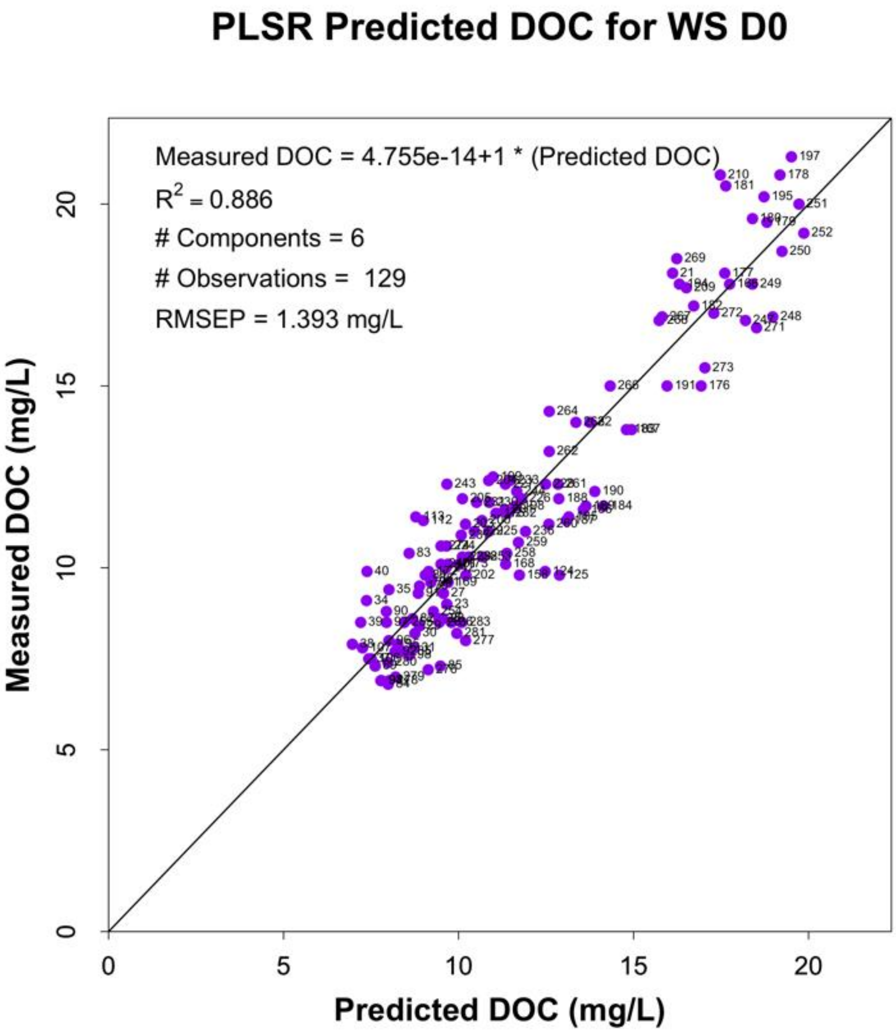

Figure B.14. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 6 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (129 measured samples).

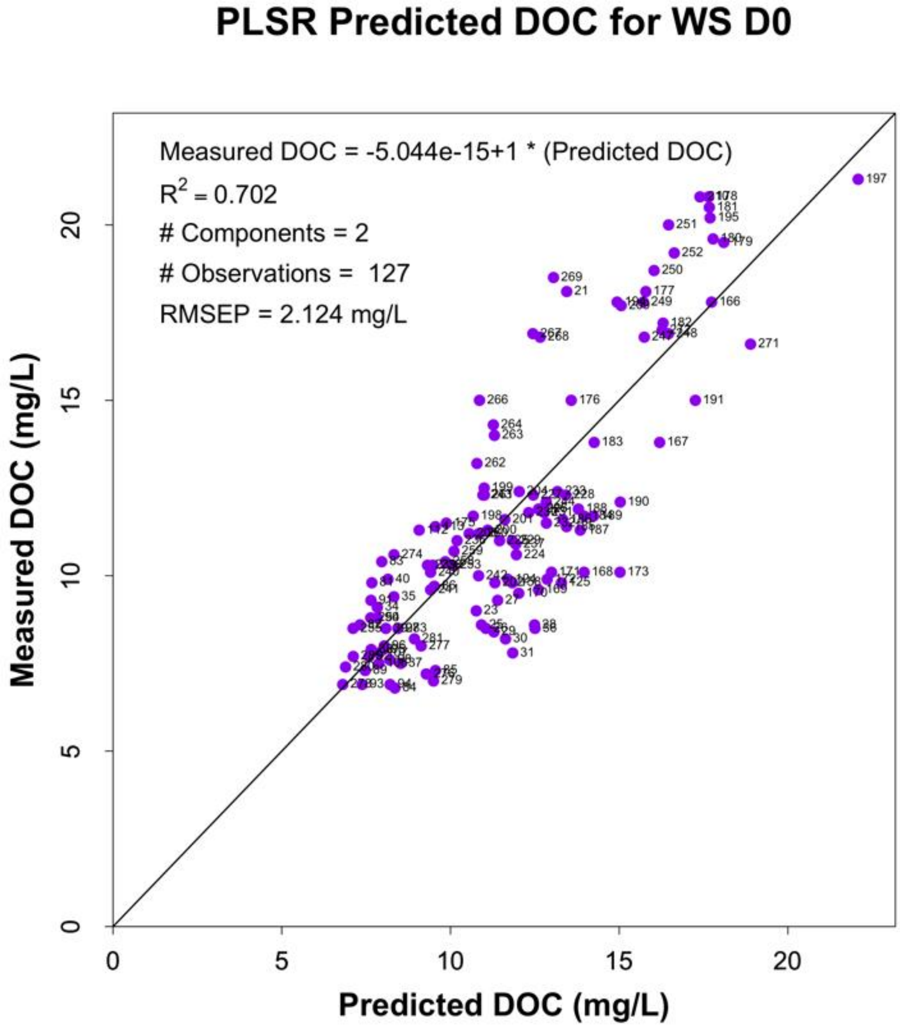

Figure B.15. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 2 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (127 measured samples).

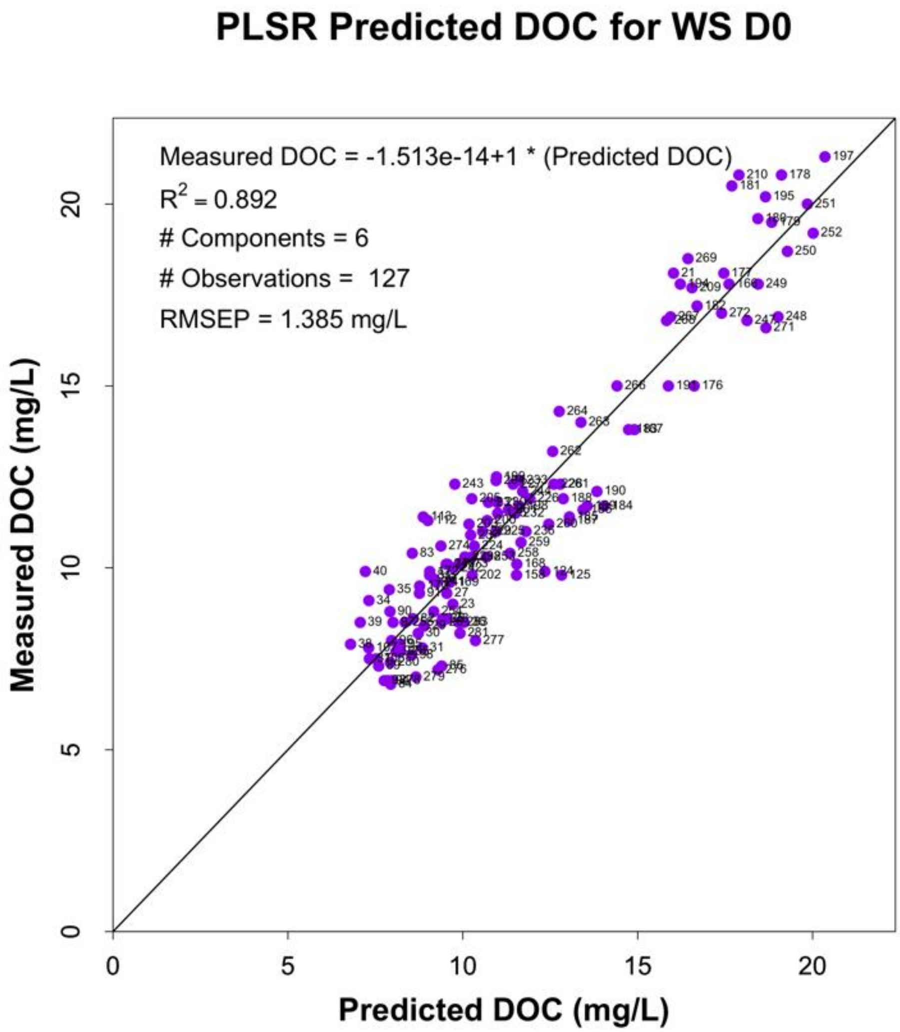

Figure B.16. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 6 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (127 measured samples).

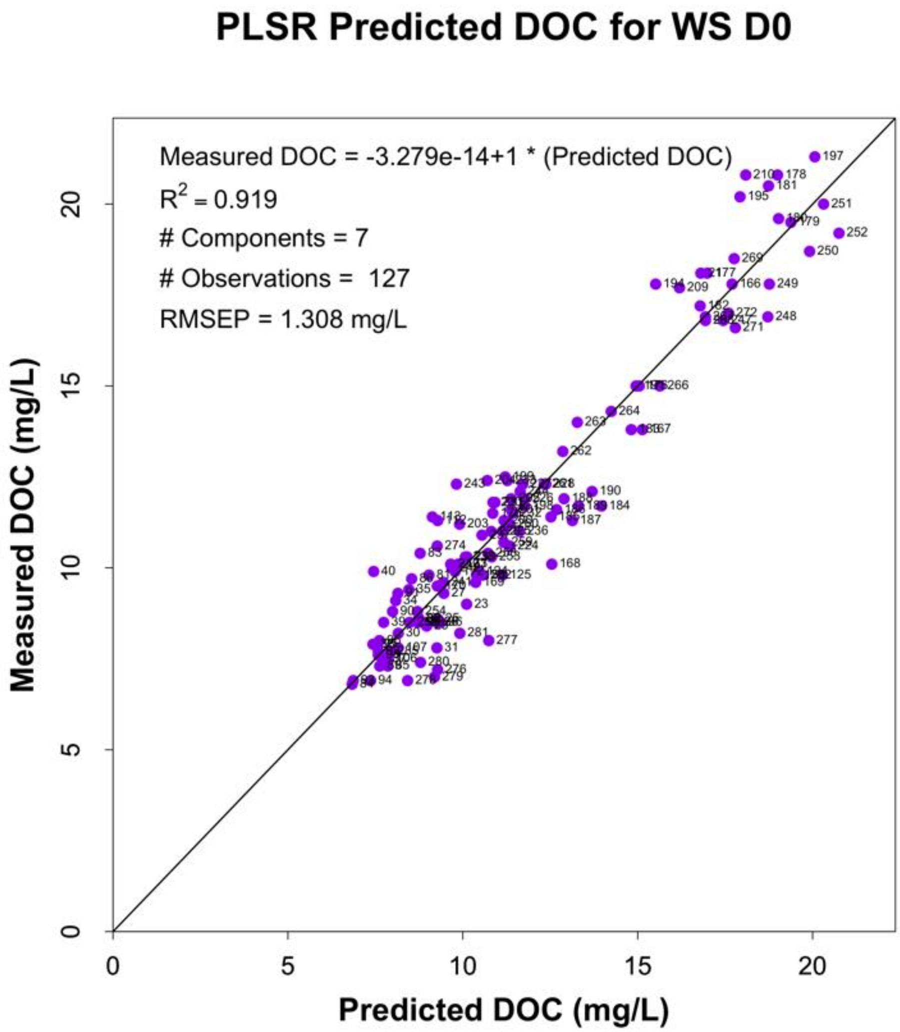

Figure B.17. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 7 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (127 measured samples).

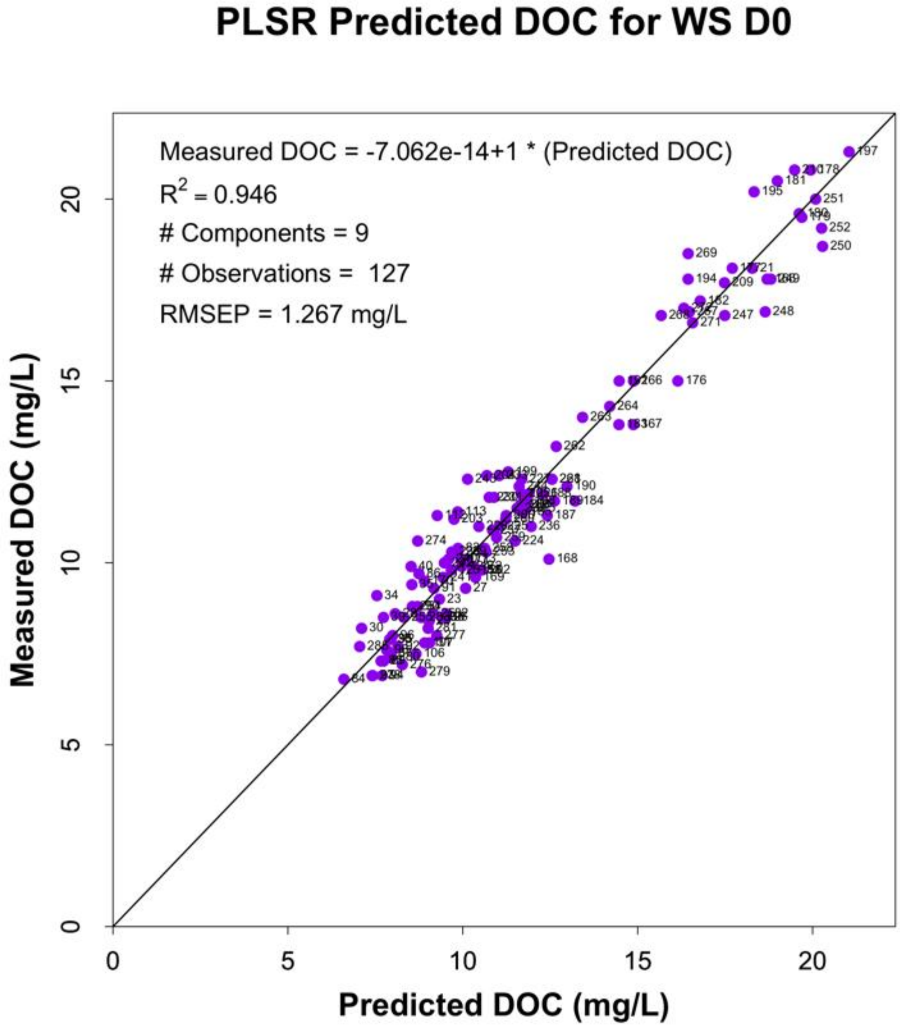

Figure B.18. Measured versus predicted dissolved organic carbon (DOC) using partial least squares regression (PLSR) with 9 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (127 measured samples).

Nitrate-nitrogen (NO_3^--N)

```
Data:   X dimension: 104 206
        Y dimension: 104 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
CV         0.08328  0.07567  0.06184  0.05557  0.05184  0.04755  0.03897  0.03693  0.03703  0.03649   0.03568   0.03927   0.04062   0.04185   0.04333
adjCV      0.08328  0.07558  0.06170  0.05548  0.05099  0.04648  0.03864  0.03698  0.03662  0.03618   0.03533   0.03831   0.03944   0.04053   0.04184
       15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.04532   0.04755   0.04844   0.04927   0.05006   0.05055
adjCV   0.04359   0.04562   0.04634   0.04711   0.04779   0.04820

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
X                       89.82     99.7    99.91    99.92    99.97    99.99    99.99    99.99    99.99    100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)    19.76     48.2    58.09    69.52    74.36    83.64    85.98    88.91    90.03     91.75     94.07     95.39      96.2     96.87
                      15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     97.54     98.04     98.48     98.73     98.98     99.22
```

Figure B.19. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first trial for nitrate (NO_3^--N) in watershed D0, used to select the number of components.

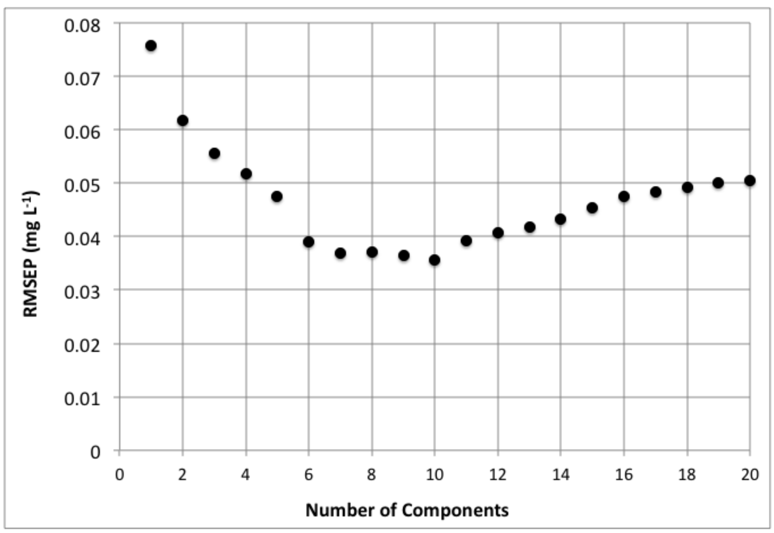

Figure B.20. Root mean square error of prediction (RMSEP, mg L^{-1}) as a function of the number of components for the first trial of the partial least squares regression model for nitrate (NO_3^--N) in watershed D0.

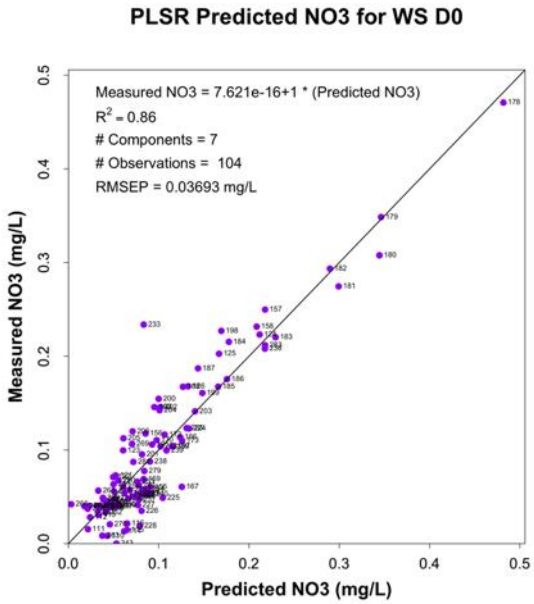

Figure B.21. Measured versus predicted nitrate (NO_3^--N) values from first partial least squares regression (PLSR) trial with 7 components for watershed D0 in Carteret County, North Carolina for data from Nov 2013 to Nov 2014 (104 measured samples).

```
Data:   X dimension: 103 206
        Y dimension: 103 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
CV          0.0826  0.07503  0.06250  0.05414  0.04904  0.04727  0.03430  0.03080  0.03007  0.02881   0.02858   0.02946   0.03202   0.03212    0.0320
adjCV       0.0826  0.07494  0.06223  0.05406  0.04846  0.04728  0.03403  0.03062  0.02969  0.02852   0.02823   0.02881   0.03100   0.03106    0.0309
       15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03323   0.03273   0.03363    0.0342   0.03439   0.03512
adjCV   0.03194   0.03142   0.03219    0.0327   0.03288   0.03351

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
X                      89.79    99.70    99.91    99.93    99.99    99.99    99.99    99.99    99.99    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)   20.13    49.34    59.68    71.49    73.40    86.76    89.44    92.24    93.13     94.41     95.91     96.99     97.54     98.01
                     15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00    100.00    100.00    100.00     100.0
as.vector(samp.conc)    98.46     98.78     99.08     99.22     99.33      99.5
```

Figure B.22. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the second trial for nitrate (NO_3^--N) in watershed D0, used to select the number of components.

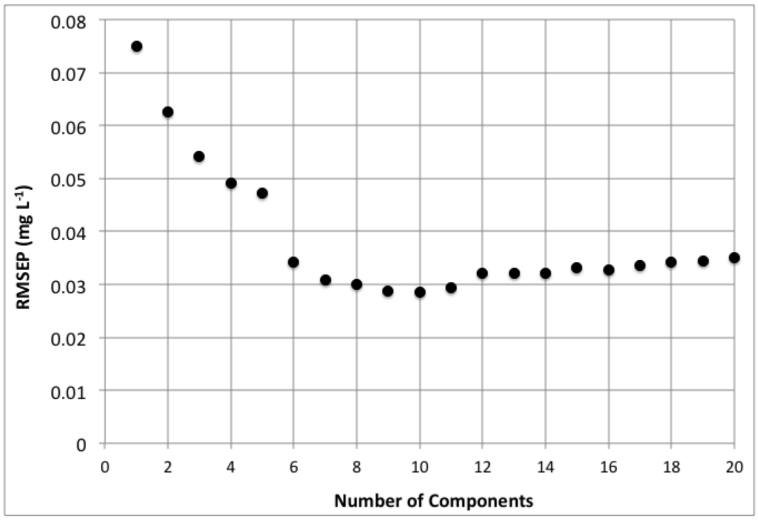

Figure B.23. Root mean square error of prediction (RMSEP, mg L^{-1}) as a function of the number of components for the second trial of the partial least squares regression model for nitrate (NO_3^--N) in watershed D0.

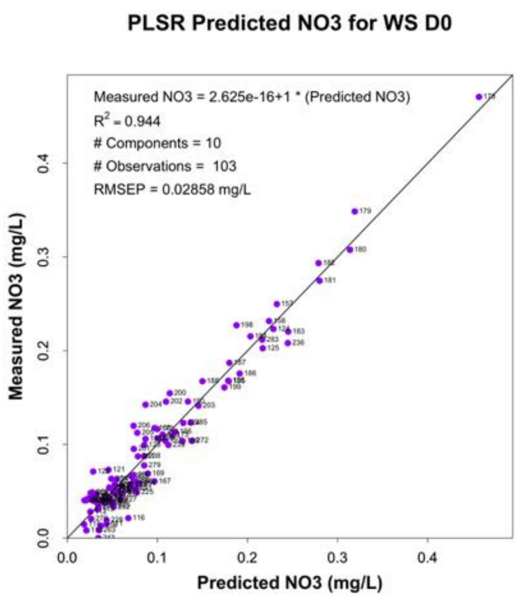

Figure B.24. Final relationship between measured and predicted nitrate (NO_3^--N) values using partial least squares regression (PLSR) trial with 10 components used to predict continuous NO_3^-N values for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (103 measured samples).

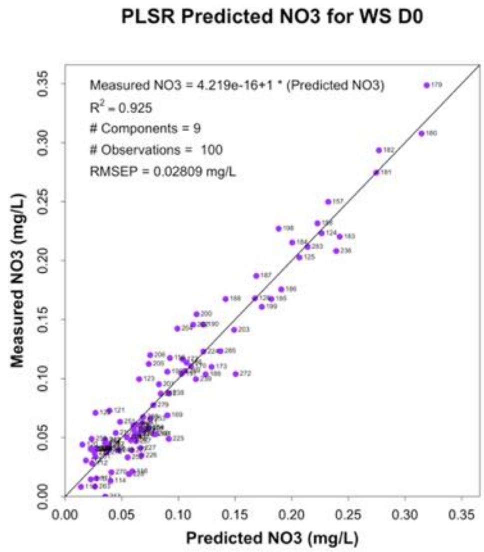

Figure B.25. Measured versus predicted nitrate (NO_3^--N) values using partial least squares regression (PLSR) trial with 9 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (103 measured samples).

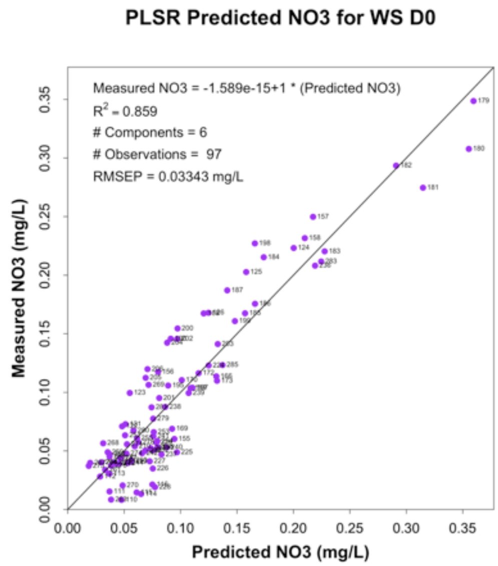

Figure B.26. Measured versus predicted nitrate (NO_3^--N) values using partial least squares regression (PLSR) trial with 6 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (97 measured samples).

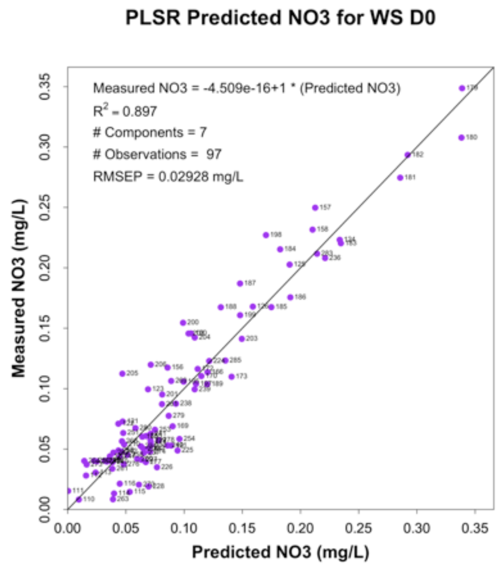

Figure B.27. Measured versus predicted nitrate (NO_3^--N) values using partial least squares regression (PLSR) trial with 7 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (97 measured samples).

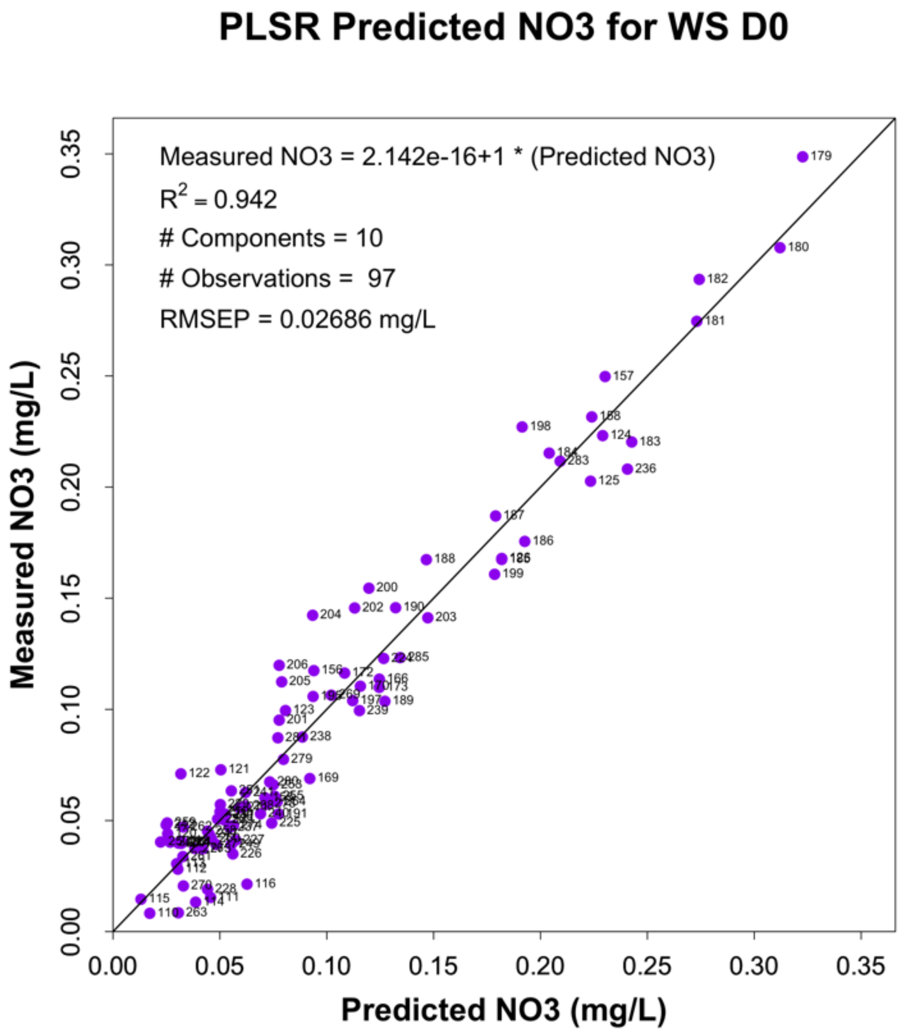

Figure B.28. Measured versus predicted nitrate (NO_3^--N) values using partial least squares regression (PLSR) trial with 10 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (97 measured samples).

Total dissolved nitrogen (TDN)

```
Data:   X dimension: 146 206
        Y dimension: 146 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
CV           0.135   0.1073  0.09097  0.07398  0.05355  0.04367  0.04004  0.03602  0.03633  0.03666   0.03917   0.04046   0.04166   0.04466   0.04561
adjCV        0.135   0.1072  0.09086  0.07352  0.05357  0.04352  0.04002  0.03589  0.03612  0.03640   0.03866   0.03978   0.04074   0.04348   0.04416
       15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.04573   0.04655   0.04753   0.04728   0.04931   0.05023
adjCV   0.04426   0.04495   0.04583   0.04550   0.04739   0.04827

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
X                        89.33    99.59    99.84    99.95    99.97    99.98    99.99    99.99    99.99     99.99     99.99    100.00    100.00    100.00
as.vector(samp.conc)     37.66    56.38    76.78    85.36    90.76    92.41    94.03    94.53    95.05     95.58     96.00     96.76     97.24     97.78
                       15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      98.05     98.34     98.53     98.73     98.85     98.96
```

Figure B.29. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first trial for total dissolved nitrogen (TDN) in watershed D0, used to select the number of components.

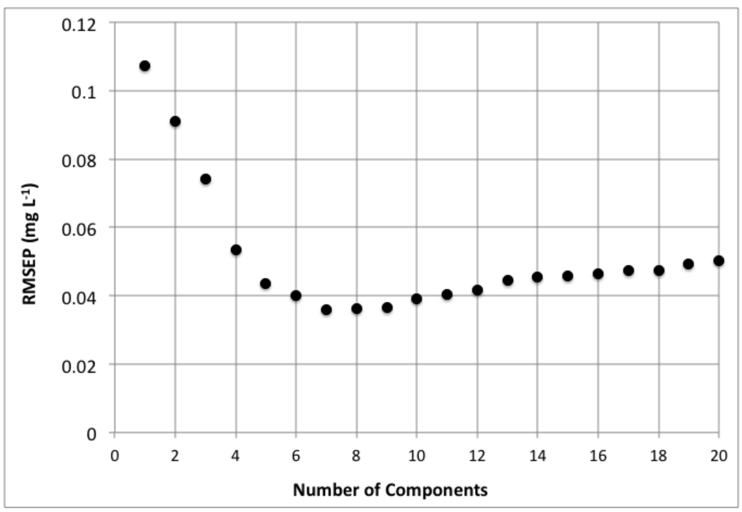

Figure B.30. Root mean square error of prediction (RMSEP, mg L^{-1}) as a function of the number of components for the first trial of the partial least squares regression model for total dissolved nitrogen (TDN) in watershed D0.

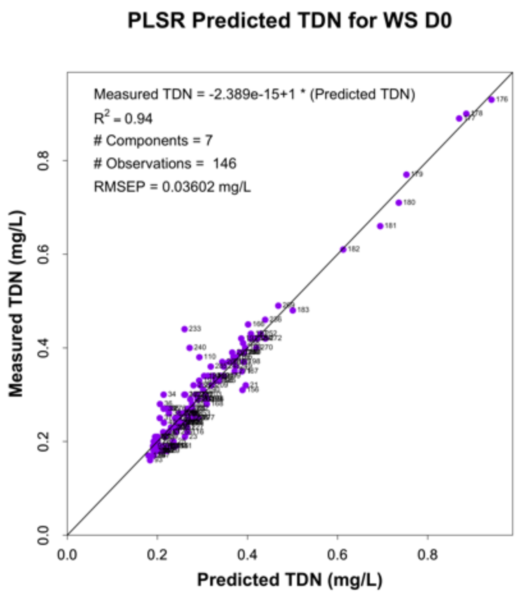

Figure B.31. Relationship between measured and predicted total dissolved nitrogen (TDN) values from first partial least squares regression (PLSR) trial for watershed D0.

```
Data:    X dimension: 143 206
         Y dimension: 143 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
CV          0.1356   0.1095  0.09166  0.07225  0.05057  0.03832  0.03444  0.02861  0.02911  0.02877   0.02930   0.03055   0.03121   0.03232   0.03373
adjCV       0.1356   0.1093  0.09146  0.07185  0.05062  0.03820  0.03439  0.02851  0.02889  0.02843   0.02885   0.03005   0.03046   0.03143   0.03255
       15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03421   0.03441   0.03469   0.03413   0.03481   0.03518
adjCV   0.03291   0.03301   0.03325   0.03268   0.03333   0.03362

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps  14 comps
X                      89.28    99.59    99.84    99.95    99.97    99.98    99.99    99.99    99.99     99.99     99.99     100.0    100.00    100.00
as.vector(samp.conc)   38.78    57.66    78.06    87.12    93.07    94.65    96.36    96.87    97.48     97.82     98.08      98.5     98.76     99.05
                     15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    99.21     99.36     99.45     99.53     99.57     99.65
```
Figure B.32. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the second trial for total dissolved nitrogen (TDN) in watershed D0, used to select the number of components.

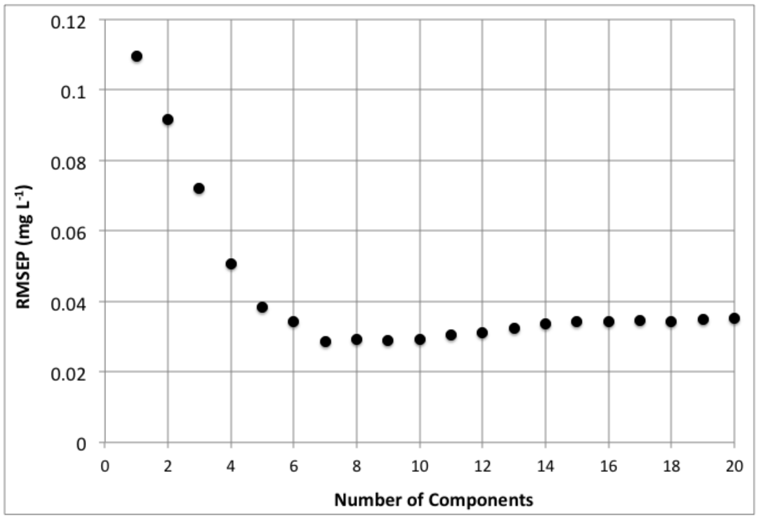

Figure B.33. Root mean square error of prediction (RMSEP, mg L^{-1}) as a function of the number of components for the second trial of the partial least squares regression model for total dissolved nitrogen (TDN) in watershed D0.

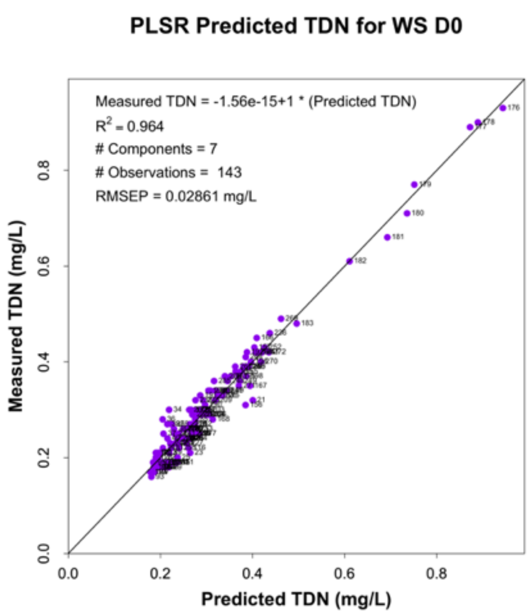

Figure B.34. Final relationship between measured and predicted values used to predict continuous total dissolved nitrogen (TDN) data for watershed D0.

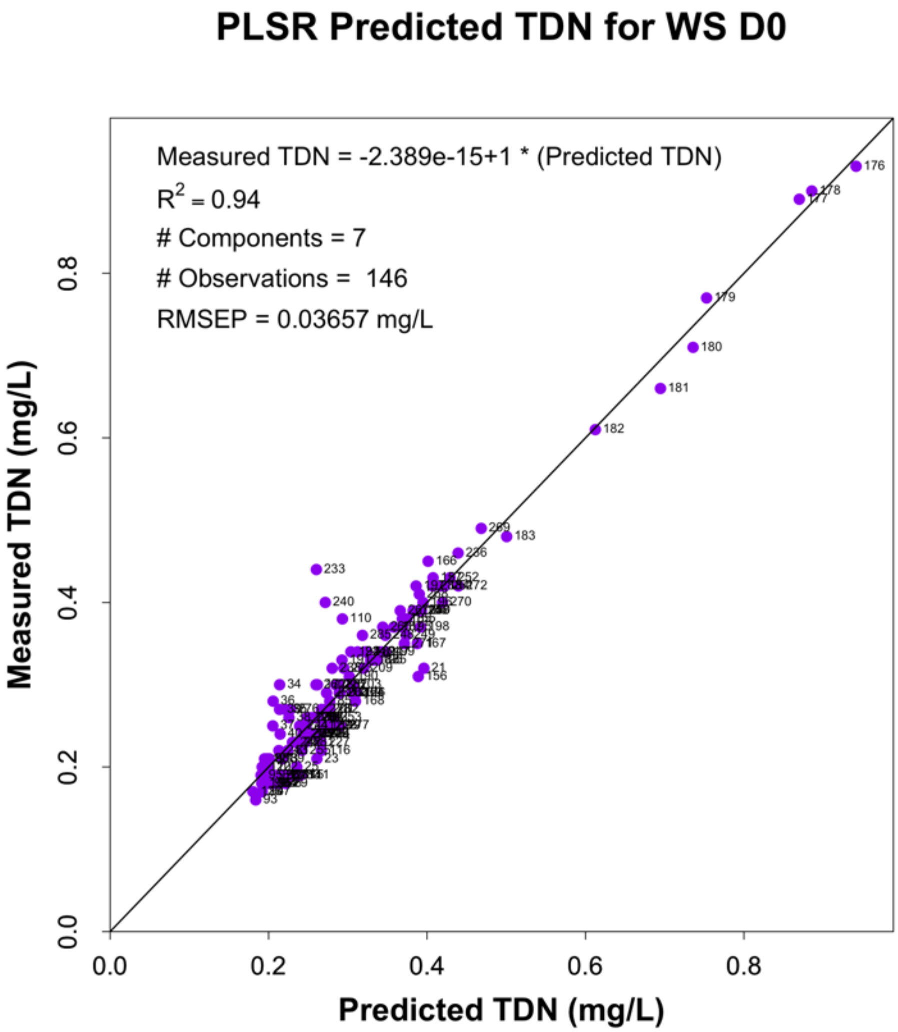

Figure B.35. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) trial with 7 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (146 measured samples).

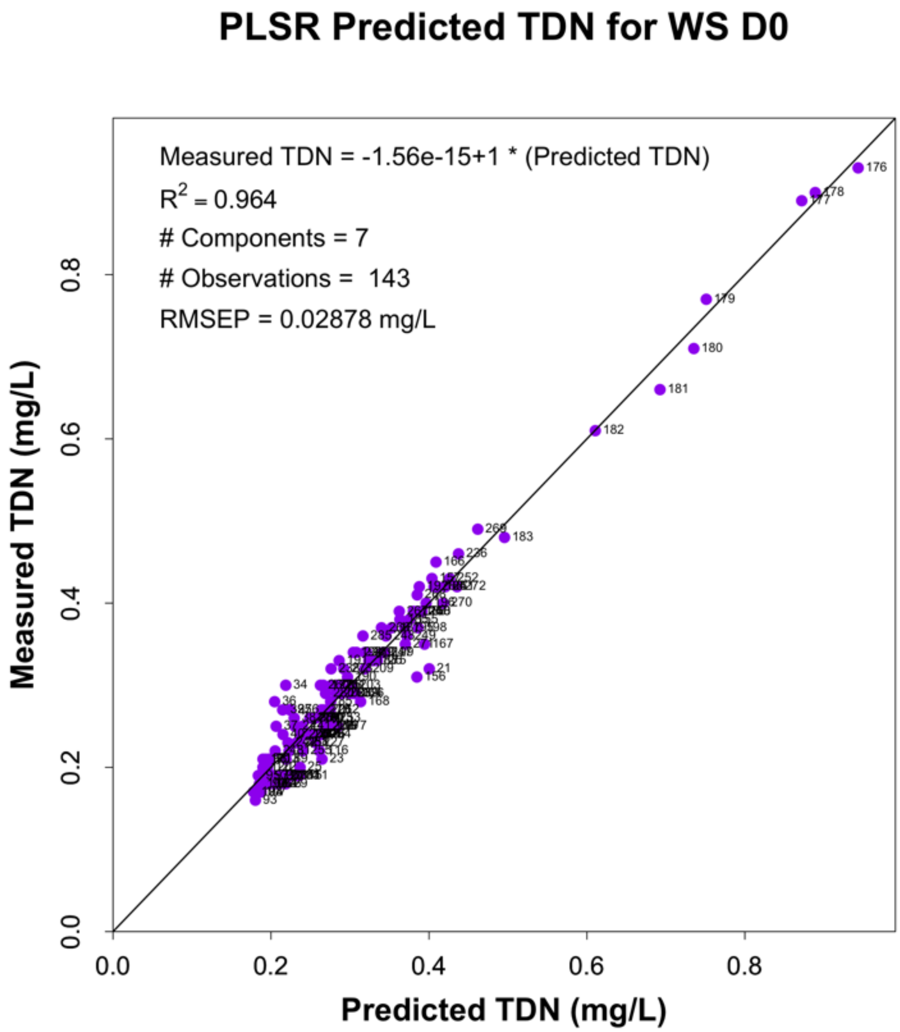

Figure B.36. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) trial with 7 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (143 measured samples).

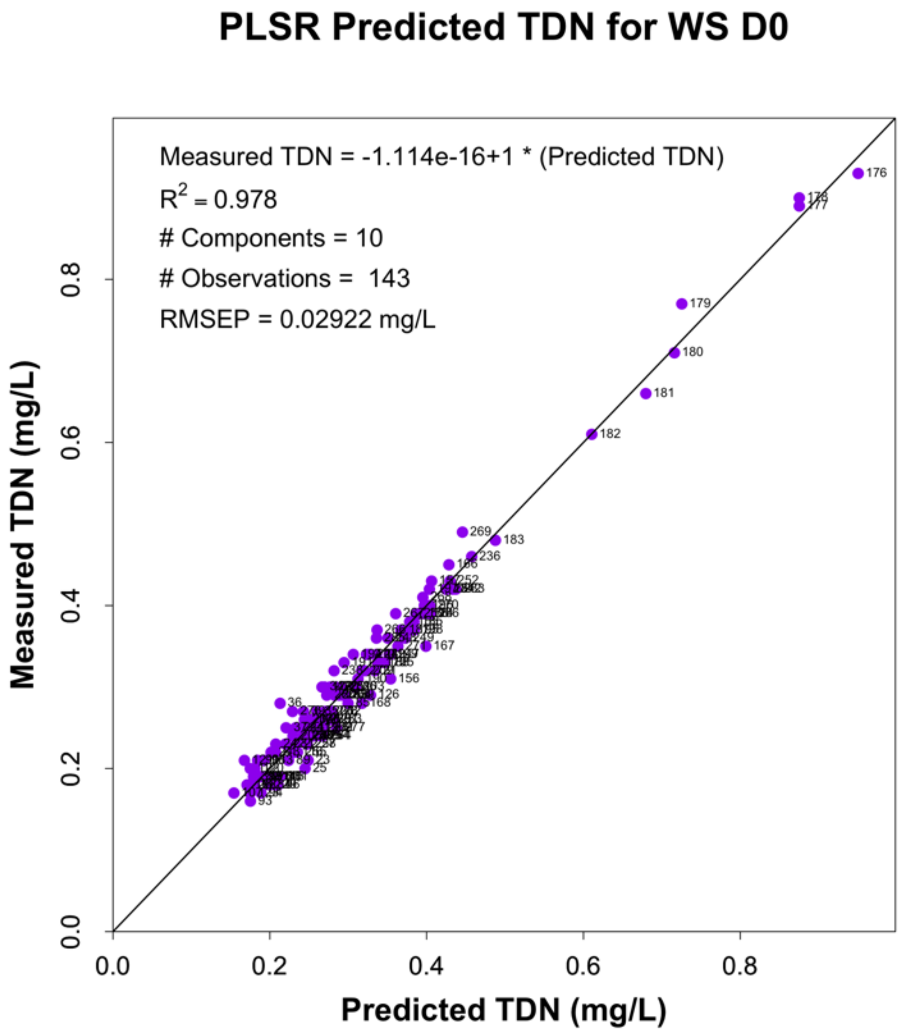

Figure B.37. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) trial with 10 components for watershed D0 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (143 measured samples).

B.2 Watershed D1

Dissolved organic carbon (DOC)

```
Data:   X dimension: 168 206
        Y dimension: 168 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           2.734    2.492    2.432    2.085    1.682    1.663    1.665    1.544    1.325    1.274     1.280     1.249     1.222     1.337
adjCV        2.734    2.490    2.446    2.047    1.677    1.657    1.647    1.519    1.260    1.265     1.266     1.231     1.196     1.305
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.318     1.308     1.380     1.370     1.394     1.486     1.525
adjCV     1.284     1.274     1.338     1.326     1.347     1.433     1.469

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      97.83    99.46    99.78    99.95    99.99    99.99   100.00    100.0   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)   18.46    26.36    59.98    66.60    68.32    76.13    79.33     83.7    84.11     86.66     88.93     91.15     92.12
                     14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.0    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     93.4     94.19     94.88     95.51     95.97     96.31     96.68
```

Figure B.38. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D1, used to select the number of components.

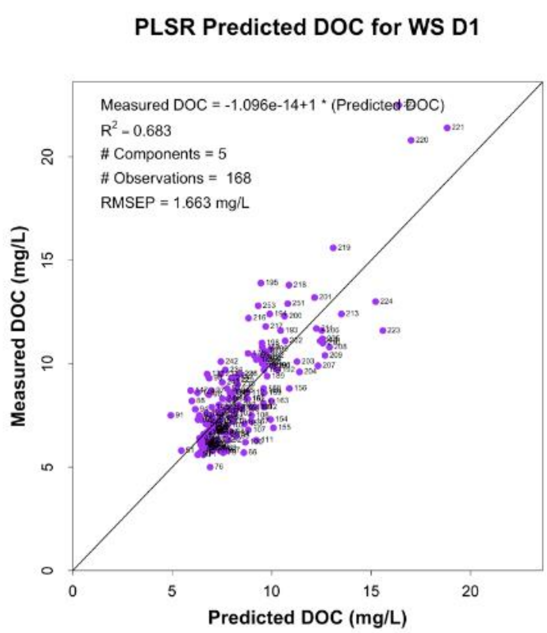

Figure B.39. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 5 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (168 measured samples).

```
Data:   X dimension: 80 206
        Y dimension: 80 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           1.909    1.795    1.687    1.132   0.8993   0.8698   0.8761   0.8662   0.7438   0.6166    0.6287    0.6700    0.7006    0.7002
adjCV        1.909    1.792    1.583    1.132   0.8974   0.8663   0.8719   0.8532   0.7308   0.6093    0.6211    0.6566    0.6801    0.6741
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        0.725    0.7482    0.7548    0.7738    0.7912    0.8362    0.8339
adjCV     0.699    0.7167    0.7246    0.7423    0.7563    0.7970    0.7945

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       96.56    98.02    99.89    99.97    99.99   100.00   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    13.62    46.12    70.20    80.24    82.17    83.77    87.39    91.74    93.73     94.53     95.59     96.67     97.59
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)     98.02     98.53     98.72     98.94     99.26      99.5     99.61
```

Figure B.40. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D1, used to select the number of components.

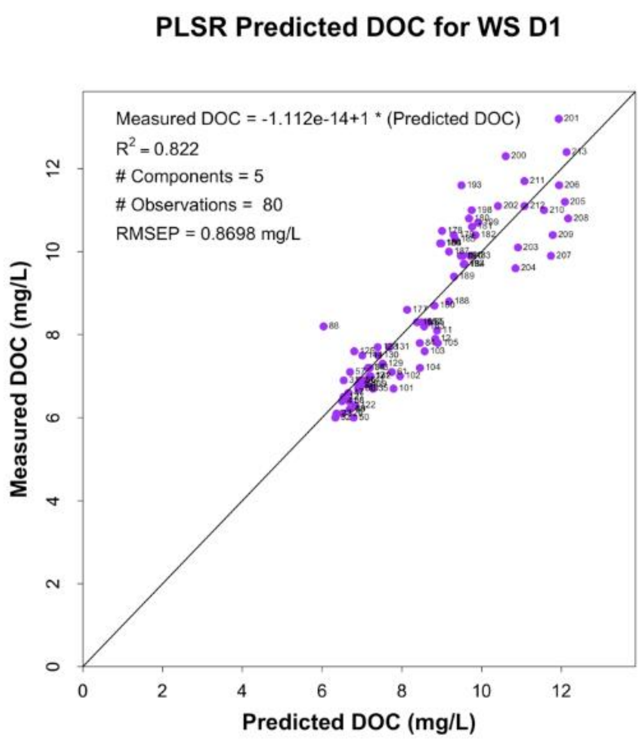

Figure B.41. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 5 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (80 measured samples).

```
Data:   X dimension: 65 206
        Y dimension: 65 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           1.647    1.545    1.528    1.102   0.6404   0.6006   0.6652   0.5277   0.6058   0.6538    0.7833    0.7838    0.7814    0.8517
adjCV        1.647    1.541    1.374    1.101   0.6351   0.5978   0.6368   0.5224   0.5952   0.6411    0.7572    0.7549    0.7524    0.8191
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV       0.9677    1.0057     1.057     1.104     1.121     1.107     1.097
adjCV    0.9263    0.9597     1.008     1.052     1.067     1.054     1.044

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                        95.99    97.24    99.90    99.97    99.99   100.00   100.00   100.00   100.00    100.00       100    100.00     100.0
as.vector(samp.conc)     16.99    47.76    61.92    87.65    88.64    92.28    93.39    93.89    94.77     96.13        97     97.62      98.1
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      98.72     99.23     99.44     99.62     99.75     99.84     99.89
```

Figure B.42. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D1, used to select the number of components.

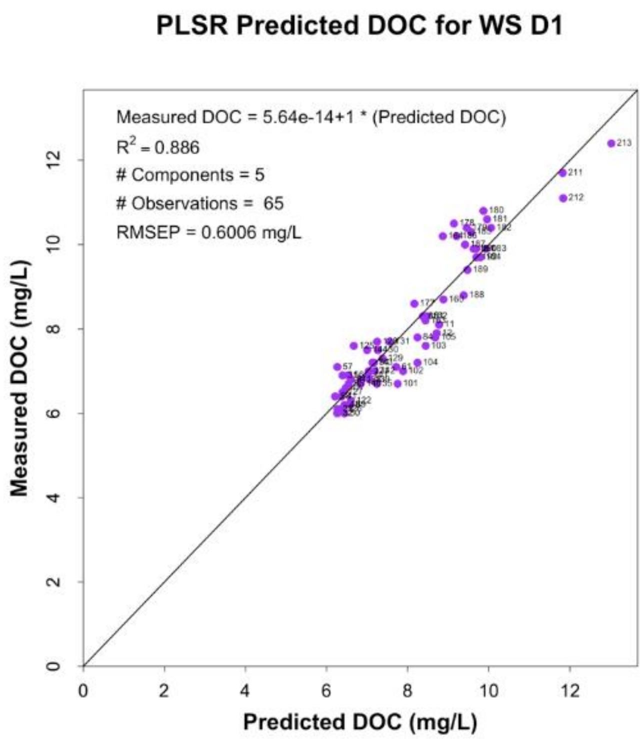

Figure B.43. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 5 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (65 measured samples).

Nitrate-nitrogen (NO_3^--N)

```
Data:   X dimension: 95 206
        Y dimension: 95 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.04299  0.04345  0.04558  0.04616  0.04752  0.04874  0.04400  0.04243  0.04048  0.04353   0.04161   0.04581   0.04317   0.04477
adjCV      0.04299  0.04341  0.04537  0.04595  0.04717  0.04678  0.04344  0.04207  0.04027  0.04283   0.04087   0.04466   0.04210   0.04361
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.04632   0.05036   0.05172   0.05429   0.05339   0.05450   0.05381
adjCV   0.04465   0.04851   0.04967   0.05196   0.05090   0.05196   0.05129

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                    98.4797  99.5919   99.895   99.972    99.97    99.99   100.00   100.00   100.00    100.00    100.00       100    100.00
as.vector(samp.conc)  0.1213   0.5236    1.239    2.529    23.53    24.41    26.47    28.97    45.96     59.45     64.05        70     75.82
                     14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00    100.00    100.00     100.0    100.00    100.00
as.vector(samp.conc)    82.28     85.24     88.95     91.41      94.3     95.15     96.11
```

Figure B.44. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D1, used to select the number of components.

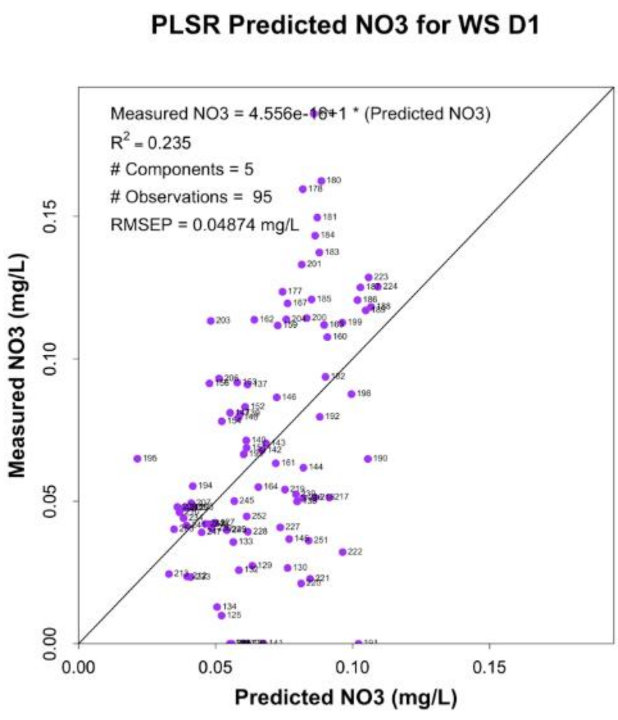

Figure B.45. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 5 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (95 measured samples).

```
Data:   X dimension: 87 206
        Y dimension: 87 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.03957  0.04036  0.04187  0.04158  0.04364  0.04549  0.04099   0.0381  0.03564  0.03548   0.03643   0.03648   0.03380   0.03386
adjCV      0.03957  0.04029  0.04170  0.04148  0.04337  0.04510  0.04046   0.0377  0.03543  0.03523   0.03575   0.03542   0.03273   0.03244
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03534   0.04070   0.04310   0.04504   0.04602   0.04780   0.04791
adjCV   0.03402   0.03905   0.04116   0.04305   0.04384   0.04555   0.04563

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                     98.26256   99.580   99.910   99.968    99.98   100.00   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)   0.05391    1.031    2.189    4.109    17.70    30.31    34.13    37.72    49.95     68.63     75.53     82.68     88.36
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00     100.0    100.00    100.00    100.00
as.vector(samp.conc)     90.23     92.23     94.42      95.2     96.81     97.29     97.96
```

Figure B.46. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D1, used to select the number of components after removing all data <0.01 mg L^{-1}.

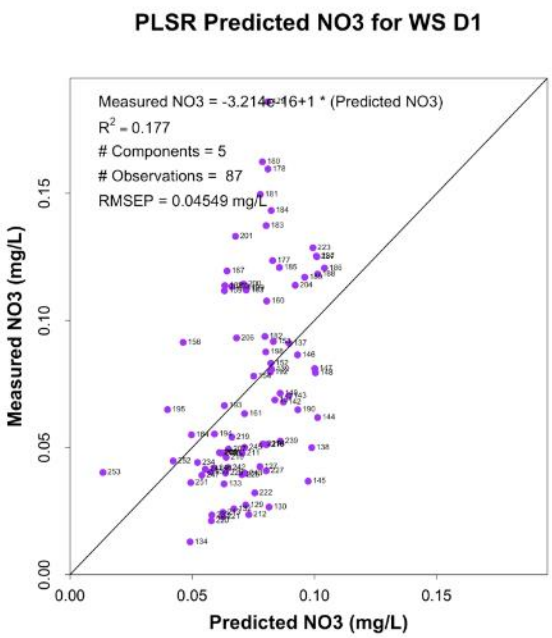

Figure B.47. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 5 components after removing all data <0.01 mg L^{-1} for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (87 measured samples).

```
Data:   X dimension: 54 206
        Y dimension: 54 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.03334  0.03350  0.03770  0.03810  0.03783  0.03613  0.03608  0.03452  0.03693  0.03587   0.03528   0.03338   0.03066   0.03418
adjCV      0.03334  0.03346  0.03734  0.03762  0.03730  0.03582  0.03559  0.03413  0.03628  0.03477   0.03387   0.03212   0.02967   0.03263
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03590   0.03844   0.03911   0.03917   0.04057   0.04076   0.04109
adjCV   0.03421   0.03654   0.03715   0.03713   0.03844   0.03859   0.03888

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      97.8300   99.475   99.945    99.98    99.99      100   100.00   100.00   100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)    0.1012    2.035    5.332    11.48    15.05       22    30.08    43.56    64.43     78.79     84.92      88.5     93.43
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00     100.0    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      95.03      96.3     97.35     98.64     99.14     99.57     99.83
```

Figure B.48. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D1, used to select the number of components after removing all data <0.05 mg L^{-1}.

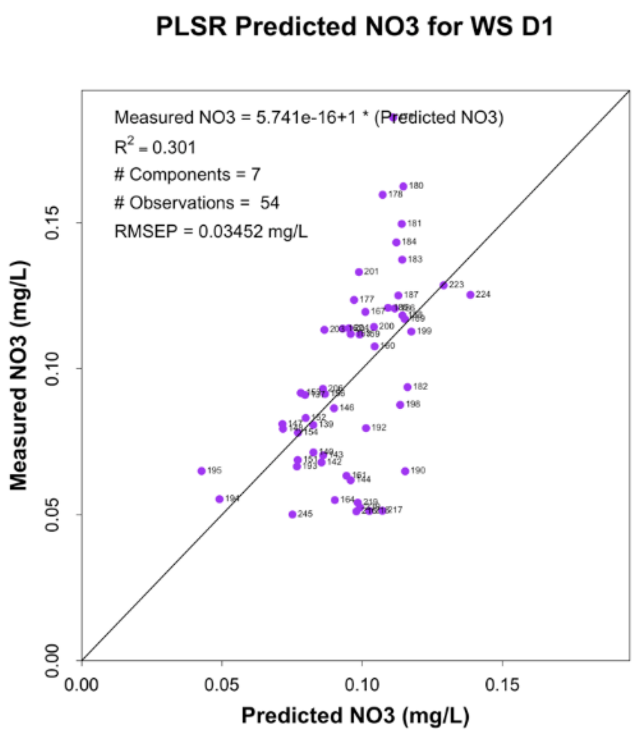

Figure B.49. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 7 components after removing all data <0.05 mg L^{-1} for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (54 measured samples).

```
Data:   X dimension: 34 206
        Y dimension: 34 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.02373  0.02390  0.02446  0.02183  0.02013  0.02251  0.02156  0.02484   0.0325  0.03687   0.04228   0.04728   0.04859   0.05111
adjCV      0.02373  0.02388  0.02444  0.02164  0.01992  0.02202  0.02130  0.02428   0.0315  0.03553   0.04066   0.04526   0.04650   0.04884
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.04964   0.05047   0.05129   0.05192   0.05200   0.05180   0.05177
adjCV   0.04739   0.04815   0.04890   0.04949   0.04957   0.04937   0.04934

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                     97.0695   99.892    99.96    99.98    99.99   100.00   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)   0.9999    7.206    36.88    48.36    51.39    51.95    59.11    67.11    75.35     82.72     90.55     93.17     95.94
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.0    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      97.8     98.78     99.75     99.94     99.97     99.99     99.99
```

Figure B.50. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D1, used to select the number of components.

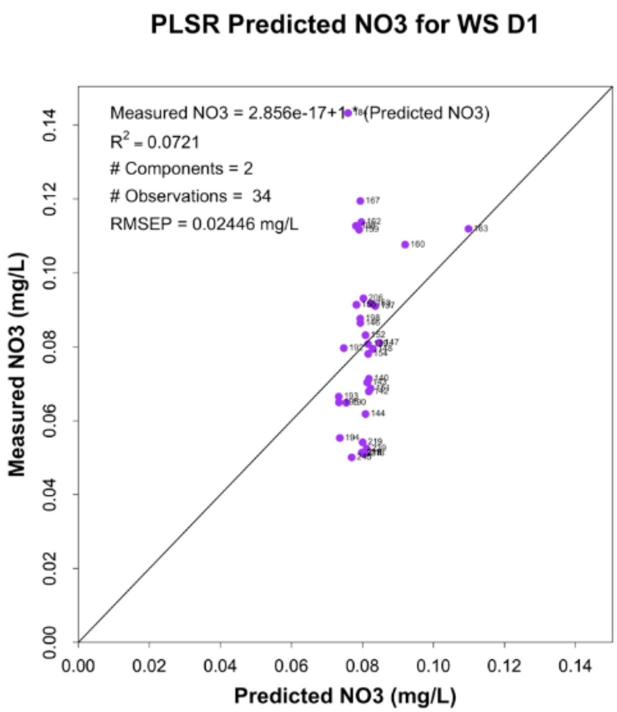

Figure B.51. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 2 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (34 measured samples).

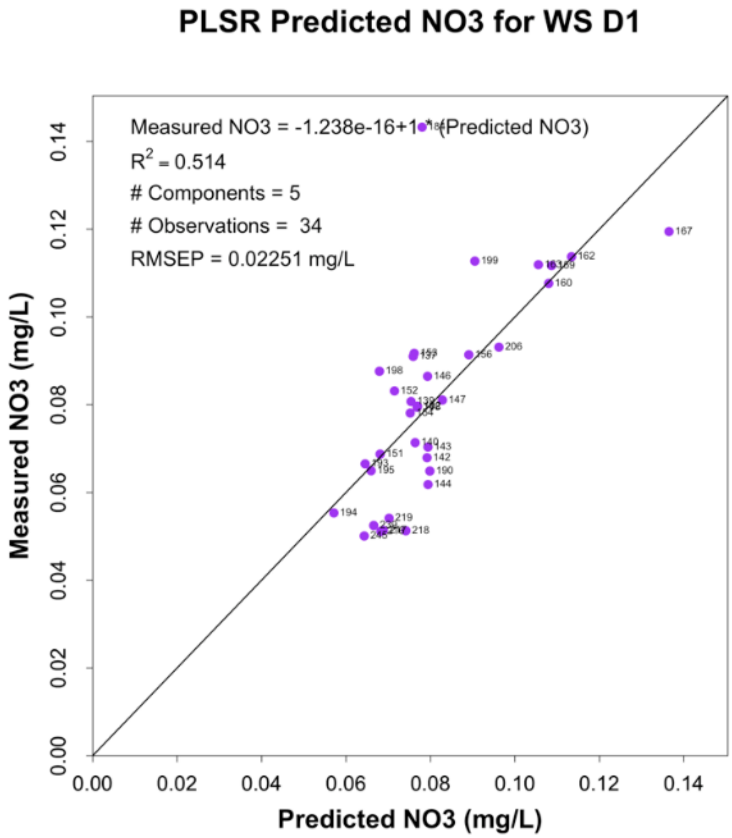

Figure B.52. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 5 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (34 measured samples).

```
Data:   X dimension: 33 206
        Y dimension: 33 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.02125  0.02095  0.02227  0.01600  0.01398  0.01545  0.01621  0.01761  0.01866  0.02299   0.02171   0.02235   0.02244   0.02322
adjCV      0.02125  0.02093  0.02214  0.01589  0.01382  0.01519  0.01591  0.01722  0.01843  0.02209   0.02079   0.02127   0.02129   0.02200
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.02313   0.02316   0.02323   0.02329   0.02331   0.02332   0.02337
adjCV   0.02189   0.02191   0.02198   0.02203   0.02204   0.02206   0.02210

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      97.014    99.89    99.96    99.98    99.99   100.00    100.0   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    1.801    14.15    55.91    70.23    70.85    71.51     74.7    78.06    86.51     91.79     96.06     97.58     98.63
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00       100
as.vector(samp.conc)     99.31     99.59     99.83     99.94     99.98     99.99       100
```

Figure B.53. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D1, used to select the number of components.

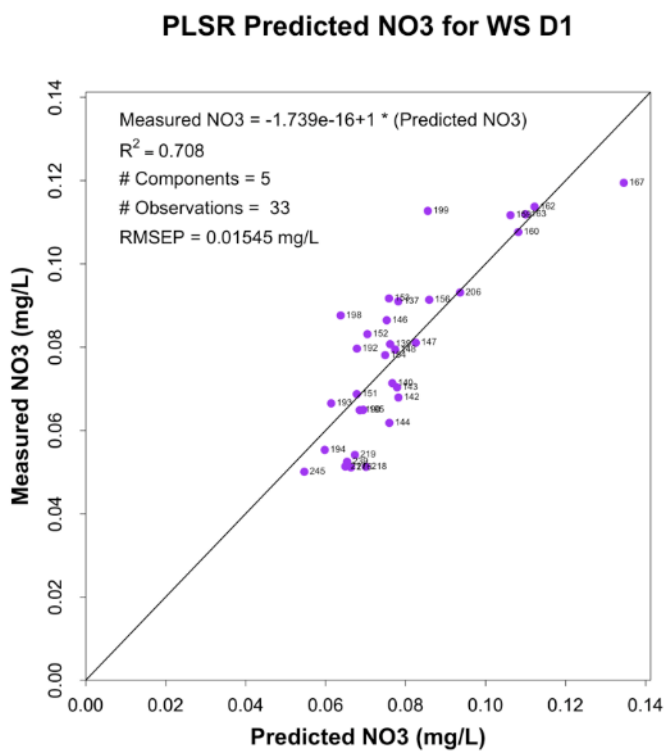

Figure B.54. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 5 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (33 measured samples).

```
Data:   X dimension: 30 206
        Y dimension: 30 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.01972  0.02049  0.01918  0.01383  0.01052  0.01105  0.01033  0.01076  0.01026  0.01038   0.01161   0.01289   0.01292   0.01455
adjCV      0.01972  0.02040  0.01903  0.01376  0.01038  0.01076  0.01017  0.01057  0.01004  0.01012   0.01121   0.01233   0.01237   0.01387
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.01481   0.01479   0.01500   0.01489   0.01492   0.01492   0.01494
adjCV   0.01409   0.01405   0.01423   0.01413   0.01415   0.01415   0.01417

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      96.232    99.92    99.97    99.99    99.99   100.00    100.0   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    2.143    22.72    61.14    79.80    81.86    85.51     87.7    90.77    93.61     95.66     97.41     98.21     99.07
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00     100.0    100.00    100.00       100       100       100
as.vector(samp.conc)     99.53      99.8     99.93     99.98       100       100       100
```

Figure B.55. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D1, used to select the number of components.

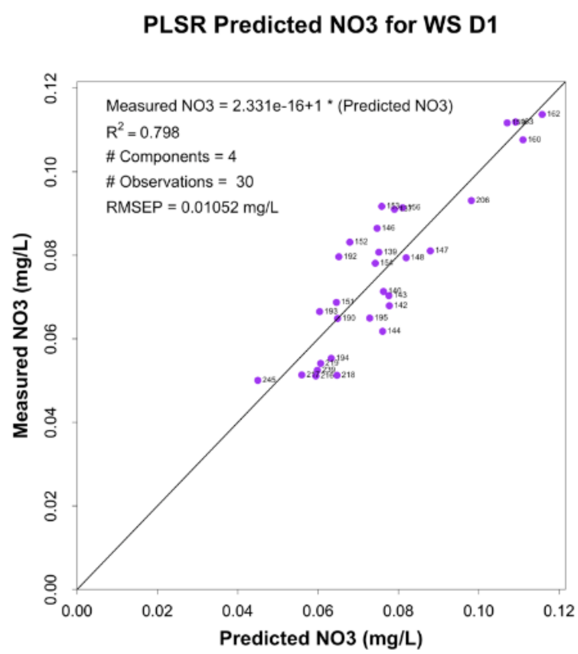

Figure B.56. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 4 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (30 measured samples).

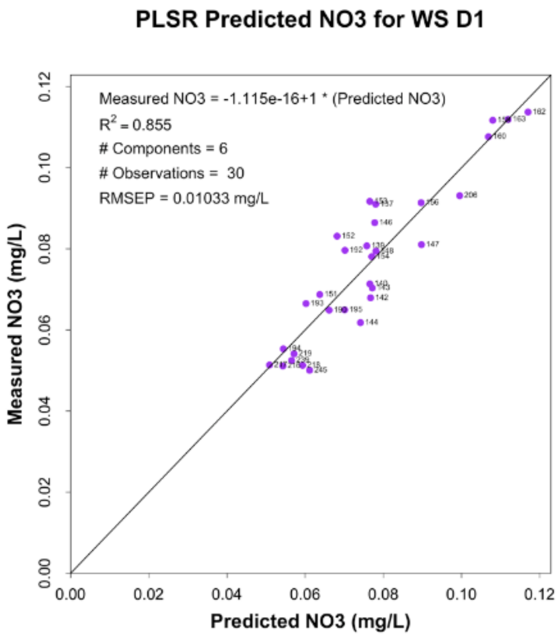

Figure B.57. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 6 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (30 measured samples).

Total dissolved nitrogen (TDN)

```
Data:   X dimension: 167 206
        Y dimension: 167 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.06234  0.05738  0.05593  0.04942  0.04437  0.04342  0.04225  0.03889  0.03693  0.03527   0.03448   0.03332   0.03311   0.03329
adjCV      0.06234  0.05734  0.05593  0.04922  0.04423  0.04333  0.04203  0.03862  0.03685  0.03515   0.03423   0.03305   0.03257   0.03267
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03214   0.03260   0.03196   0.03093   0.03023   0.03124   0.03257
adjCV   0.03142   0.03169   0.03104   0.03013   0.02935   0.03020   0.03140

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      97.93     99.6    99.81    99.96    99.99    99.99   100.00    100.0   100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)   16.84     21.7    46.70    54.60    56.21    62.29    66.64     68.2    72.76     77.59     82.68      86.3     88.29
                     14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.0    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     90.8     92.61     93.68     94.47     95.34     95.93     96.43
```

Figure B.58. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for total dissolved nitrogen (TDN) in watershed D1, used to select the number of components.

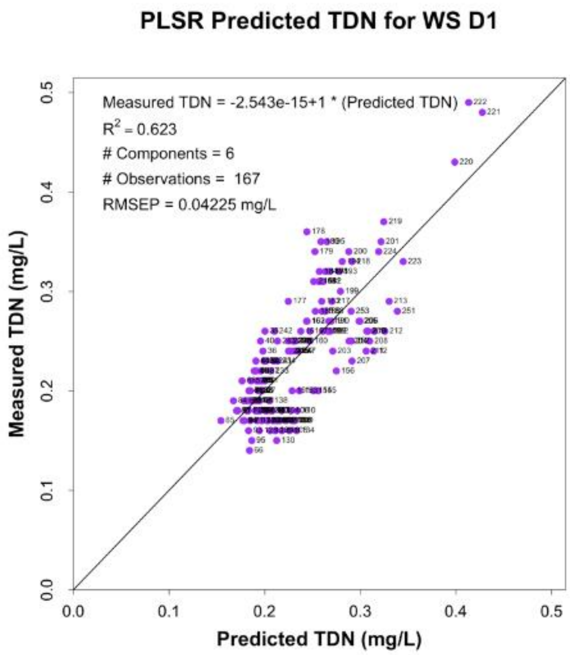

Figure B.59. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 6 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (167 measured samples).

```
Data:   X dimension: 149 206
        Y dimension: 149 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.0465  0.04522  0.04464  0.03955  0.03735  0.03615  0.03509  0.03453  0.03206  0.03089   0.02936   0.02821   0.02692   0.02551
adjCV       0.0465  0.04518  0.04462  0.03945  0.03723  0.03614  0.03499  0.03441  0.03177  0.03065   0.02924   0.02778   0.02639   0.02490
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.02476   0.02542   0.02511   0.02458   0.02486   0.02518   0.02547
adjCV   0.02413   0.02473   0.02432   0.02383   0.02397   0.02429   0.02449

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                        96.88    99.71    99.86    99.95    99.99   100.00   100.00   100.00    100.0     100.0    100.00    100.00    100.00
as.vector(samp.conc)      6.82    10.19    34.94    42.12    44.38    49.26    51.88    62.34     67.2      72.8     81.01     85.63     89.28
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00     100.0
as.vector(samp.conc)      91.74     93.07     94.48     95.13     96.02     96.47      97.1
```

Figure B.60. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for total dissolved nitrogen (TDN) in watershed D1, used to select the number of components.

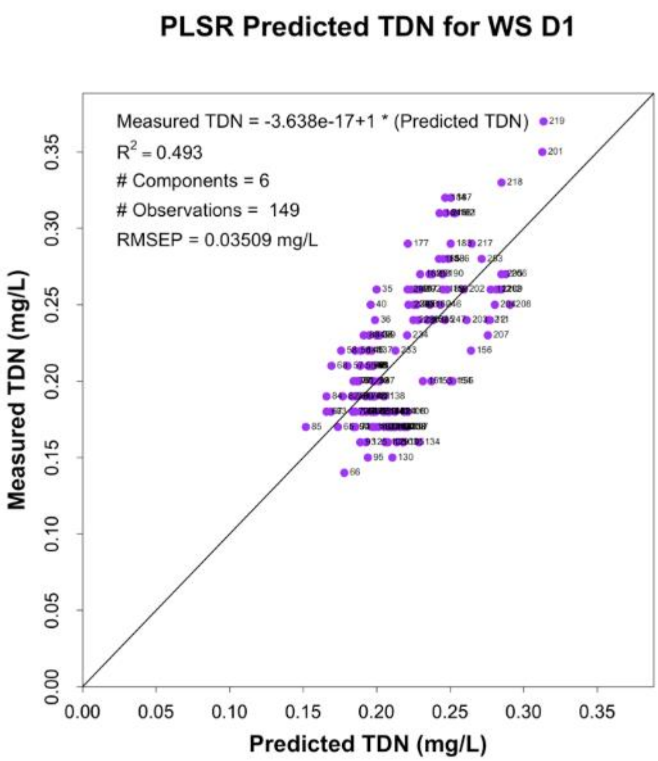

Figure B.61. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 6 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (149 measured samples).

```
Data:   X dimension: 139 206
        Y dimension: 139 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.04519  0.04351  0.04289  0.03709  0.03525  0.03407  0.03345  0.03262  0.03123  0.02934   0.02982   0.03405   0.03152   0.02937
adjCV      0.04519  0.04350  0.04288  0.03703  0.03517  0.03408  0.03333  0.03251  0.03096  0.02922   0.02954   0.03314   0.03058   0.02847
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.02851   0.02927   0.02749   0.02754   0.02824   0.02757   0.02747
adjCV   0.02758   0.02824   0.02648   0.02653   0.02716   0.02653   0.02640

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       96.945    99.70    99.86    99.96    99.98   100.00   100.00   100.00   100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)     7.327    10.29    36.54    43.43    47.22    51.87    54.54    64.51    69.04     73.95     81.84      86.5     89.72
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00       100    100.00    100.00    100.00    100.00
as.vector(samp.conc)      92.24     93.63        95     95.66     96.31     96.75     97.27
```

Figure B.62. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for total dissolved nitrogen (TDN) in watershed D1, used to select the number of components.

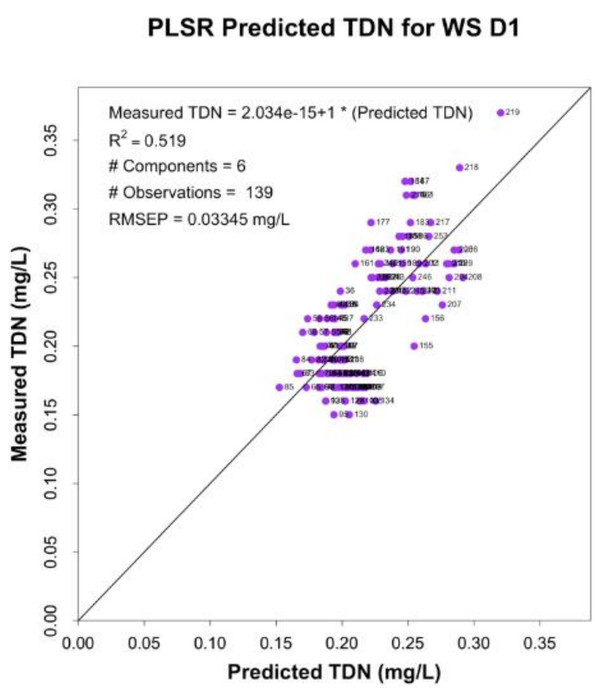

Figure B.63. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 6 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (139 measured samples).

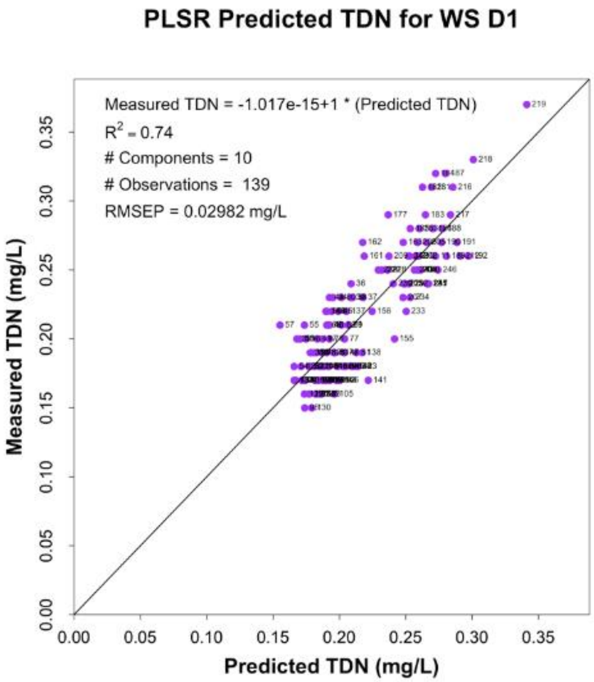

Figure B.64. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 10 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (139 measured samples).

```
Data:   X dimension: 123 206
        Y dimension: 123 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV         0.04615  0.04407  0.04336  0.03779  0.03576  0.03391  0.03430  0.03251  0.03154  0.02885   0.03071   0.03592   0.03293   0.03011
adjCV      0.04615  0.04405  0.04336  0.03763  0.03562  0.03397  0.03408  0.03236  0.03117  0.02859   0.03024   0.03472   0.03181   0.02903
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03116   0.02926   0.02795   0.02865   0.02859   0.02897   0.02877
adjCV   0.02991   0.02809   0.02680   0.02746   0.02738   0.02770   0.02745

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       97.496    99.73    99.86    99.96    99.98   100.00   100.00   100.00    100.0    100.00    100.00    100.00     100.0
as.vector(samp.conc)     9.146    12.83    41.43    46.74    51.90    56.42    59.97    69.53     75.3     79.61     86.36     89.66      92.6
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00     100.0
as.vector(samp.conc)      94.67     95.82     96.83     97.23     97.67     98.11      98.6
```

Figure B.65. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for total dissolved nitrogen (TDN) in watershed D1, used to select the number of components.

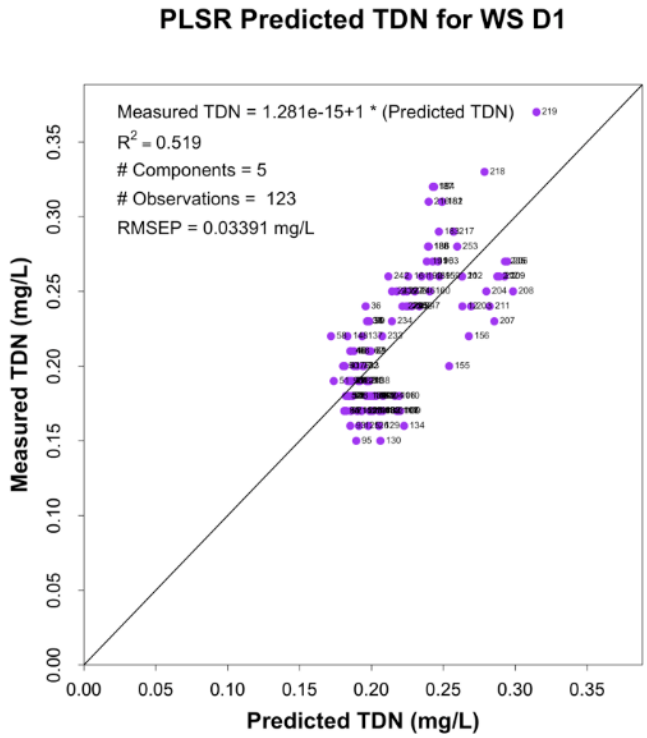

Figure B.66. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 5 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (123 measured samples).

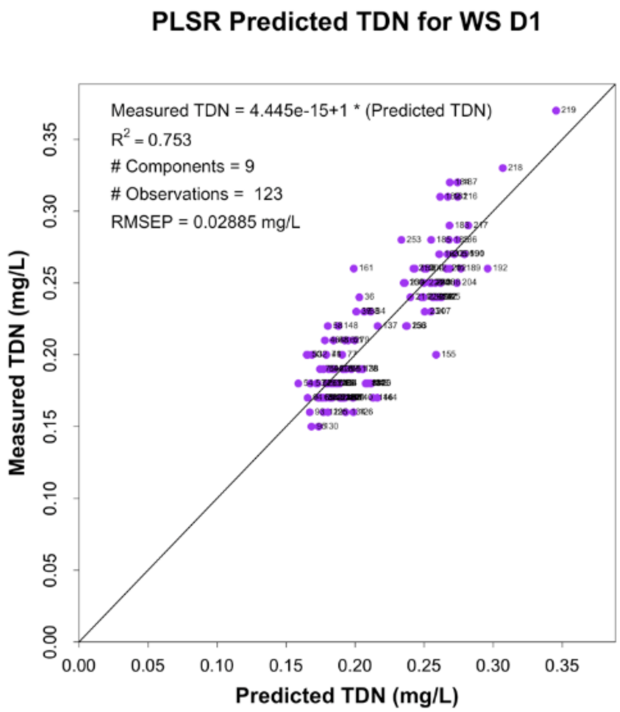

Figure B.67. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 9 components for watershed D1 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (123 measured samples).

B.3 Watershed D2

Dissolved organic carbon (DOC)

```
Data:   X dimension: 159 206
        Y dimension: 159 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps
CV           2.703    2.654    2.661    2.553    2.476    2.395    2.204    2.167    2.181    2.144     2.175     2.169     2.204
adjCV        2.703    2.652    2.658    2.552    2.465    2.384    2.196    2.160    2.165    2.128     2.134     2.133     2.162
       13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        2.519     2.686     2.843     3.163     3.306     3.619     3.753     3.797
adjCV     2.455     2.612     2.747     3.047     3.178     3.467     3.586     3.627

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps
X                       98.682   99.454    99.78    99.93    99.98   100.00   100.00   100.00    100.0    100.00    100.00    100.00
as.vector(samp.conc)     4.536    8.456    18.37    28.92    33.51    41.29    44.02    49.89     54.3     62.26     65.23     68.37
                       13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00       100     100.0
as.vector(samp.conc)      71.58     75.23     78.29     79.99     82.59     84.92        87      88.1
```

Figure B.68. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

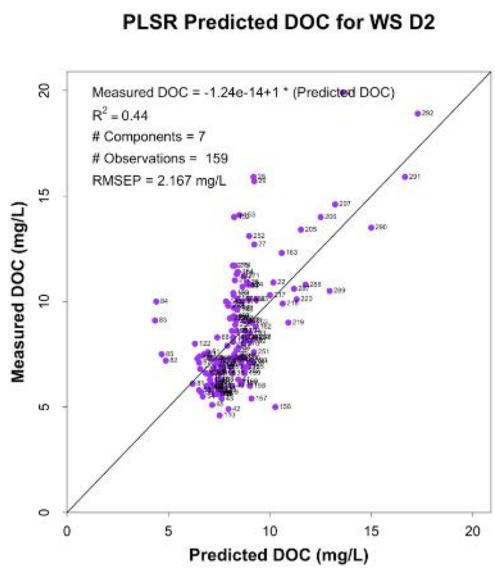

Figure B.69. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 7 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (159 measured samples).

```
Data:   X dimension: 147 206
        Y dimension: 147 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           2.354    2.274    2.366    2.156    2.102    1.791    1.684    1.627    1.623    1.717     1.711     1.722     1.765     1.869
adjCV        2.354    2.273    2.322    2.040    2.079    1.719    1.680    1.619    1.613    1.695     1.690     1.688     1.737     1.818
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.974     1.944     2.148     2.311     2.435     2.576     2.613
adjCV     1.914     1.892     2.075     2.225     2.342     2.472     2.505

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      98.775    98.98    99.17    99.93    99.94    99.99   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    7.474    21.24    37.62    39.59    54.17    55.16    60.05    62.02    65.85     69.33     73.71     75.82     80.35
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00     100.0    100.00     100.0    100.00
as.vector(samp.conc)     82.13     83.27     85.51      86.9     88.22      89.7     90.63
```

Figure B.70. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

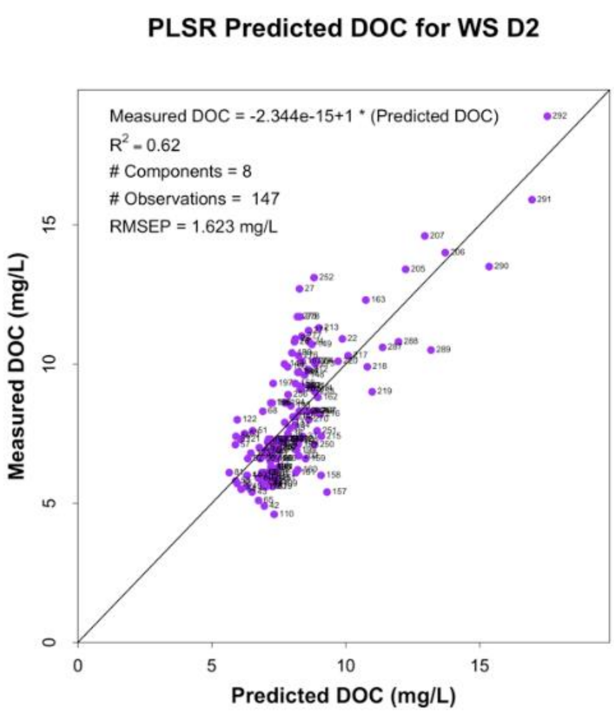

Figure B.71. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 8 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (147 measured samples).

```
Data:    X dimension: 144 206
         Y dimension: 144 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           2.299    2.207    2.191    2.000    1.916    1.618    1.538    1.450    1.443    1.492     1.507     1.555     1.681     1.731
adjCV        2.299    2.206    2.194    1.998    1.900    1.537    1.514    1.445    1.436    1.476     1.489     1.532     1.643     1.686
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.778     1.791     1.901     2.047     2.079     2.204     2.409
adjCV     1.725     1.741     1.833     1.970     2.001     2.117     2.307

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      98.828    99.55    99.75    99.94    99.94    99.98   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    8.217    12.96    33.24    42.96    58.61    60.54    64.62    66.85    70.25     72.87     76.26     79.27     82.34
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     84.45     85.68     88.32     89.48     90.47     91.52     92.53
```

Figure B.72. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

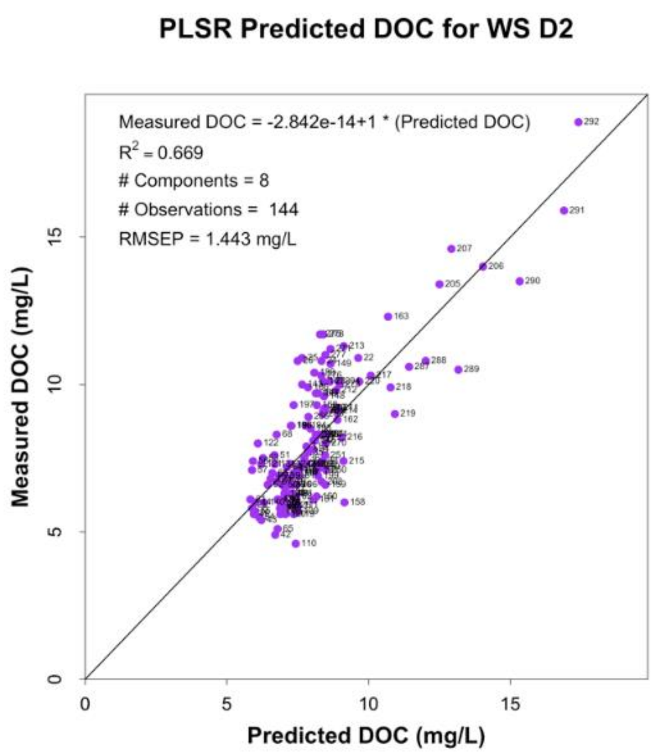

Figure B.73. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 8 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (144 measured samples).

```
Data:   X dimension: 138 206
        Y dimension: 138 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           2.265    2.157    2.077    1.961    1.839    1.488    1.442    1.355    1.335    1.453     1.656     1.626     1.615     1.704
adjCV        2.265    2.155    2.085    1.962    1.824    1.439    1.444    1.349    1.328    1.440     1.613     1.591     1.581     1.661
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.966     2.100     2.379     2.668     3.019     3.181     3.151
adjCV     1.900     2.024     2.284     2.551     2.881     3.030     3.002

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       98.71    99.43    99.76    99.93    99.94    99.99   100.00   100.00   100.00     100.0    100.00    100.00    100.00
as.vector(samp.conc)    10.57    16.96    33.44    47.41    60.92    63.93    69.18    71.04    73.03      77.1     79.77     82.21     83.98
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00       100    100.00
as.vector(samp.conc)     85.77     87.41     89.09     90.57     91.49        93     93.67
```
Figure B.74. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

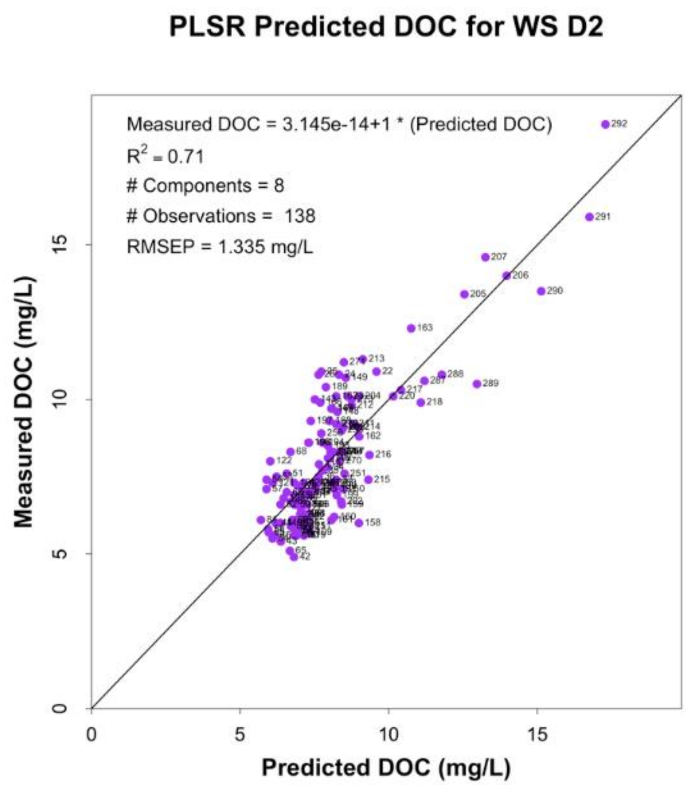

Figure B.75. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 8 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (138 measured samples).

```
Data:   X dimension: 135 206
        Y dimension: 135 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           2.223    2.097    2.059    1.940    1.868    1.506    1.401    1.304    1.279    1.345     1.518     1.792     1.889      2.17
adjCV        2.223    2.095    2.067    1.938    1.850    1.444    1.405    1.299    1.273    1.334     1.486     1.741     1.829      2.09
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        2.413     2.700     2.951     3.292     3.620     3.783      3.64
adjCV     2.316     2.584     2.818     3.136     3.444     3.595      3.46

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       98.72    99.43    99.75    99.93    99.95    99.99   100.00   100.00   100.00     100.0    100.00    100.00    100.00
as.vector(samp.conc)    12.07    17.91    33.79    45.25    60.26    63.79    70.06    72.34    74.29      77.3     79.88     82.64     84.11
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     86.06     87.69     89.32     90.84     91.77     93.37     93.88
```

Figure B.76. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

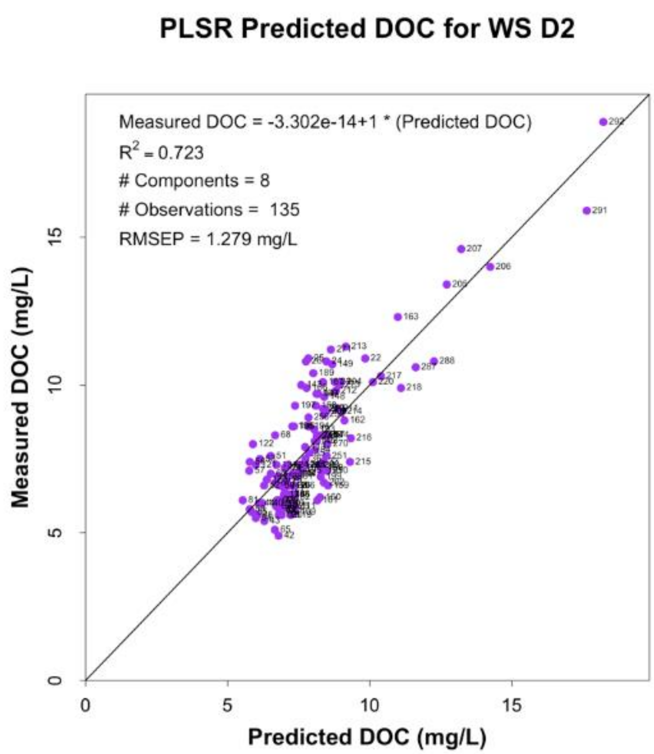

Figure B.77. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 8 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (135 measured samples).

```
Data:   X dimension: 16 206
        Y dimension: 16 1
Fit method: kernelpls
Number of components considered: 10

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps
CV           1.189    1.338    1.460    1.324   0.8613    1.235     1.27    1.176    1.179    1.194     1.204
adjCV        1.189    1.326    1.413    1.300   0.8511    1.196     1.20    1.107    1.107    1.119     1.128

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps
X                     99.9074    99.95    99.99   100.00      100   100.00   100.00   100.00   100.00    100.00
as.vector(samp.conc)   0.5988    37.04    44.73    64.69       74    92.49    98.09    99.45    99.93     99.99
```

Figure B.78. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 10 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

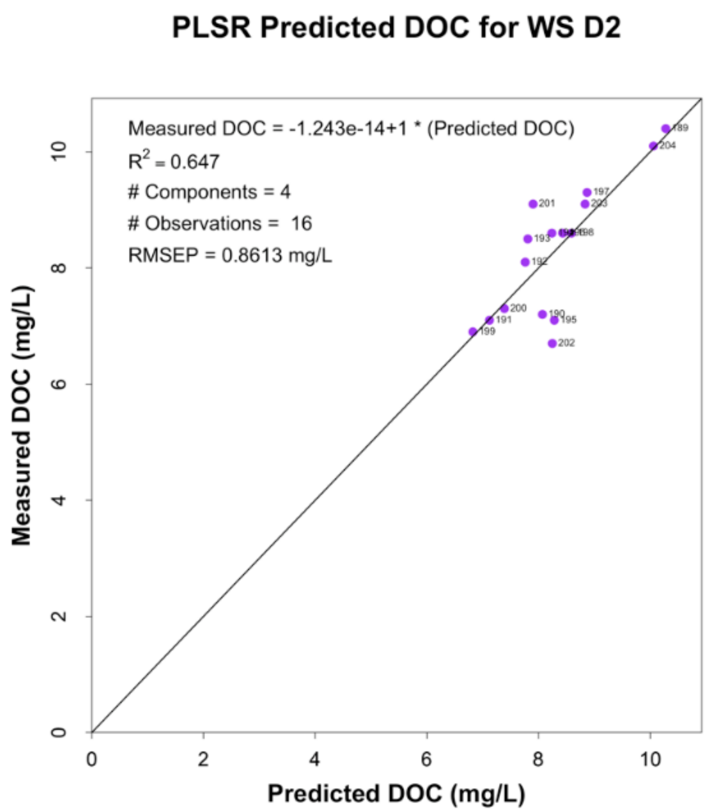

Figure B.79. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 4 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (16 measured samples).

```
Data:   X dimension: 13 206
        Y dimension: 13 1
Fit method: kernelpls
Number of components considered: 10

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps
CV           1.163    1.337    1.324    1.444   0.9858    1.197    1.124    1.112    1.109    1.109     1.109
adjCV        1.163    1.320    1.259    1.382   0.9229    1.113    1.037    1.025    1.022    1.022     1.022

TRAINING: % variance explained
                        1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps
X                        99.890    99.93    99.99    100.0   100.00   100.00   100.00   100.00      100       100
as.vector(samp.conc)      2.014    53.75    61.87     91.2    94.48    99.27    99.87    99.99      100       100
```

Figure B.80. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 10 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

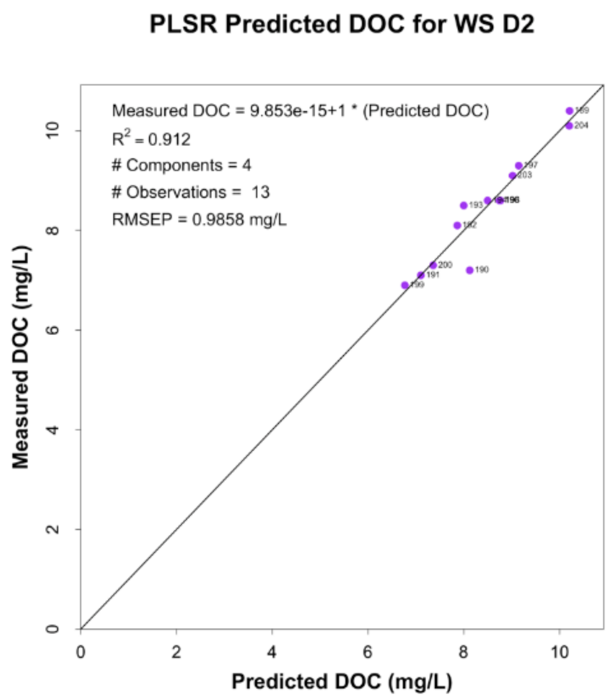

Figure B.81. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 4 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (13 measured samples).

```
Data:   X dimension: 52 206
        Y dimension: 52 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps
CV           2.492    2.499    2.525    2.604    2.163    1.989    2.181    2.502    2.789    2.856     2.948     3.019     3.014
adjCV        2.492    2.494    2.518    2.546    2.163    1.967    2.145    2.437    2.677    2.731     2.806     2.868     2.861
       13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        3.009     3.101     3.055     3.018     3.004     2.985     2.989     2.979
adjCV     2.852     2.933     2.886     2.851     2.837     2.819     2.823     2.814

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps
X                      94.745   99.262    99.60    99.96    99.98   100.00   100.00   100.00   100.00    100.00    100.00       100
as.vector(samp.conc)    2.235    4.549    23.41    35.83    57.10    57.66    59.65    75.65    83.98     91.61     94.37        96
                      13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     97.61     98.75     99.49     99.78     99.88     99.94     99.98     99.99
```

Figure B.82. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components, after using data subset used for NO3 (although leaving in values where NO3 values <0.05 were removed).

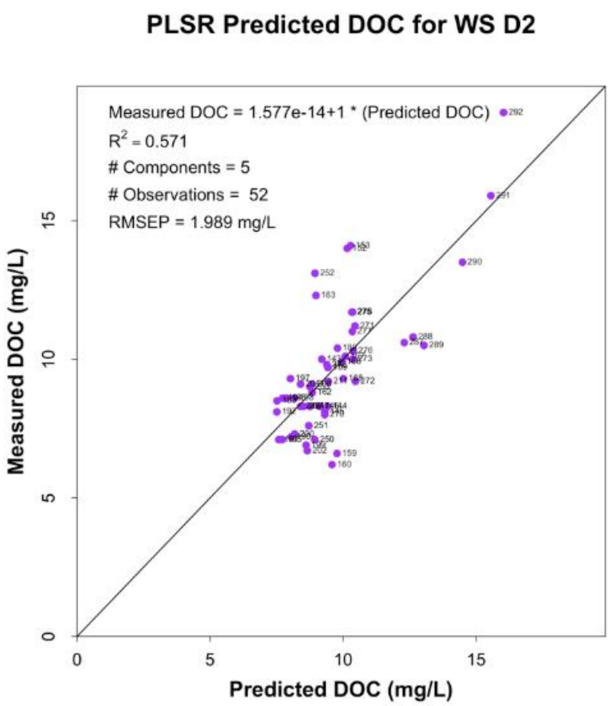

Figure B.83. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 5 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (52 measured samples).

```
Data:   X dimension: 33 206
        Y dimension: 33 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps
CV           1.069    1.111    1.090    1.027   0.9871   0.9972   0.9361    1.228    1.403    1.558     1.547     1.586     1.593
adjCV        1.069    1.100    1.087    1.021   0.9793   0.9850   0.9207    1.172    1.297    1.476     1.462     1.496     1.502
       13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.570     1.556     1.559     1.557     1.556     1.557     1.557     1.557
adjCV     1.479     1.466     1.468     1.466     1.465     1.466     1.466     1.466

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps
X                      50.064   98.920    99.92    99.97   100.00   100.00      100   100.00   100.00    100.00    100.00    100.00
as.vector(samp.conc)    4.722    9.047    23.79    39.33    45.57    61.15       75    89.92    91.67     96.49     98.44     99.27
                      13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00       100       100       100       100
as.vector(samp.conc)     99.67     99.88     99.94     99.99       100       100       100       100
```

Figure B.84. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

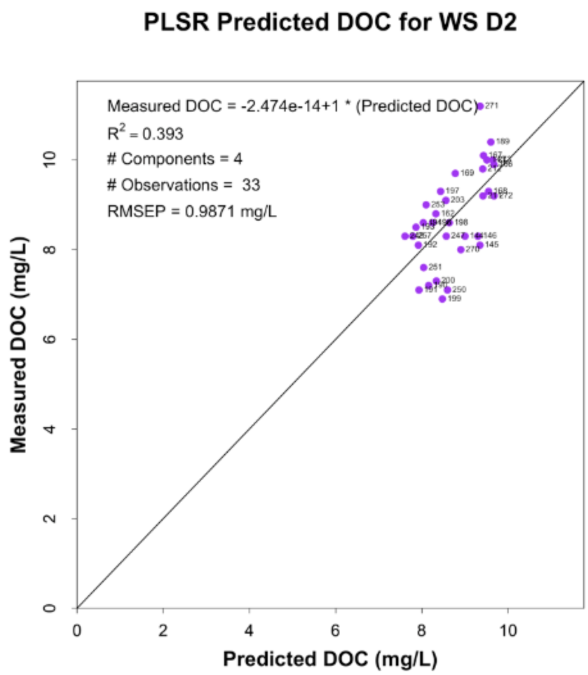

Figure B.85. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 4 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (33 measured samples).

```
Data:   X dimension: 32 206
        Y dimension: 32 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps
CV          0.9854    1.062   1.0010   0.9308   0.8842   0.9253   0.8947    1.131    1.233    1.337     1.309     1.329     1.342
adjCV       0.9854    1.057   0.9977   0.9256   0.8783   0.9163   0.8816    1.083    1.189    1.278     1.249     1.266     1.276
       13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.339     1.321     1.315     1.313     1.313     1.312     1.312     1.312
adjCV     1.273     1.256     1.250     1.248     1.248     1.247     1.248     1.248

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps
X                      83.03   98.779    99.93    99.97   100.00   100.00   100.00   100.00   100.00    100.00    100.00     100.0
as.vector(samp.conc)    1.70    9.062    24.56    38.92    43.94    57.64    76.14    81.44    92.33     96.76     98.69      99.7
                     13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00    100.00       100       100       100       100       100
as.vector(samp.conc)    99.87     99.96     99.99       100       100       100       100       100
```

Figure B.86. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

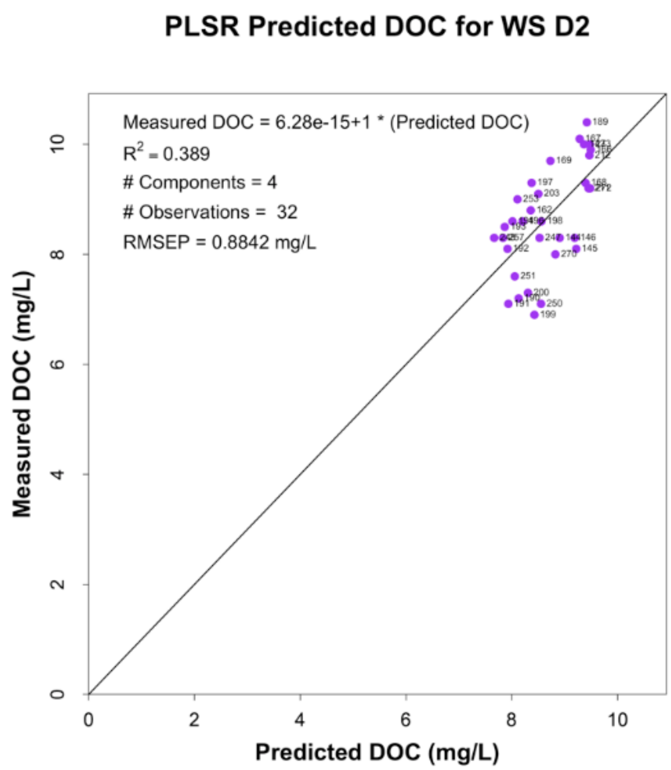

Figure B.87. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 4 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (32 measured samples).

```
Data:   X dimension: 56 206
        Y dimension: 56 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           2.373    2.395    2.350    2.286    1.810    1.280     1.29    1.292    1.263    1.453     1.287     1.252     1.460     1.735
adjCV        2.373    2.391    2.347    2.298    1.785    1.282     1.28    1.274    1.256    1.407     1.249     1.219     1.401     1.648
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.819     1.818     1.766     1.764     1.768     1.764     1.765
adjCV     1.731     1.725     1.673     1.672     1.676     1.673     1.673

TRAINING: % variance explained
                        1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       97.5453   99.261    99.85    99.95    99.97   100.00   100.00    100.0   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     0.7165    6.872    20.21    60.99    73.79    78.15    82.25     83.4    89.65     92.51     93.97     96.15     98.06
                        14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                         100.00    100.00    100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)       98.61     99.28     99.71     99.78     99.87      99.9     99.94
```
Figure B.88. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

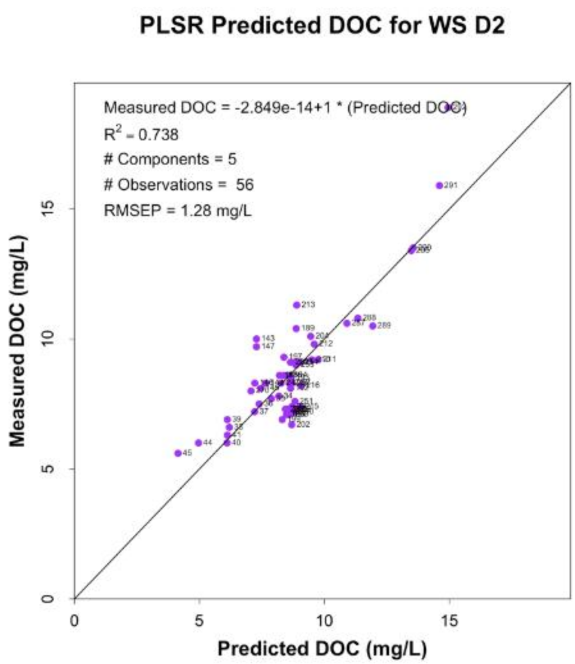

Figure B.89. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) with 5 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (58 measured samples after removing certain date ranges and additional outliers).

```
Data:   X dimension: 49 206
        Y dimension: 49 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           1.883    1.934    1.845    1.768    1.479    1.059    1.015   0.9914    1.030    1.300     1.651     1.775     1.749     1.985
adjCV        1.883    1.927    1.840    1.766    1.451    1.068    1.011   0.9832    1.017    1.266     1.592     1.700     1.673     1.885
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        2.060     2.108     2.135     2.126     2.126     2.148     2.146
adjCV     1.954     2.000     2.024     2.016     2.016     2.036     2.034

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      97.521    99.28    99.93    99.96    99.98   100.00   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    2.202    11.59    19.60    59.85    71.25    75.79    80.37    82.52    86.15     89.83     93.45     95.13     98.18
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00     100.0    100.00    100.00    100.00    100.00
as.vector(samp.conc)     98.93     99.19      99.6     99.72     99.84     99.91     99.97
```

Figure B.90. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

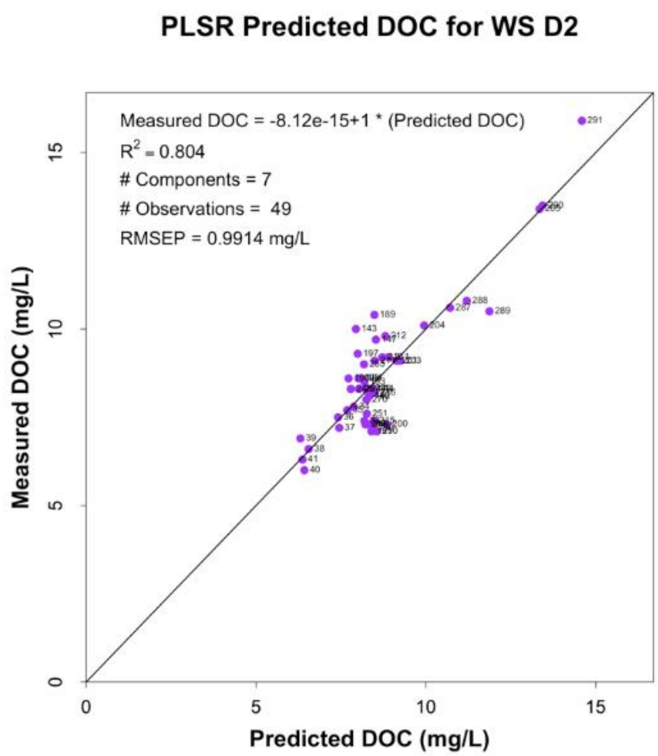

Figure B.91. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) with 5 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (49 measured samples after removing certain date ranges and additional outliers).

```
Data:   X dimension: 44 206
        Y dimension: 44 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           1.561    1.594    1.515    1.446    1.232   0.9284   0.8275   0.7502   0.7748    1.103     1.273     1.385     1.433     1.496
adjCV        1.561    1.587    1.509    1.439    1.212   0.9052   0.8251   0.7444   0.7636    1.064     1.217     1.319     1.361     1.417
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.560     1.561     1.555     1.550     1.556     1.549     1.548
adjCV     1.476     1.476     1.469     1.464     1.469     1.462     1.461

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      97.611    99.18    99.94    99.97    99.98   100.00   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    7.805    19.19    27.51    60.17    75.58    76.82    83.66    86.02    89.74     93.02     95.25     96.82     98.33
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00     100.0    100.00    100.00    100.00    100.00
as.vector(samp.conc)     99.02     99.39      99.7     99.85     99.92     99.97     99.99
```

Figure B.92. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

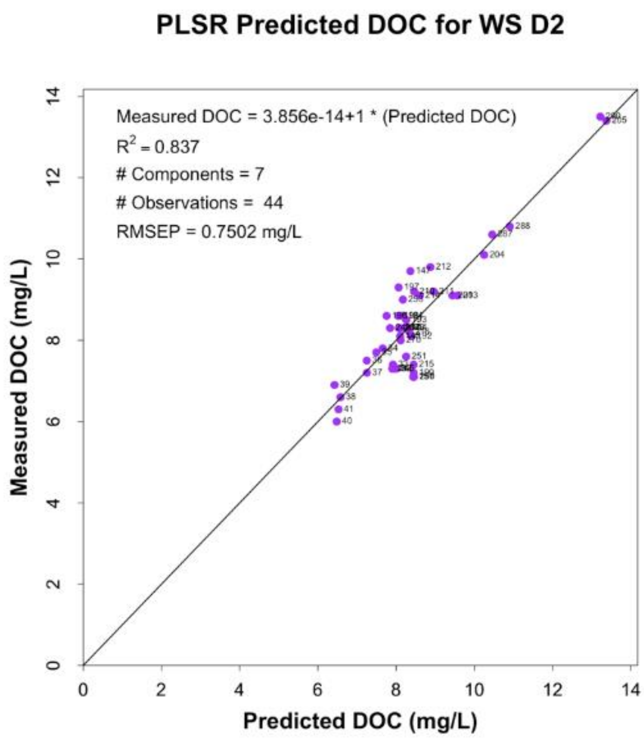

Figure B.93. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) with 7 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (44 measured samples after removing certain date ranges and additional outliers).

```
Data:    X dimension: 39 206
         Y dimension: 39 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           1.604    1.644    1.534    1.416    1.199   0.8744   0.7219   0.6772   0.5942   0.8314     1.154     1.219     1.263     1.324
adjCV        1.604    1.635    1.529    1.413    1.183   0.8457   0.7162   0.6649   0.5877   0.8045     1.102     1.163     1.203     1.259
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.332     1.333     1.328      1.33     1.323     1.314     1.310
adjCV     1.264     1.264     1.259      1.26     1.254     1.245     1.241

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       97.28    98.85    99.93    99.96    99.97   100.00   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    11.85    23.21    31.23    67.43    85.01    86.09    90.61    92.05    94.47     96.86     97.74     98.61     99.23
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00       100
as.vector(samp.conc)     99.61     99.78     99.93     99.96     99.98     99.99       100
```

Figure B.94. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

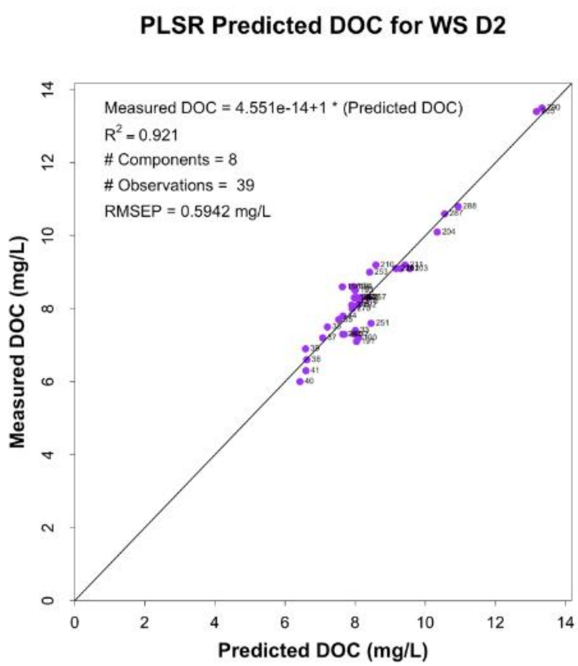

Figure B.95. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) with 8 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (39 measured samples after removing certain date ranges and additional outliers).

Nitrate-nitrogen (NO_3^--N)

```
Data:   X dimension: 76 206
        Y dimension: 76 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           0.305   0.3038   0.2848   0.2803   0.2779   0.2349   0.1465   0.1494   0.1797   0.1942    0.2050    0.2224    0.2673    0.2755
adjCV        0.305   0.3036   0.2845   0.2803   0.2773   0.2320   0.1458   0.1477   0.1748   0.1865    0.1968    0.2128    0.2543    0.2617
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV       0.2830    0.2894    0.2970    0.2942    0.2954    0.2950    0.2992
adjCV    0.2684    0.2744    0.2816    0.2789    0.2799    0.2796    0.2835

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                     98.8520    99.70    99.88    99.99    99.99    99.99   100.00   100.00   100.00     100.0    100.00    100.00     100.0
as.vector(samp.conc)   0.9234    14.57    18.70    23.68    56.71    82.83    86.48    91.26    94.63      95.5     96.54     97.54      98.5
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00     100.0    100.00    100.00
as.vector(samp.conc)     99.07     99.31     99.45     99.61      99.7     99.76     99.84
```

Figure B.96. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D2, used to select the number of components.

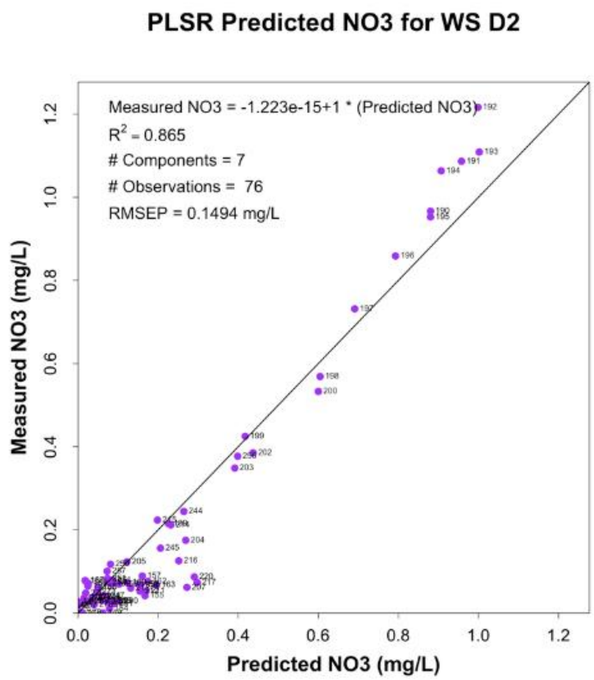

Figure B.97. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 7 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (76 measured samples).

```
Data:   X dimension: 71 206
        Y dimension: 71 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.3145   0.3156   0.2955   0.2905   0.2628   0.2052   0.1842   0.1440   0.1065  0.07513   0.07082   0.06187   0.05566   0.05263
adjCV       0.3145   0.3154   0.2948   0.2898   0.2615   0.2010   0.1827   0.1408   0.1033  0.07228   0.06794   0.05936   0.05355   0.05026
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.05731   0.05820   0.05767   0.05841   0.05789   0.05852   0.05804
adjCV   0.05478   0.05531   0.05488   0.05549   0.05497   0.05552   0.05506

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      97.0421    99.48    99.90    99.98    99.99   100.00   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    0.9367    17.28    23.98    45.60    78.18    80.52    90.88    96.46    98.73     99.12     99.39     99.54     99.74
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      99.78     99.86     99.89     99.92     99.95     99.97     99.98
```

Figure B.98. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D2, used to select the number of components.

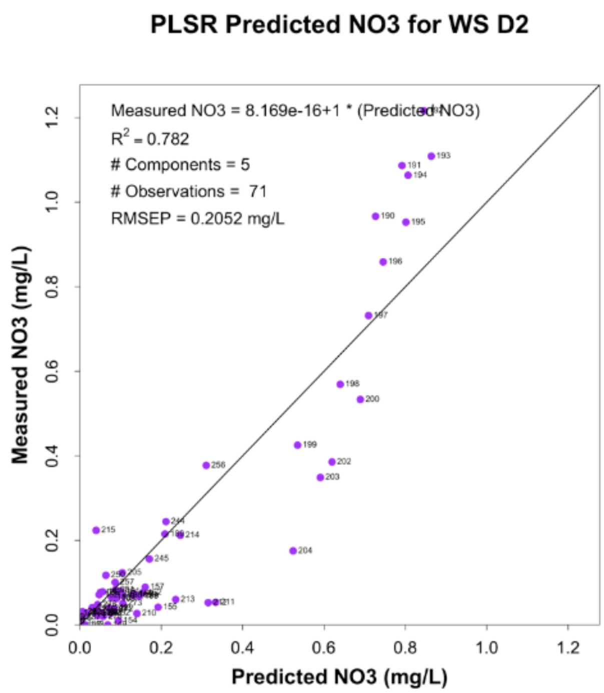

Figure B.99. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 5 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (71 measured samples).

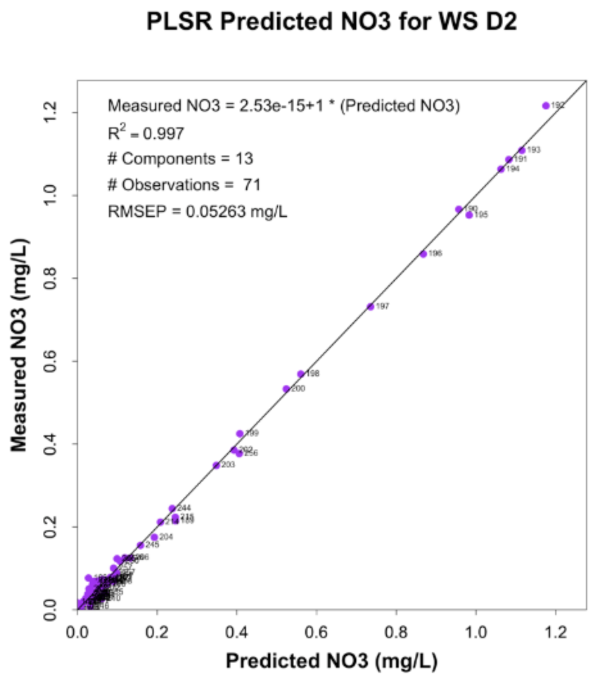

Figure B.100. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 13 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (71 measured samples).

```
Data:   X dimension: 60 206
        Y dimension: 60 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.3359   0.3475   0.3197   0.3045   0.2548   0.1878   0.1844   0.1601  0.08677  0.07849   0.07273   0.06761   0.06897   0.06751
adjCV       0.3359   0.3462   0.3185   0.3028   0.2548   0.1849   0.1819   0.1564  0.08434  0.07549   0.06976   0.06484   0.06614   0.06439
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.07254   0.07258   0.07262   0.07360   0.07347   0.07336   0.07427
adjCV   0.06900   0.06905   0.06904   0.06991   0.06978   0.06963   0.07048

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       94.730    99.56    99.91    99.95    99.98   100.00   100.00   100.00   100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)     1.573    19.47    33.04    62.38    82.72    84.71    91.58    97.98    99.12     99.44     99.62      99.7     99.84
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                         100.0    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)       99.9     99.93     99.95     99.97     99.98     99.99     99.99
```
Figure B.101. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D2, used to select the number of components.

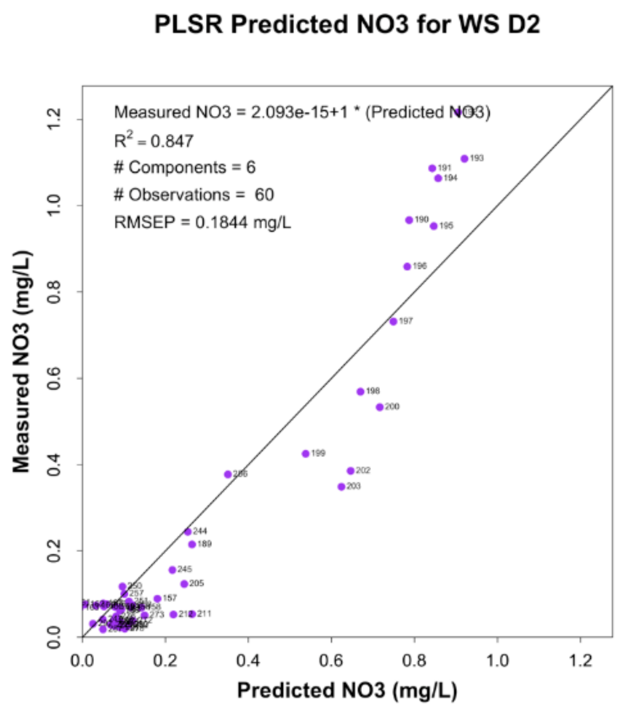

Figure B.102. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 6 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (60 measured samples).

```
Data:   X dimension: 40 206
        Y dimension: 40 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.3758   0.3761   0.3260   0.2874   0.2333   0.1846   0.1609   0.1265  0.09983  0.09502   0.08490   0.08521   0.08739   0.08460
adjCV       0.3758   0.3749   0.3244   0.2856   0.2302   0.1812   0.1572   0.1210  0.09658  0.09095   0.08147   0.08124   0.08326   0.08051
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.08604   0.08733   0.08770   0.08803    0.0879   0.08782   0.08779
adjCV   0.08171   0.08288   0.08322   0.08352    0.0834   0.08332   0.08328

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                     97.871    99.61    99.94    99.98   100.00   100.00   100.00   100.00   100.00     100.0     100.0    100.00    100.00
as.vector(samp.conc)   7.451    35.60    52.93    77.90    88.84    93.31    98.22    98.65    99.41      99.6      99.8     99.87     99.93
                     14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00       100       100       100       100       100
as.vector(samp.conc)    99.98     99.99       100       100       100       100       100
```

Figure B.103. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D2, used to select the number of components (after removing all points <0.05 [half MDL]).

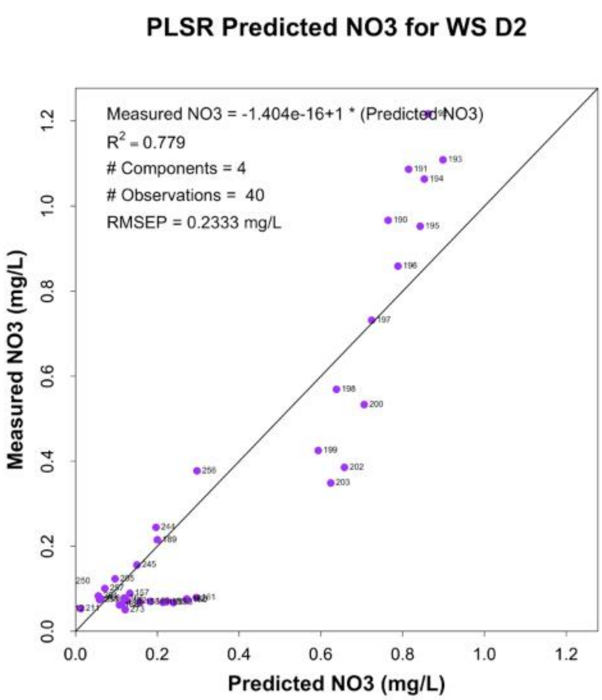

Figure B.104. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 4 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (40 measured samples after removing all points <0.05 [half MDL]).

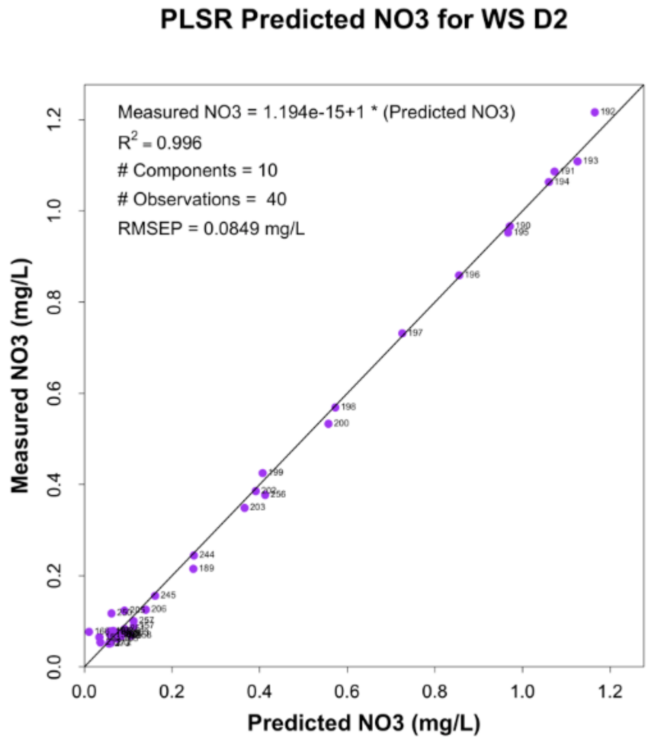

Figure B.105. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 10 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (40 measured samples after removing all points <0.05 [half MDL]).

```
Data:   X dimension: 36 206
        Y dimension: 36 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.3933   0.3795   0.3198   0.2944   0.2466   0.1973   0.1692   0.1306  0.09469  0.09590   0.08689   0.08798   0.08942   0.08862
adjCV       0.3933   0.3788   0.3187   0.2927   0.2426   0.1932   0.1653   0.1239  0.09126  0.09136   0.08287   0.08351   0.08486   0.08398
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.09114   0.09216   0.09298   0.09304   0.09313   0.09311   0.09310
adjCV   0.08622   0.08716   0.08789   0.08794   0.08801   0.08799   0.08798

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       97.747    99.60    99.94    99.98   100.00   100.00   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     8.723    38.97    54.36    78.75    88.95    93.29    98.59    99.01    99.51     99.68     99.84     99.89     99.95
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00       100       100       100       100       100
as.vector(samp.conc)      99.98     99.99       100       100       100       100       100
```

Figure B.106. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D2, used to select the number of components.

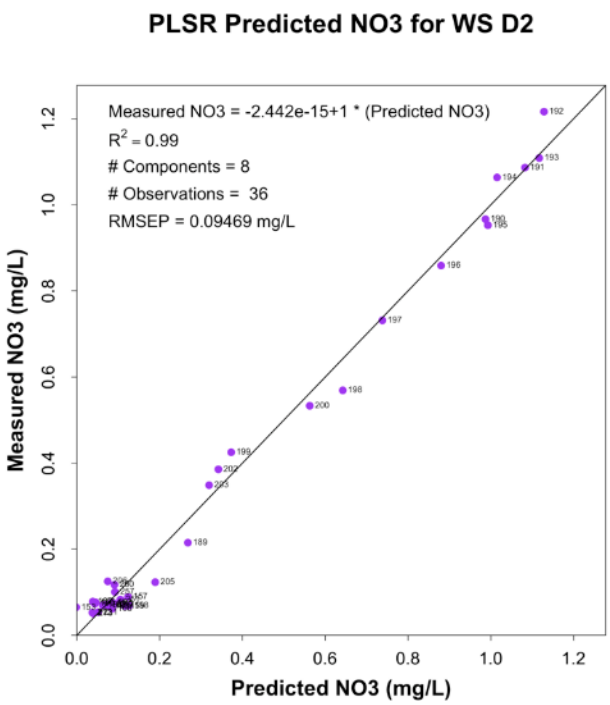

Figure B.107. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 8 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (36 measured samples).

```
Data:   X dimension: 35 206
        Y dimension: 35 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.3964   0.3922   0.3428   0.2958   0.2508   0.1945   0.1506   0.1188   0.1055  0.09837   0.09341   0.08906   0.09006   0.08841
adjCV       0.3964   0.3911   0.3409   0.2945   0.2471   0.1911   0.1474   0.1169   0.1020  0.09470   0.08995   0.08546   0.08627   0.08444
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.09150   0.09162   0.09121   0.09133   0.09126   0.09116   0.09112
adjCV   0.08727   0.08735   0.08693   0.08703   0.08696   0.08686   0.08682

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      97.757    99.61    99.94    99.98    100.0   100.00   100.00   100.00   100.00     100.0    100.00     100.0    100.00
as.vector(samp.conc)    8.958    38.89    54.21    79.14     89.9    95.38    97.35    99.08    99.54      99.7     99.83      99.9     99.96
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00       100       100       100       100       100
as.vector(samp.conc)     99.98     99.99       100       100       100       100       100
```

Figure B.108. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D2, used to select the number of components.

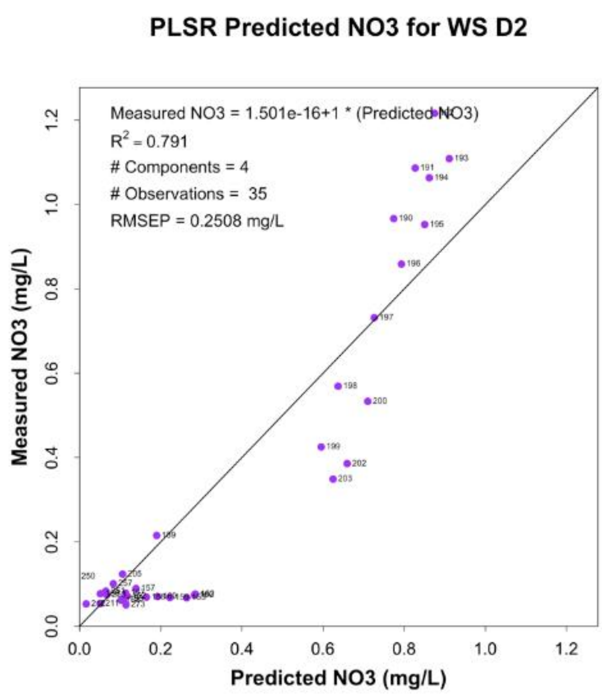

Figure B.109. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 4 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (35 measured samples).

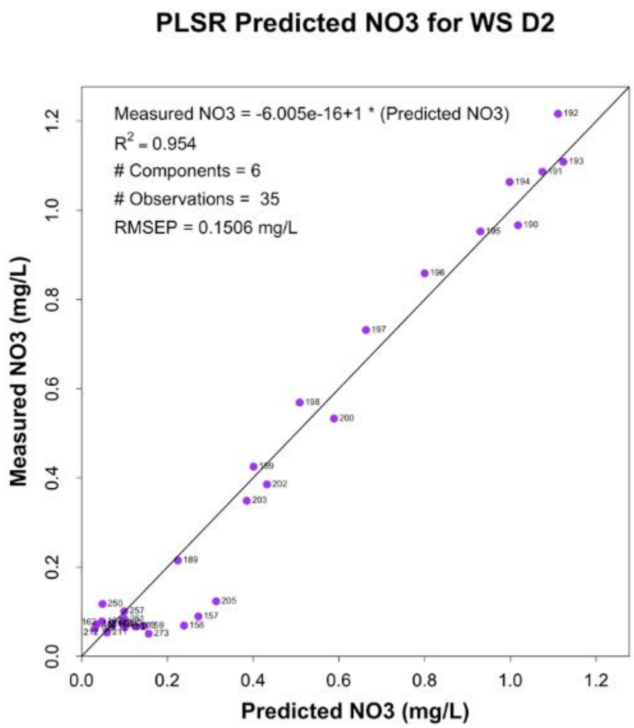

Figure B.110. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 6 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (35 measured samples).

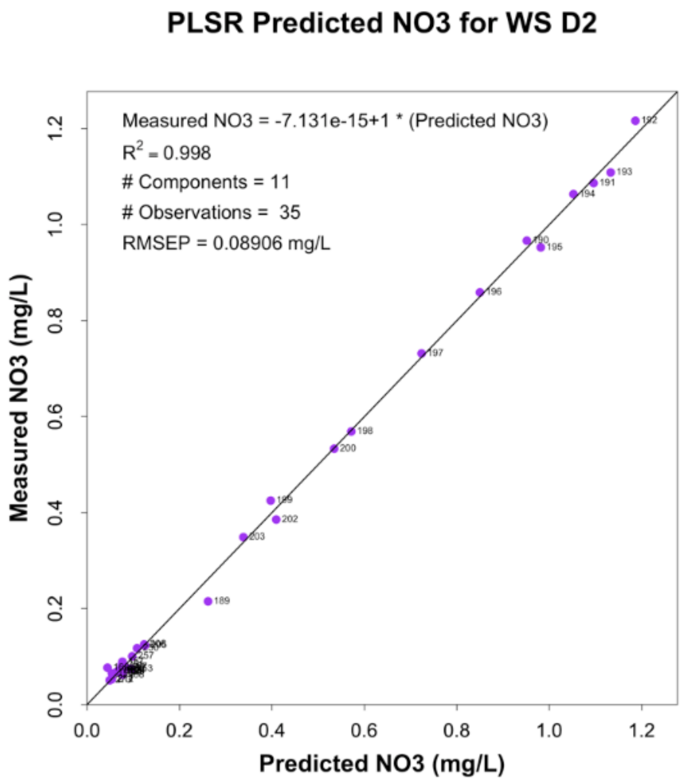

Figure B.111. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 11 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (35 measured samples).

```
Data:   X dimension: 31 206
        Y dimension: 31 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.4116   0.4010   0.3362   0.3009  0.07177  0.06549  0.04646  0.04120  0.04939  0.04666   0.04899   0.05305   0.05366   0.05450
adjCV       0.4116   0.3999   0.3348   0.2991  0.07105  0.06610  0.04594  0.04055  0.04775  0.04485   0.04671   0.05043   0.05091   0.05169
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.05481   0.05470   0.05489   0.05492   0.05493   0.05493   0.05493
adjCV   0.05195   0.05184   0.05202   0.05204   0.05205   0.05205   0.05205

TRAINING: % variance explained
                        1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                        95.104    99.35    99.94    99.98   100.00   100.00   100.00   100.00   100.00    100.00    100.00    100.00       100
as.vector(samp.conc)      9.779    40.20    56.03    97.62    98.22    99.22    99.54    99.76    99.87     99.95     99.98     99.99       100
                        14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                            100       100       100       100       100       100       100
as.vector(samp.conc)         100       100       100       100       100       100       100
```

Figure B.112. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D2, used to select the number of components.

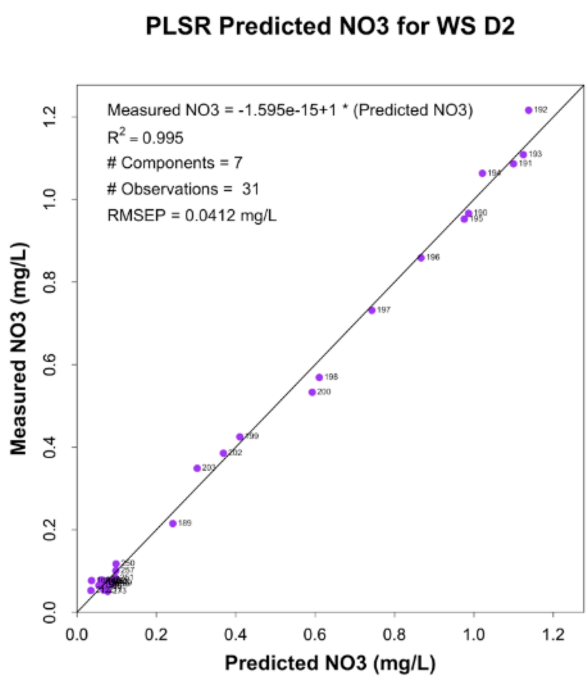

Figure B.113. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 7 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (31 measured samples, removed more outliers based on the previous plot with 6 comps, validated with continuous time series).

Total dissolved nitrogen (TDN)

```
Data:   X dimension: 158 206
        Y dimension: 158 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.2439   0.2452   0.2373   0.2270   0.2177   0.2120   0.1920   0.1281   0.1144   0.1311    0.1595    0.1657    0.1681    0.1933
adjCV       0.2439   0.2451   0.2369   0.2265   0.2171   0.2114   0.1911   0.1275   0.1135   0.1283    0.1527    0.1582    0.1605    0.1845
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV       0.2010    0.2086    0.2110    0.2080    0.2050    0.1910    0.1941
adjCV    0.1913    0.1984    0.2006    0.1977    0.1948    0.1816    0.1844

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                     98.1689   99.595    99.80    99.94    99.99    99.99   100.00   100.00   100.00    100.00    100.00       100    100.00
as.vector(samp.conc)   0.3157    9.529    19.82    28.16    33.60    53.88    78.46    83.86    88.67     93.23     95.02        96     96.55
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.0    100.00    100.00    100.00     100.0    100.00    100.00
as.vector(samp.conc)      97.4     97.81     98.07     98.37      98.6     98.79     98.97
```

Figure B.114. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for total dissolved nitrogen (TDN) in watershed D2, used to select the number of components.

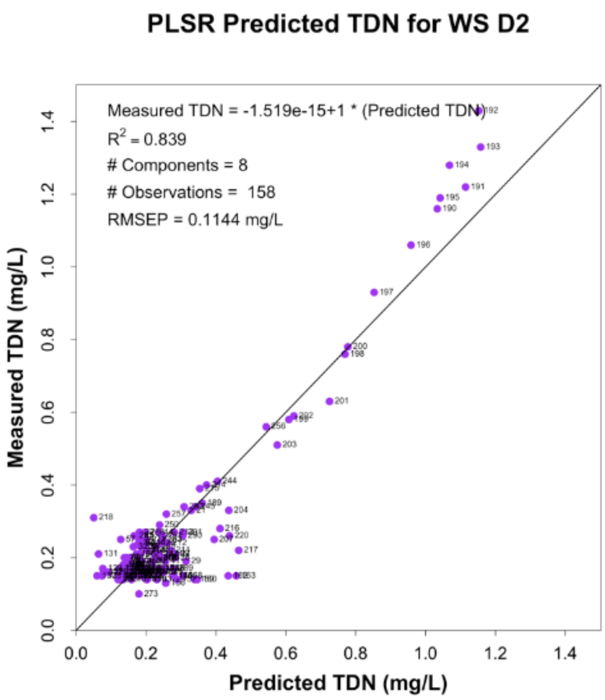

Figure B.115. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 8 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (158 measured samples).

```
Data:    X dimension: 148 206
         Y dimension: 148 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           0.251   0.2498   0.2409   0.2236   0.1923   0.1736   0.2017   0.2106   0.1424   0.1424    0.1414    0.1320    0.1215    0.1215
adjCV        0.251   0.2502   0.2407   0.2228   0.1919   0.1752   0.1967   0.2009   0.1402   0.1376    0.1354    0.1259    0.1159    0.1159
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV       0.1246    0.1229    0.1245    0.1253    0.1317    0.1306    0.1343
adjCV    0.1188    0.1171    0.1185    0.1193    0.1254    0.1243    0.1277

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                    95.4577    99.36    99.69    99.89    99.96    99.99    99.99   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)  0.7137    10.68    29.91    44.93    58.06    76.73    88.96    89.56    94.08     96.67     97.89     98.24     98.54
                     14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00    100.00     100.0    100.00    100.00    100.00
as.vector(samp.conc)    98.74     98.96     99.13      99.2     99.29     99.36     99.45
```

Figure B.116. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D2, used to select the number of components.

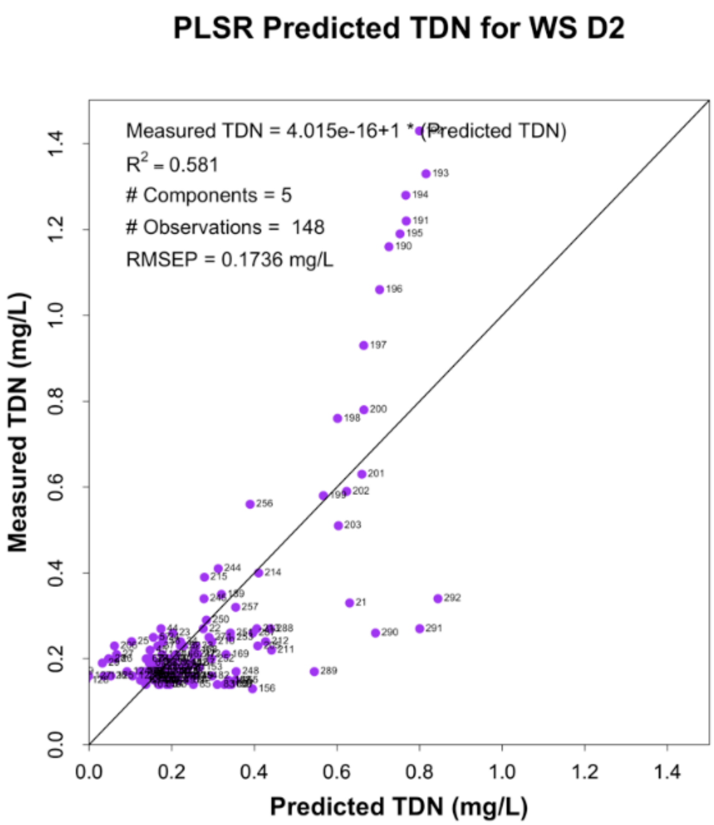

Figure B.117. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 5 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (148 measured samples).

```
Data:   X dimension: 145 206
        Y dimension: 145 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.2532   0.2523   0.2438   0.2201   0.1909   0.1717   0.1448   0.1331   0.1040  0.08714   0.06937   0.06582   0.06323   0.05865
adjCV       0.2532   0.2528   0.2435   0.2194   0.1904   0.1720   0.1433   0.1272   0.1026  0.08578   0.06782   0.06379   0.06114   0.05680
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.05588   0.05742   0.06153   0.06301   0.06278   0.06514   0.06648
adjCV   0.05420   0.05548   0.05926   0.06062   0.06041   0.06257   0.06373

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      95.4475    99.37    99.69    99.89    99.97    99.99    99.99   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    0.7234    10.88    32.28    49.24    59.68    78.22    89.61    90.18    94.33     97.14     98.21     98.49     98.74
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      98.91     99.09     99.24     99.31     99.39     99.45     99.53
```

Figure B.118. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D2, used to select the number of components.

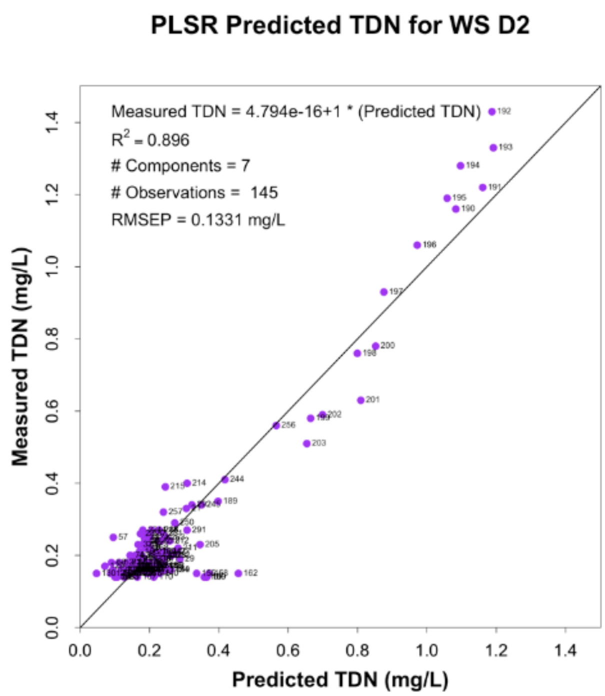

Figure B.119. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 7 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (145 measured samples).

```
Data:   X dimension: 139 206
        Y dimension: 139 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.2574   0.2560   0.2456   0.2264   0.1981   0.1815   0.1471   0.1293  0.09238  0.08257   0.06836   0.06286   0.05915   0.05374
adjCV       0.2574   0.2561   0.2454   0.2256   0.1971   0.1812   0.1452   0.1228  0.09123  0.08138   0.06652   0.06064   0.05711   0.05209
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.05057   0.05091   0.05306   0.05212   0.05246   0.05343   0.05399
adjCV   0.04901   0.04927   0.05111   0.05021   0.05053   0.05142   0.05180

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                     95.8839    99.38    99.68    99.89    99.97    99.99    99.99   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)   0.7661    11.37    34.53    50.73    61.39    80.29    91.20    92.31    94.81     97.56     98.57     98.76     98.94
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     99.09     99.24     99.39     99.46     99.52     99.56     99.65
```

Figure B.120. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D2, used to select the number of components.

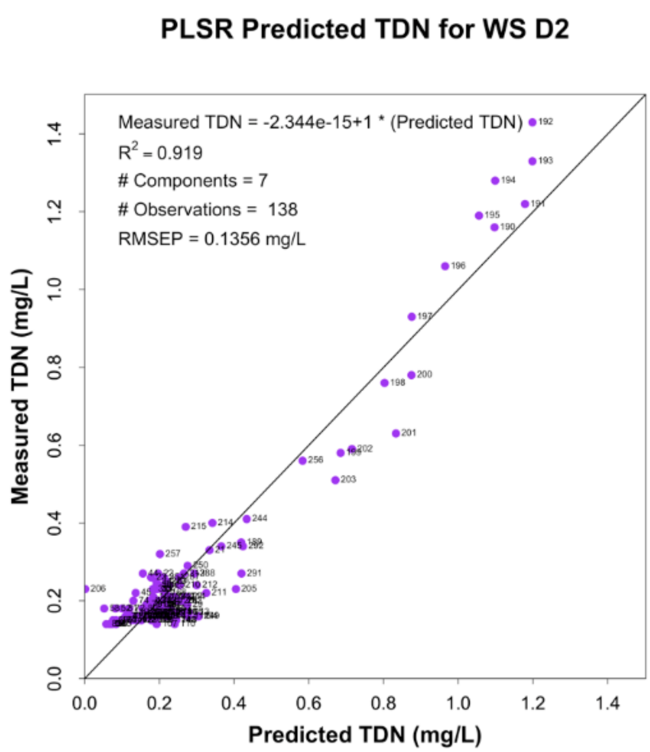

Figure B.121. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 7 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (138 measured samples).

```
Data:   X dimension: 133 206
        Y dimension: 133 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.2625   0.2593   0.2484   0.2224   0.1945   0.1524  0.07149  0.04946  0.04435  0.04317    0.0399   0.03825   0.03665   0.03811
adjCV       0.2625   0.2598   0.2481   0.2218   0.1935   0.1514  0.07084  0.04916  0.04400  0.04284    0.0395   0.03771   0.03605   0.03739
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03960   0.04064   0.04262   0.04280   0.04438   0.04587   0.04701
adjCV   0.03859   0.03946   0.04123   0.04142   0.04280   0.04413   0.04514

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       91.479    99.14    99.62    99.85    99.93    99.99   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     1.654    13.07    36.75    54.42    74.96    94.35    97.13    97.95    98.24     98.61     98.92     99.13     99.24
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00     100.0    100.00    100.00    100.00
as.vector(samp.conc)      99.39     99.48     99.56      99.6     99.66     99.72     99.77
```

Figure B.122. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D2, used to select the number of components.

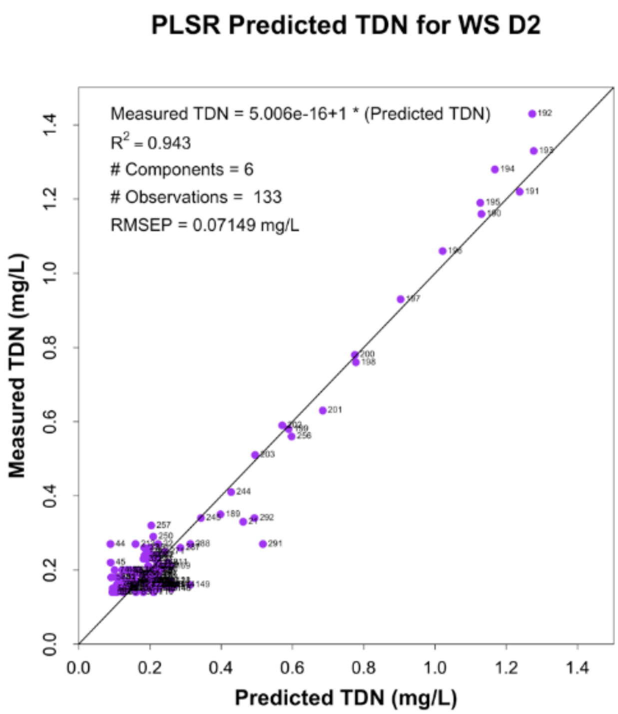

Figure B.123. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 6 components for watershed D2 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (133 measured samples).

B.4 Watershed D3

Dissolved organic carbon (DOC)

```
Data:   X dimension: 70 206
        Y dimension: 70 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           2.618    2.418    2.340    2.342    2.176    2.100    1.972    1.852    1.828    1.734     1.597     1.543     1.606     1.622
adjCV        2.618    2.415    2.332    2.317    2.148    2.088    1.961    1.841    1.814    1.704     1.568     1.506     1.557     1.559
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.597     1.545     1.566     1.550     1.555     1.548     1.564
adjCV     1.529     1.478     1.495     1.476     1.478     1.471     1.486

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       83.89    99.83    99.88    99.91    99.99    99.99   100.00    100.0   100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)    17.37    27.60    39.73    47.58    49.96    55.91    64.84     69.9    82.49     87.21     90.97      94.1     96.34
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00     100.0    100.00     100.0
as.vector(samp.conc)     97.67     98.29     98.78     99.26      99.6     99.71      99.8
```
Figure B.124. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

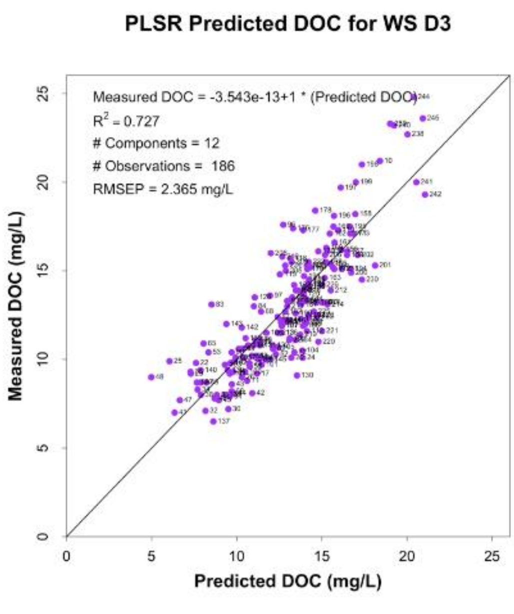

Figure B.125. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 12 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (186 measured samples).

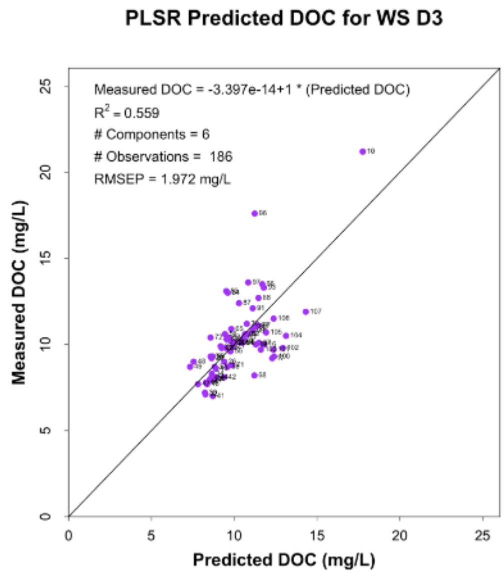

Figure B.126. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 6 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (186 measured samples).

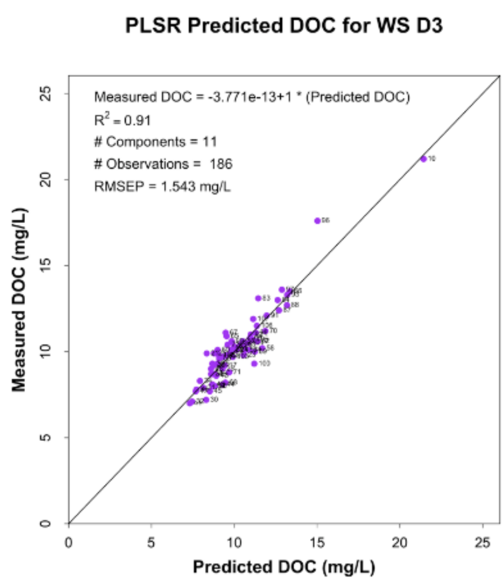

Figure B.127. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 11 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (186 measured samples).

```
Data:    X dimension: 67 206
         Y dimension: 67 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           1.601    1.340    1.309    1.242    1.246    1.271    1.283    1.428    1.332    1.354     1.415     1.411     1.400     1.424
adjCV        1.601    1.337    1.306    1.239    1.242    1.265    1.277    1.403    1.319    1.332     1.380     1.375     1.352     1.369
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.405     1.392     1.388     1.379     1.374     1.378     1.375
adjCV     1.348     1.332     1.325     1.313     1.307     1.309     1.306

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                      87.62    99.84    99.93    99.97    99.99    99.99   100.00      100   100.00    100.00     100.0    100.00    100.00
as.vector(samp.conc)   33.59    36.76    45.45    46.57    47.55    50.91    60.93       66    71.67     79.85      83.3     88.79     92.21
                     14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00    100.00     100.0    100.00    100.00    100.00
as.vector(samp.conc)    94.92     96.65     97.69      98.6     99.06     99.41     99.63
```

Figure B.128. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

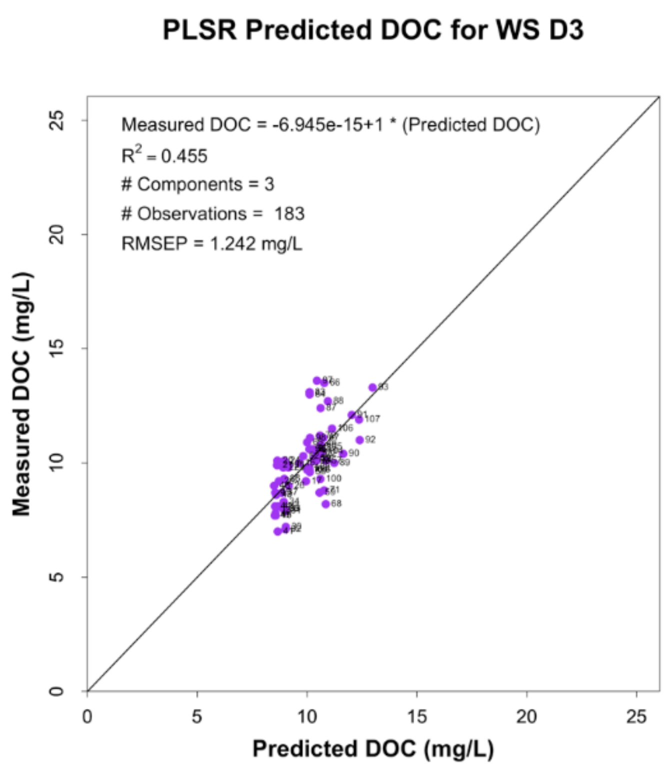

Figure B.129. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 3 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (183 measured samples).

```
Data:   X dimension: 43 206
        Y dimension: 43 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           1.269   0.9742    1.023   0.8487   0.8455   0.8904   0.8891   0.9408    1.109   0.9794     1.042    0.9831    0.9594    0.9717
adjCV        1.269   0.9722    1.018   0.8441   0.8421   0.8821   0.8784   0.9196    1.048   0.9521     1.003    0.9449    0.9136    0.9231
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV       0.9589    0.9638    0.9604    0.9635    0.9671    0.9670    0.9659
adjCV    0.9103    0.9139    0.9099    0.9126    0.9160    0.9159    0.9149

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                        89.26    99.75    99.93    99.98    99.98    99.99   100.00    100.0    100.0    100.00    100.00    100.00    100.00
as.vector(samp.conc)     43.82    44.64    62.08    62.85    69.52    72.53    77.22     86.4     88.3     92.19     94.71     97.88     99.02
                       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00       100       100
as.vector(samp.conc)      99.44     99.72     99.91     99.97     99.99       100       100
```

Figure B.130. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

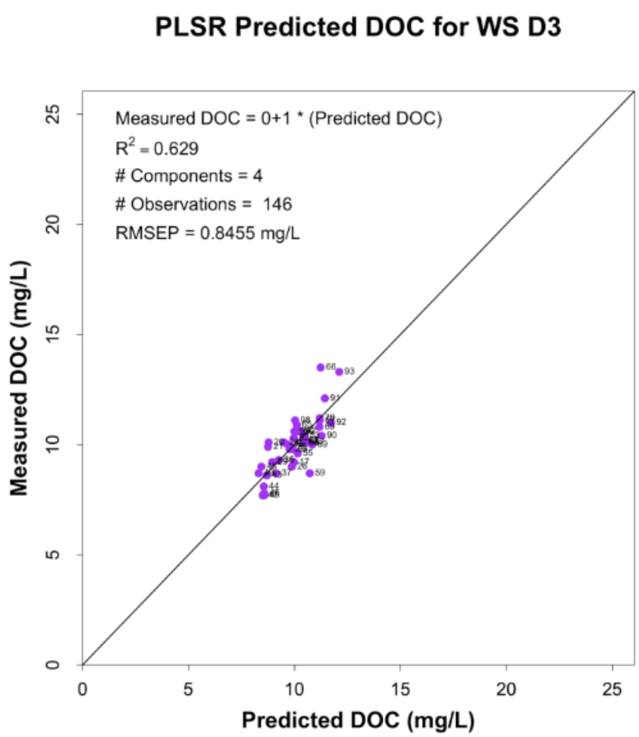

Figure B.131. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 4 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (146 measured samples).

```
Data:   X dimension: 40 206
        Y dimension: 40 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           1.027   0.7574   0.7478   0.6586   0.6716   0.6860   0.7793   0.8041   0.8016   0.7785    0.7513    0.7842    0.7627    0.7563
adjCV        1.027   0.7555   0.7543   0.6545   0.6671   0.6858   0.7580   0.7666   0.7741   0.7559    0.7292    0.7500    0.7278    0.7201
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV       0.7545    0.7577    0.7653    0.7665    0.7653    0.7640    0.7637
adjCV    0.7171    0.7195    0.7264    0.7272    0.7260    0.7248    0.7245

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       90.79    99.55    99.92    99.97    99.99    99.99    99.99   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    48.05    49.16    66.64    67.43    69.41    78.14    83.75    86.87    89.47     92.87     96.85     98.31     99.16
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00       100       100       100
as.vector(samp.conc)     99.62     99.84     99.93     99.98       100       100       100
```

Figure B.132. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

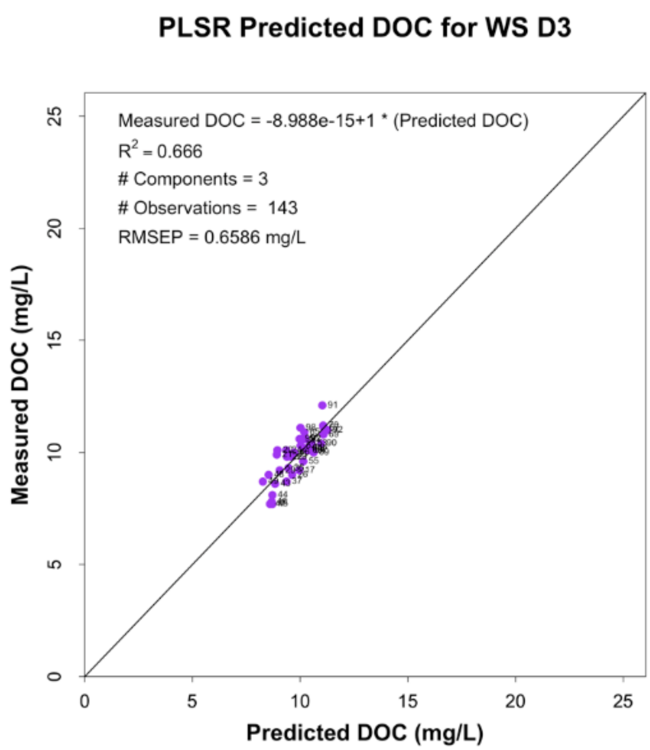

Figure B.133. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 4 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (146 measured samples).

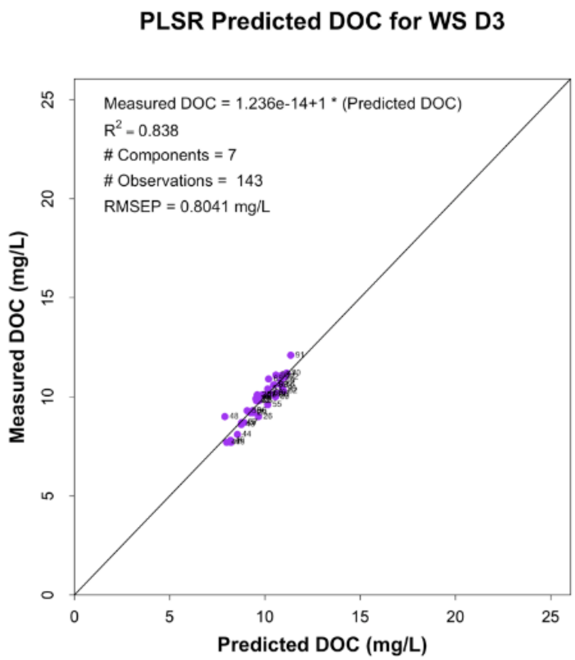

Figure B.134. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 7 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (143 measured samples).

```
Data:   X dimension: 33 206
        Y dimension: 33 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV          0.7306   0.5158   0.5239   0.5181   0.5212   0.5513   0.5147   0.5373   0.6519   0.6615    0.5967    0.5737    0.5583    0.5732
adjCV       0.7306   0.5135   0.5200   0.5134   0.5158   0.5371   0.5081   0.5342   0.6415   0.6309    0.5690    0.5480    0.5321    0.5447
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV       0.5765    0.5798    0.5833    0.5836    0.5842    0.5842    0.5842
adjCV    0.5474    0.5502    0.5534    0.5536    0.5543    0.5542    0.5542

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       91.14    99.88    99.94    99.98    99.98    99.99   100.00   100.00   100.00    100.00    100.00     100.0    100.00
as.vector(samp.conc)    55.78    59.11    63.93    65.11    71.20    72.24    74.51    79.99    94.46     97.07     98.07      98.9     99.57
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00       100       100       100
as.vector(samp.conc)     99.79     99.93     99.98     99.99       100       100       100
```

Figure B.135. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

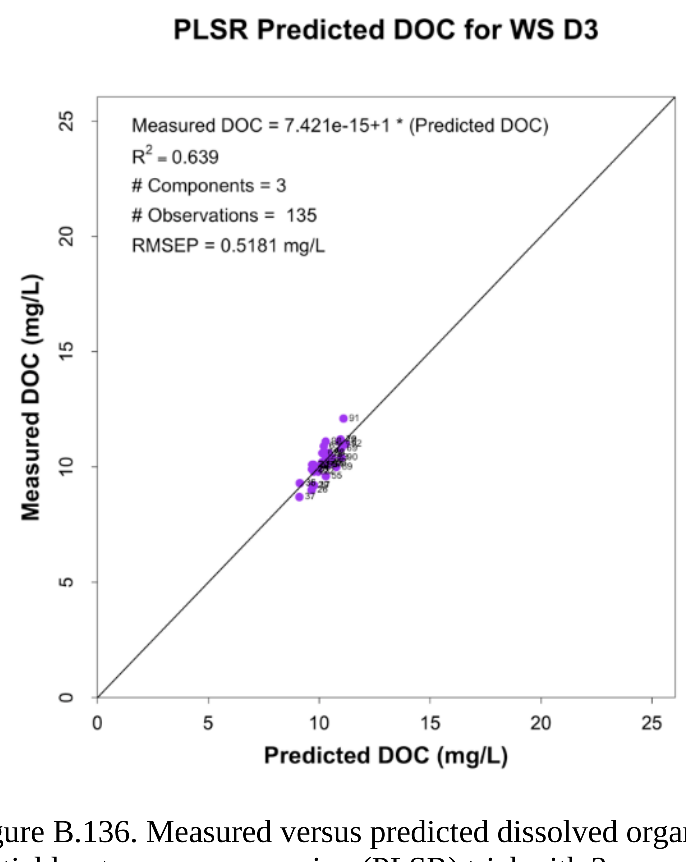

Figure B.136. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 3 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (135 measured samples).

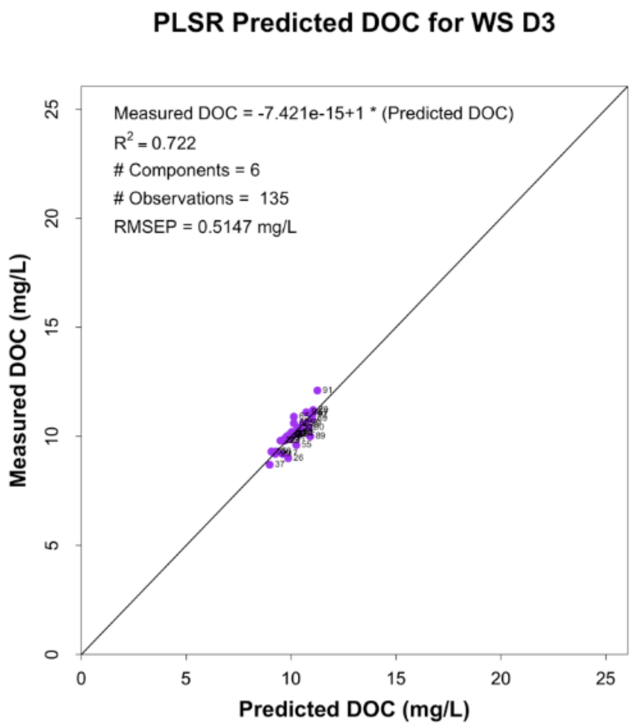

Figure B.137. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 6 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (135 measured samples).

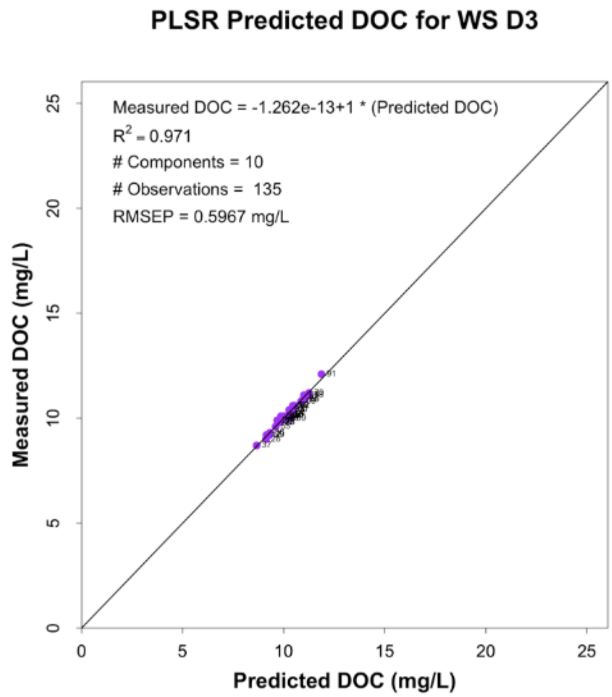

Figure B.138. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 10 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (135 measured samples).

```
Data:   X dimension: 137 205
        Y dimension: 137 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps
CV            2.63    2.406    2.384    2.337    1.930    1.836    1.731    1.730    1.832    1.757     1.688
adjCV         2.63    2.405    2.382    2.338    1.925    1.831    1.724    1.721    1.798    1.731     1.642
       11 comps  12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.700     1.747     1.799     1.796     1.837     1.805     1.831     1.914     2.002     2.168
adjCV     1.675     1.724     1.758     1.755     1.784     1.749     1.771     1.845     1.922     2.081

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps
X                        78.18    99.42    99.94    99.96    99.99    99.99   100.00   100.00   100.00    100.00
as.vector(samp.conc)     16.90    19.30    22.88    51.06    56.34    63.12    64.85    68.99    72.39     76.09
                       11 comps  12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps
X                        100.00    100.00    100.00     100.0    100.00     100.0    100.00     100.0    100.00
as.vector(samp.conc)      77.53     81.01     84.02      85.9     88.04      90.1     91.03      92.2     93.33
                       20 comps
X                        100.00
as.vector(samp.conc)      93.91
```

Figure B.139. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

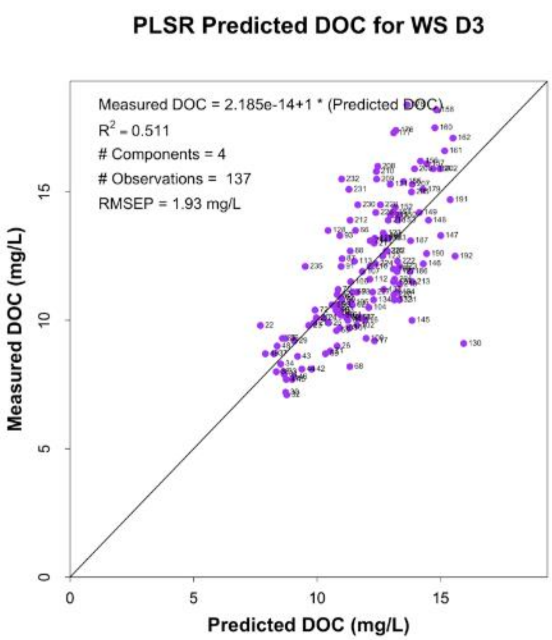

Figure B.140. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 4 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (137 measured samples).

```
Data:   X dimension: 123 205
        Y dimension: 123 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
CV           2.448    2.211    2.220    2.159    1.476    1.407    1.347    1.337    1.389    1.420     1.416     1.390     1.386     1.376
adjCV        2.448    2.209    2.217    2.156    1.471    1.406    1.343    1.332    1.381    1.403     1.400     1.361     1.352     1.346
       14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.342     1.345     1.344     1.368     1.379     1.383     1.381
adjCV     1.310     1.309     1.303     1.324     1.329     1.329     1.326

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps  12 comps  13 comps
X                       82.79    99.35    99.95    99.97    99.99    99.99   100.00   100.00   100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)    20.49    21.43    26.50    66.06    69.37    73.07    74.39    77.05    80.31     81.89     85.64     88.36     89.73
                      14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.0    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      91.9     93.14     94.19     95.07     95.95     96.75     97.36
```

Figure B.141. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

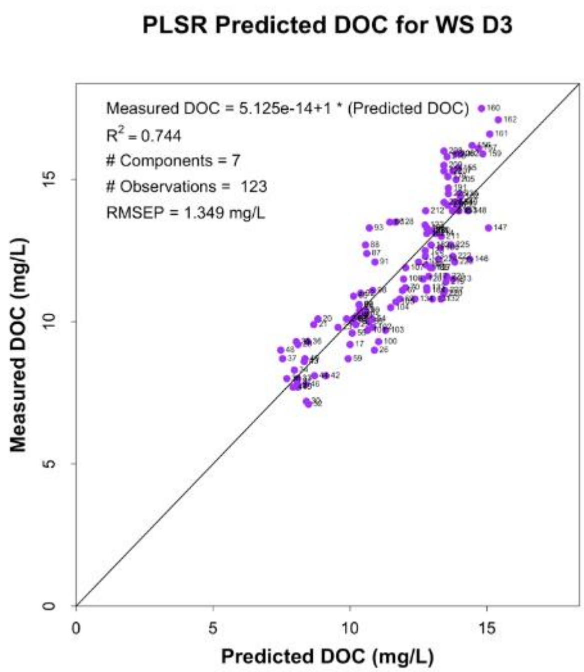

Figure B.142. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 7 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (123 measured samples).

```
Data:    X dimension: 114 205
         Y dimension: 114 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV           2.413    2.197    2.195    2.099    1.444    1.380    1.329    1.333    1.386    1.353     1.361     1.364
adjCV        2.413    2.195    2.194    2.106    1.441    1.389    1.325    1.327    1.368    1.343     1.365     1.336
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV        1.391     1.352     1.373     1.375     1.389     1.408     1.445     1.432     1.487
adjCV     1.359     1.322     1.343     1.333     1.343     1.363     1.391     1.373     1.421

TRAINING: % variance explained
                        1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                         83.65    99.34    99.93    99.97    99.99    99.99   100.00   100.00   100.00    100.00    100.00
as.vector(samp.conc)      18.71    19.05    24.44    65.43    68.77    72.88    74.19    78.08    80.13     81.77     86.64
                        12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                         100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)       88.48     90.18     91.57     93.54     94.73     95.45     96.42     97.38     97.96
```

Figure B.143. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for dissolved organic carbon (DOC) in watershed D2, used to select the number of components.

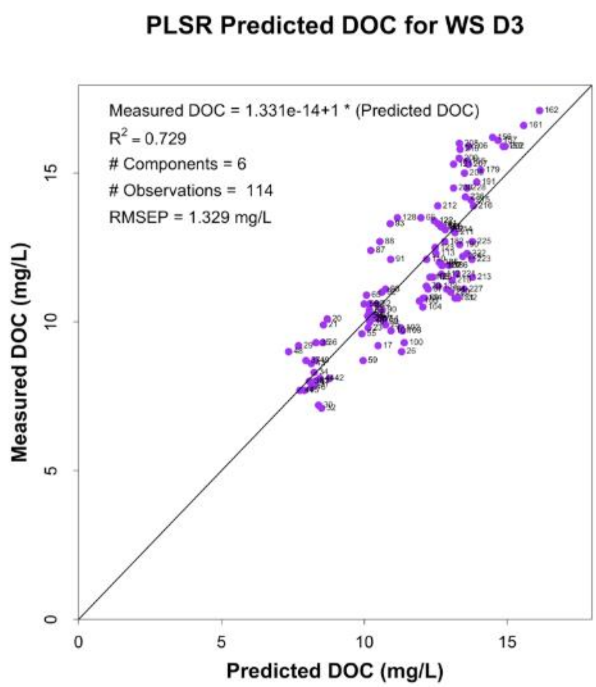

Figure B.144. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 6 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (114 measured samples).

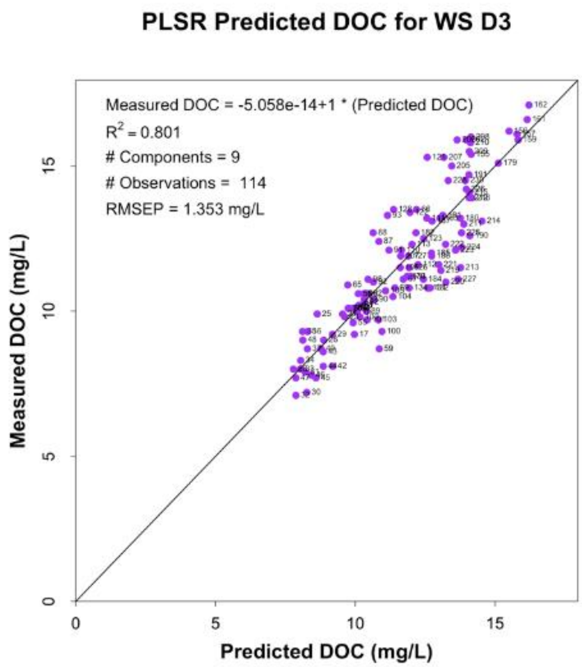

Figure B.145. Measured versus predicted dissolved organic carbon (DOC) values using partial least squares regression (PLSR) trial with 9 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (114 measured samples).

Nitrate-nitrogen (NO_3^--N)

```
Data:   X dimension: 123 205
        Y dimension: 123 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.07882  0.07791  0.07666  0.07533  0.07363  0.07560  0.07743  0.07655   0.0732  0.07385   0.07421   0.07275
adjCV      0.07882  0.07788  0.07659  0.07522  0.07347  0.07546  0.07700  0.07609   0.0727  0.07309   0.07282   0.07109
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.07208   0.07433   0.07637   0.08391   0.08096   0.07899   0.08045   0.08224   0.08181
adjCV   0.07111   0.07229   0.07435   0.08068   0.07814   0.07579   0.07723   0.07876   0.07823

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                       59.136   99.332    99.93    99.98    99.99   100.00   100.00   100.00   100.00    100.00    100.00
as.vector(samp.conc)     4.208    7.441    12.07    18.84    20.68    23.47    35.54    43.59    48.64     57.58     65.39
                       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      67.97     76.15     78.62     83.88     85.71     89.17     90.49     91.92     93.05
```

Figure B.146. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for nitrate-nitrogen (NO_3^--N) in watershed D3, used to select the number of components.

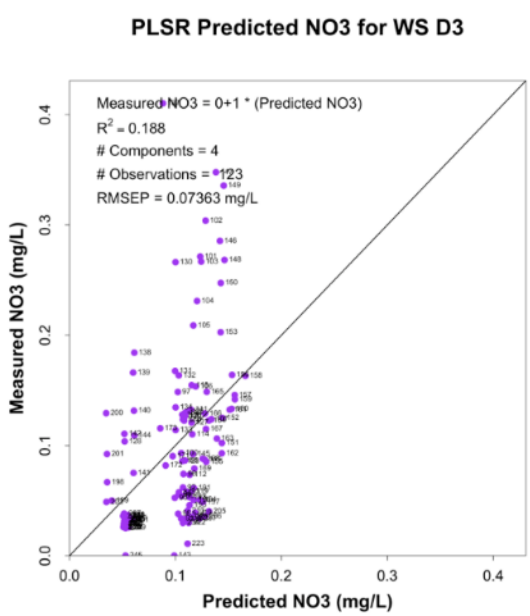

Figure B.147. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 4 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (123 measured samples).

```
Data:   X dimension: 108 205
        Y dimension: 108 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.06316  0.06168  0.05976  0.05907  0.05814  0.05950  0.06444  0.05945  0.05546  0.05728   0.05684   0.05787
adjCV      0.06316  0.06146  0.05969  0.05895  0.05799  0.05934  0.06380  0.05857  0.05431  0.05648   0.05619   0.05657
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.05868   0.05964   0.06057   0.06358   0.06559   0.06918   0.07048   0.07313   0.07746
adjCV   0.05734   0.05769   0.05824   0.06095   0.06302   0.06632   0.06760   0.07005   0.07393

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                       33.52    99.33    99.94    99.98    99.99   100.00   100.00   100.00   100.00    100.00    100.00
as.vector(samp.conc)    10.45    13.04    17.97    22.86    24.14    30.74    43.83    51.09    56.14     59.39     70.15
                      12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00    100.00     100.0     100.0
as.vector(samp.conc)     73.28     79.98     83.37     86.11     87.99     90.24     91.87      93.1      95.3
```

Figure B.148. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for nitrate-nitrogen (NO_3^--N) in watershed D3, used to select the number of components.

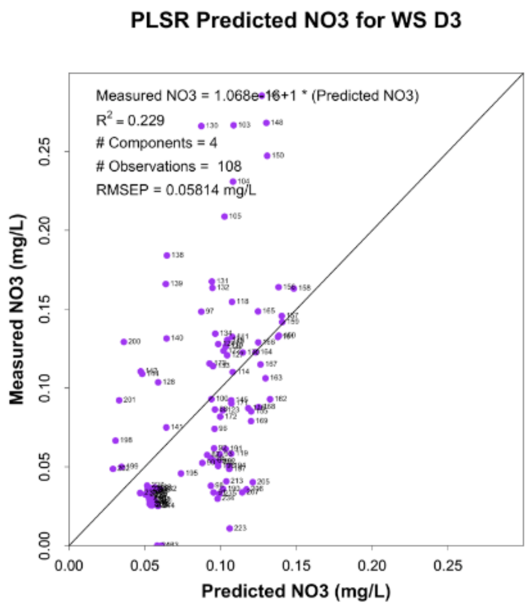

Figure B.149. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 4 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (108 measured samples).

```
Data:   X dimension: 86 205
        Y dimension: 86 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.05356  0.05143  0.05038  0.04551  0.04257  0.04544  0.04792  0.04428  0.04238  0.04223   0.03909   0.03824
adjCV      0.05356  0.05151  0.05024  0.04541  0.04245  0.04510  0.04672  0.04333  0.04188  0.04150   0.03824   0.03723
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03642   0.03480   0.03645    0.0361   0.03557   0.03480   0.03520   0.03608   0.03627
adjCV   0.03553   0.03396   0.03509    0.0347   0.03414   0.03332   0.03359   0.03435   0.03447

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                      66.412    99.54    99.94    99.98    99.99   100.00   100.00    100.0   100.00    100.00    100.00
as.vector(samp.conc)    8.554    18.52    32.80    43.14    44.29    53.46    60.49     66.9    71.45     79.91     85.38
                      12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     88.04     91.49     94.03     95.27     96.38     97.45     98.24     98.84     99.29
```

Figure B.150. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for nitrate-nitrogen (NO_3^--N) in watershed D3, used to select the number of components (removed all data points <0.01).

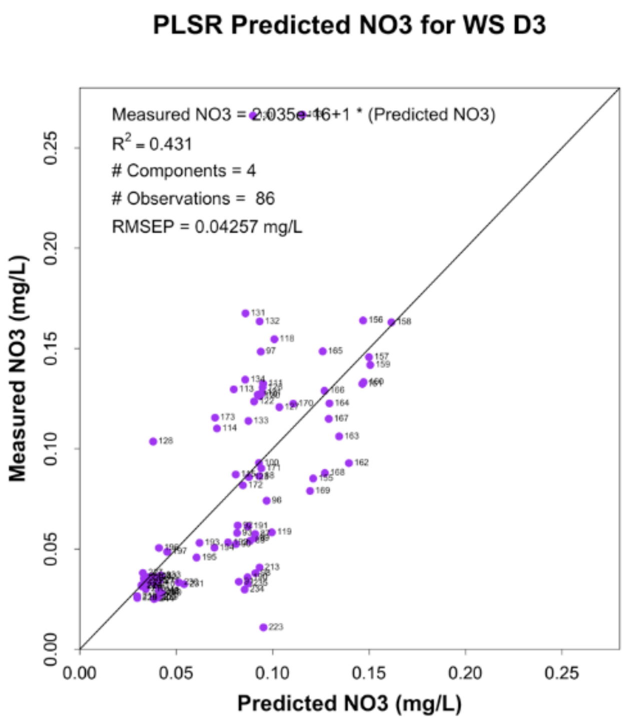

Figure B.151. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 4 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (108 measured samples after removing all data points <0.01).

```
Data:    X dimension: 79 205
         Y dimension: 79 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.04564  0.04055  0.03902  0.03506  0.02887  0.02940  0.02751  0.02787  0.02697  0.02698   0.02749   0.02828
adjCV      0.04564  0.04051  0.03886  0.03488  0.02882  0.02918  0.02753  0.02785  0.02683  0.02673   0.02701   0.02758
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.02792   0.02988   0.02944   0.02921   0.02961   0.02924   0.02986   0.03108   0.03227
adjCV   0.02727   0.02883   0.02834   0.02808   0.02837   0.02802   0.02857   0.02964   0.03073

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                        40.74     99.5    99.93    99.98    99.99   100.00    100.0   100.00   100.00     100.0    100.00
as.vector(samp.conc)     25.05     34.8    49.49    62.08    65.78    66.96     70.3    75.48    78.56      84.1     88.48
                       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00       100     100.0    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      89.93     93.42        95      96.2     97.25     97.75     98.29     98.87     99.24
```

Figure B.152. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for nitrate-nitrogen (NO_3^--N) in watershed D3, used to select the number of components.

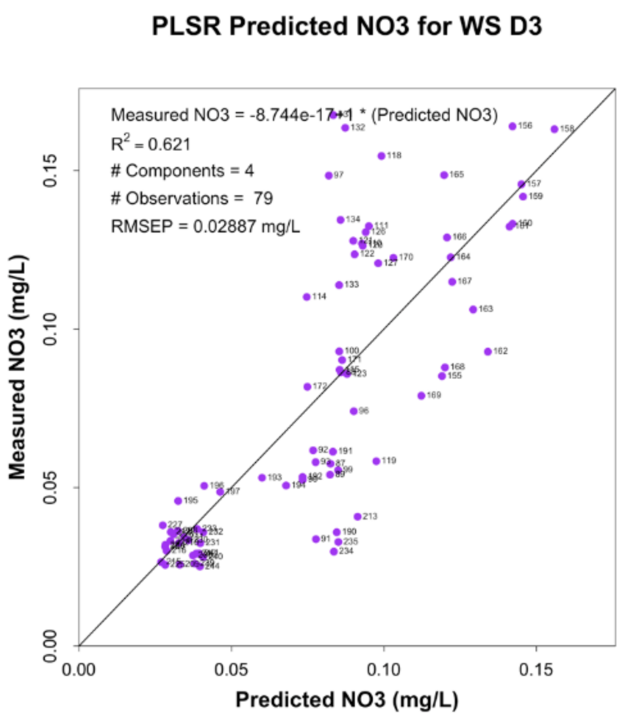

Figure B.153. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 4 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (79 measured samples).

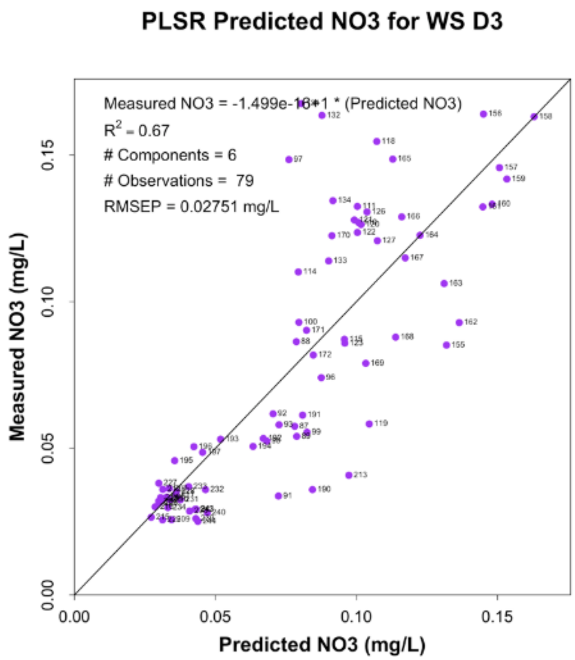

Figure B.154. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 6 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (79 measured samples).

```
Data:   X dimension: 62 205
        Y dimension: 62 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.04478  0.04252  0.03171  0.02575  0.02208  0.02208  0.02094  0.02048  0.02099  0.02082   0.02424   0.02357
adjCV      0.04478  0.04227  0.03150  0.02561  0.02196  0.02171  0.02071  0.02023  0.02049  0.02029   0.02353   0.02283
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.02601   0.02507   0.02352   0.02329   0.02379   0.02286   0.02335   0.02308   0.02307
adjCV   0.02499   0.02410   0.02256   0.02233   0.02274   0.02178   0.02224   0.02196   0.02194

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                      83.95    99.69    99.94    99.98    99.99   100.00   100.00   100.00   100.00    100.00     100.0
as.vector(samp.conc)   26.49    59.65    72.83    80.77    85.89    86.87    88.23    91.07    92.53     93.59      94.9
                     12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00     100.0    100.00     100.0    100.00    100.00    100.00    100.00
as.vector(samp.conc)    96.18     97.09      97.9     98.37      98.9     99.41     99.58     99.74     99.83
```

Figure B.155. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for nitrate-nitrogen (NO_3^--N) in watershed D3, used to select the number of components.

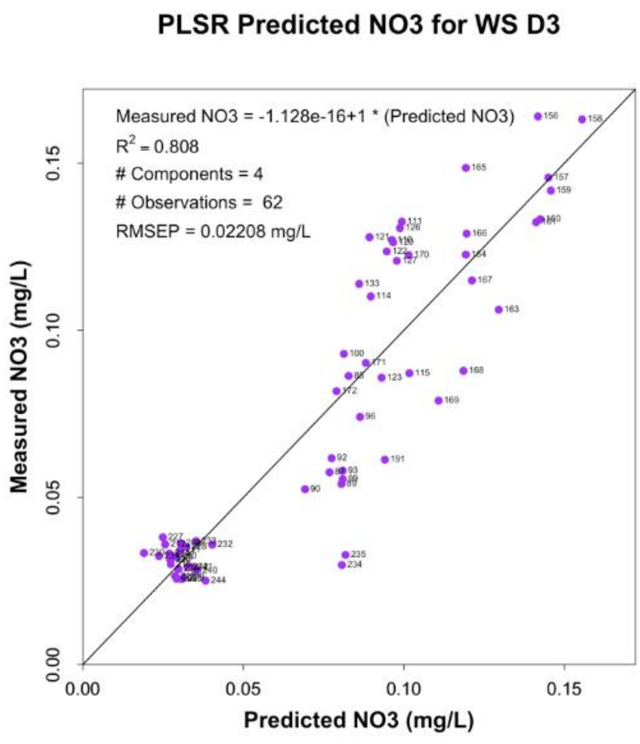

Figure B.156. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 4 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (62 measured samples).

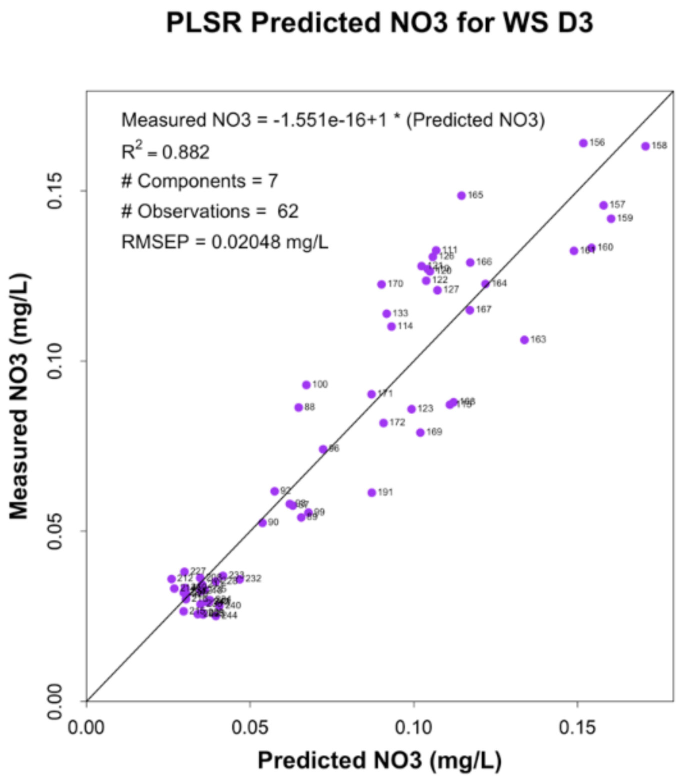

Figure B.157. Measured versus predicted nitrate-nitrogen (NO_3^--N) values using partial least squares regression (PLSR) with 7 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (62 measured samples).

Total dissolved nitrogen (TDN)

```
Data:   X dimension: 186 205
        Y dimension: 186 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV          0.1458   0.1425   0.1408   0.1399   0.1366   0.1325   0.1288   0.1280   0.1270   0.1252    0.1276    0.1188
adjCV       0.1458   0.1425   0.1407   0.1400   0.1365   0.1323   0.1286   0.1277   0.1268   0.1246    0.1269    0.1172
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV       0.1127    0.1172    0.1177    0.1168    0.1232    0.1301    0.1319    0.1412    0.1456
adjCV    0.1116    0.1154    0.1152    0.1145    0.1205    0.1263    0.1280    0.1370    0.1410

TRAINING: % variance explained
                       1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                       81.219    99.39   99.916    99.97    99.99    99.99   100.00   100.00   100.00    100.00     100.0
as.vector(samp.conc)     4.377     7.34    8.433    14.74    21.66    26.53    28.45    33.14    40.93     45.39      57.4
                       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)      61.47     66.24     70.82     72.14     73.96     77.07     78.44     79.41     81.35
```

Figure B.158. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for the first iteration for total dissolved nitrogen (TDN) in watershed D3, used to select the number of components.

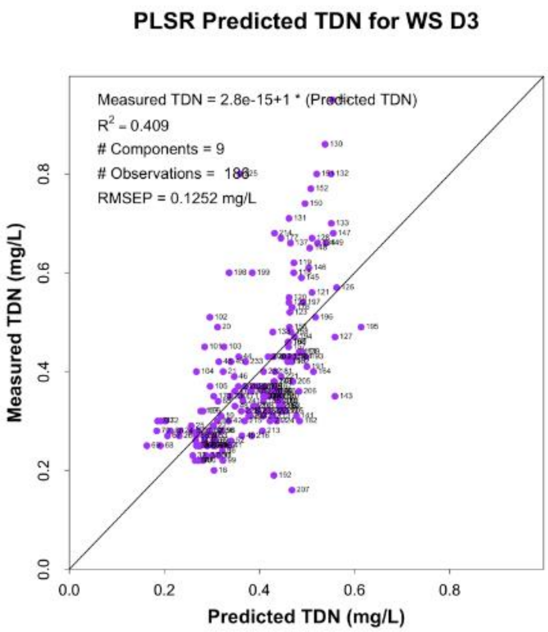

Figure B.159. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 9 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (186 measured samples).

```
Data:   X dimension: 175 205
        Y dimension: 175 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV          0.1164   0.1138   0.1125   0.1114   0.1063   0.1023  0.09921  0.09767  0.09720  0.09633   0.09824   0.09279
adjCV       0.1164   0.1137   0.1124   0.1113   0.1063   0.1021  0.09905  0.09750  0.09696  0.09582   0.09767   0.09140
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.08968   0.09317   0.09411   0.09676   0.10056    0.1037    0.1091    0.1138    0.1201
adjCV   0.08859   0.09175   0.09180   0.09454   0.09805    0.1003    0.1057    0.1103    0.1160

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                      84.376   99.389    99.94    99.97    99.99    99.99   100.00   100.00   100.00    100.00    100.00
as.vector(samp.conc)    5.829    9.096    10.87    19.78    27.47    32.13    34.97    38.55    44.97     48.87     61.51
                      12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                        100.0    100.00    100.00    100.00     100.0    100.00    100.00    100.00    100.00
as.vector(samp.conc)      65.3     68.93     74.23     75.54      76.9     79.73     80.74     82.15     83.96
```

Figure B.160. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D3, used to select the number of components.

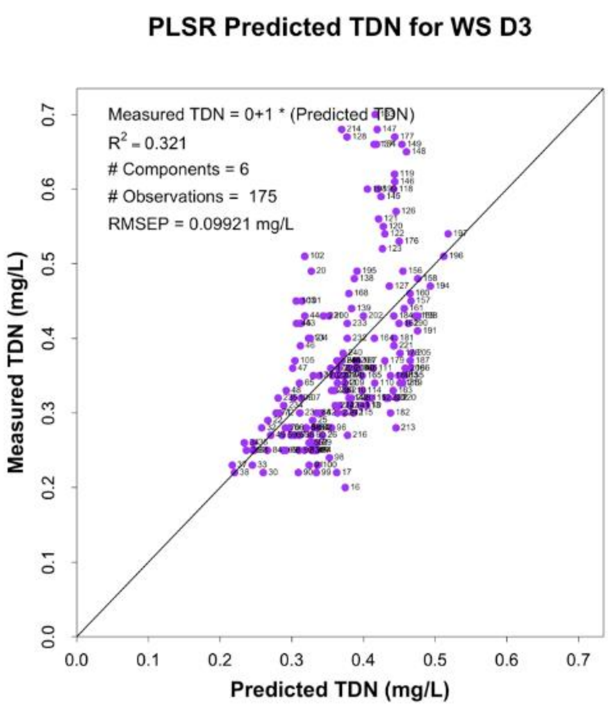

Figure B.161. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 6 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (175 measured samples).

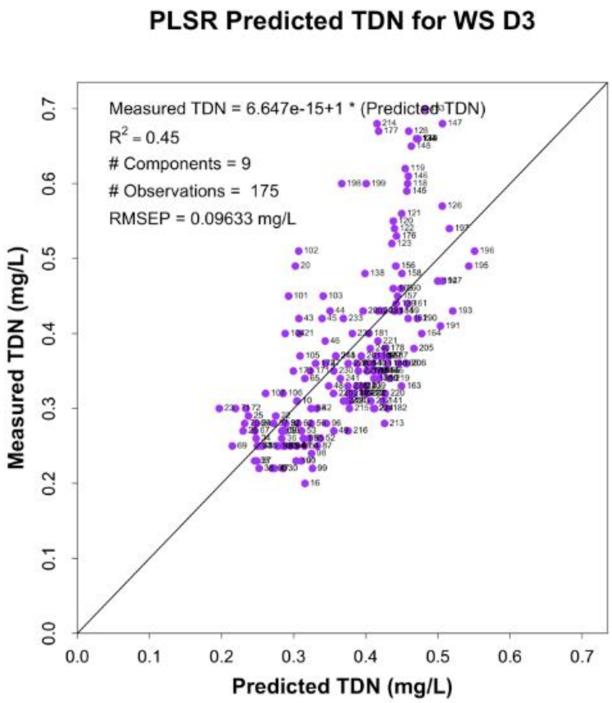

Figure B.162. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 9 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (175 measured samples).

```
Data:   X dimension: 157 205
        Y dimension: 157 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.08682  0.08441  0.08259  0.08384  0.07848  0.07508  0.07292  0.07177  0.07097  0.07005   0.06833   0.06693
adjCV      0.08682  0.08436  0.08253  0.08339  0.07843  0.07490  0.07278  0.07154  0.07072  0.06966   0.06816   0.06629
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.06575   0.06621   0.06674   0.06961   0.07200   0.07503   0.07916   0.08395   0.08757
adjCV   0.06479   0.06504   0.06546   0.06793   0.06994   0.07289   0.07669   0.08097   0.08423

TRAINING: % variance explained
                     1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                     82.585    99.48    99.82    99.97    99.99    99.99   100.00   100.00   100.00     100.0    100.00
as.vector(samp.conc)   6.788    11.08    14.44    21.55    30.89    35.57    39.46    42.53    47.57      51.1     63.92
                     12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                      100.00    100.00    100.00    100.00    100.00    100.00     100.0    100.00    100.00
as.vector(samp.conc)    70.55     74.66     77.57     80.18     82.57     83.72      85.6     87.51     88.91
```

Figure B.163. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D3, used to select the number of components.

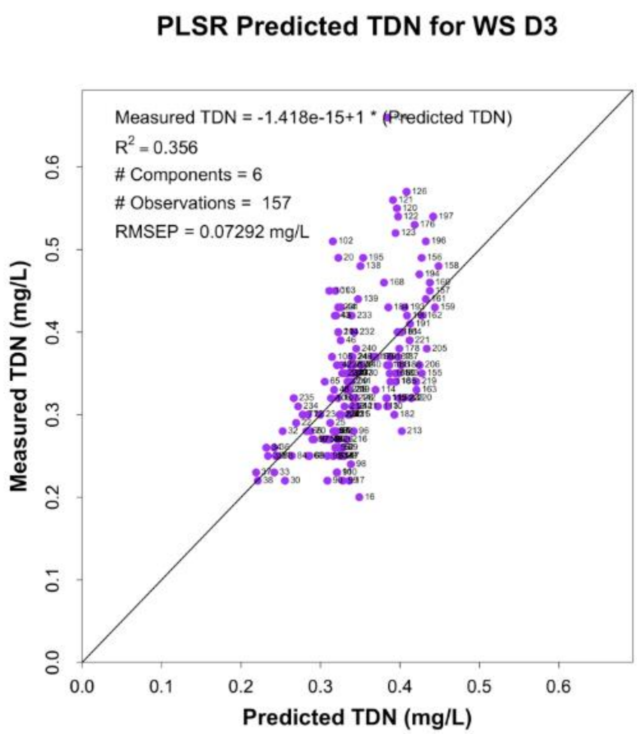

Figure B.164. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 6 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (157 measured samples).

```
Data:   X dimension: 154 205
        Y dimension: 154 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.08242  0.07956  0.07847  0.07756  0.07398  0.07025  0.06843  0.06703  0.06621  0.06502   0.06336   0.06593
adjCV      0.08242  0.07953  0.07837  0.07809  0.07396  0.07008  0.06826  0.06680  0.06598  0.06476   0.06341   0.06499
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.06340   0.06193   0.06328   0.06675   0.06918   0.07440   0.07798   0.08343   0.09005
adjCV   0.06243   0.06107   0.06218   0.06522   0.06742   0.07223   0.07550   0.08044   0.08659

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                      82.631    99.48    99.83    99.97    99.99    99.99   100.00   100.00   100.00    100.00     100.0
as.vector(samp.conc)    7.689    12.34    16.01    23.95    33.49    37.41    41.52    44.46    48.91     51.87      64.6
                      12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00    100.00    100.00       100     100.0    100.00    100.00    100.00
as.vector(samp.conc)     71.21     74.63     77.48     79.85        82      83.3     85.12     87.03     88.39
```

Figure B.165. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D3, used to select the number of components.

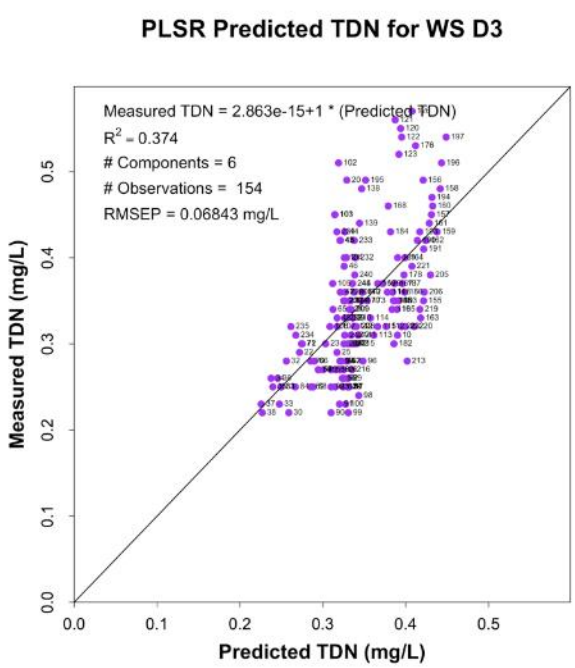

Figure B.166. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 6 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (154 measured samples).

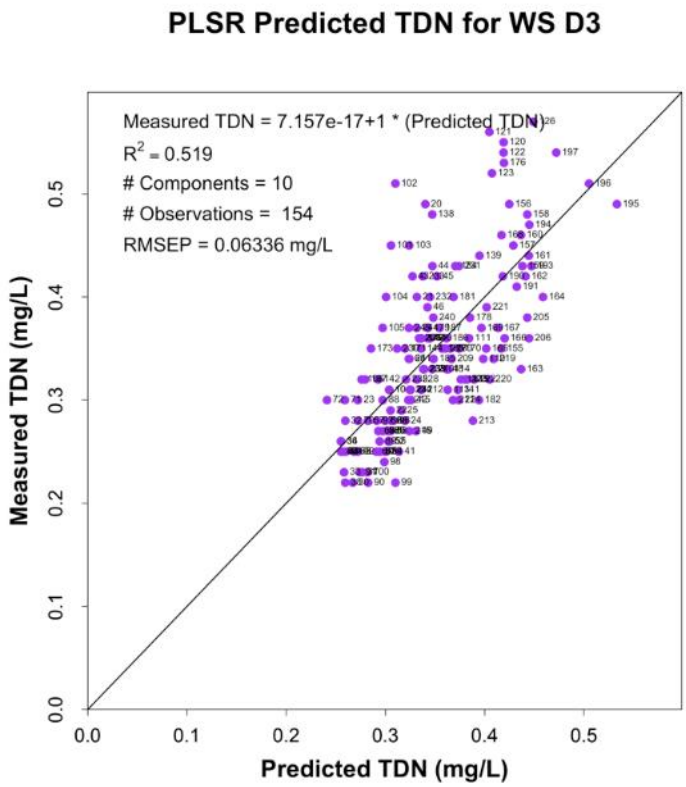

Figure B.167. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 10 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (154 measured samples).

```
Data:    X dimension: 142 205
         Y dimension: 142 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.06714  0.06336  0.06263  0.06389  0.05816  0.05589  0.05337  0.05117  0.05065  0.04865   0.04680   0.04569
adjCV      0.06714  0.06332  0.06253  0.06391  0.05815  0.05567  0.05318  0.05095  0.05033  0.04820   0.04657   0.04532
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.04727   0.04729   0.04873   0.04977   0.05143   0.05611   0.06172   0.06440   0.06824
adjCV   0.04660   0.04675   0.04795   0.04881   0.05028   0.05448   0.05950   0.06203   0.06561

TRAINING: % variance explained
                        1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                         83.40    99.48    99.84    99.97    99.99    99.99   100.00   100.00   100.00    100.00    100.00
as.vector(samp.conc)      12.88    17.18    20.74    30.85    39.88    45.94    51.94    56.11    61.67     64.52     69.93
                        12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                         100.00    100.00    100.00    100.00    100.00     100.0    100.00    100.00    100.00
as.vector(samp.conc)       74.72     77.88     80.57     82.02     83.85      85.8     88.28     89.36     90.33
```

Figure B.168. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D3, used to select the number of components.

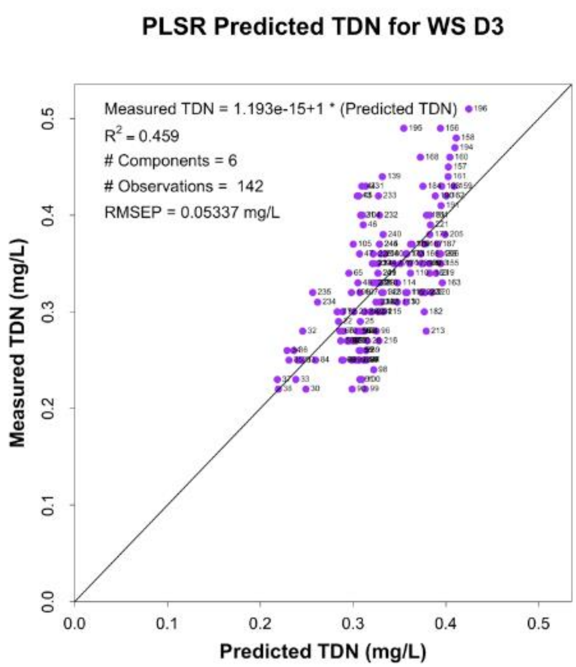

Figure B.169. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 6 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (142 measured samples).

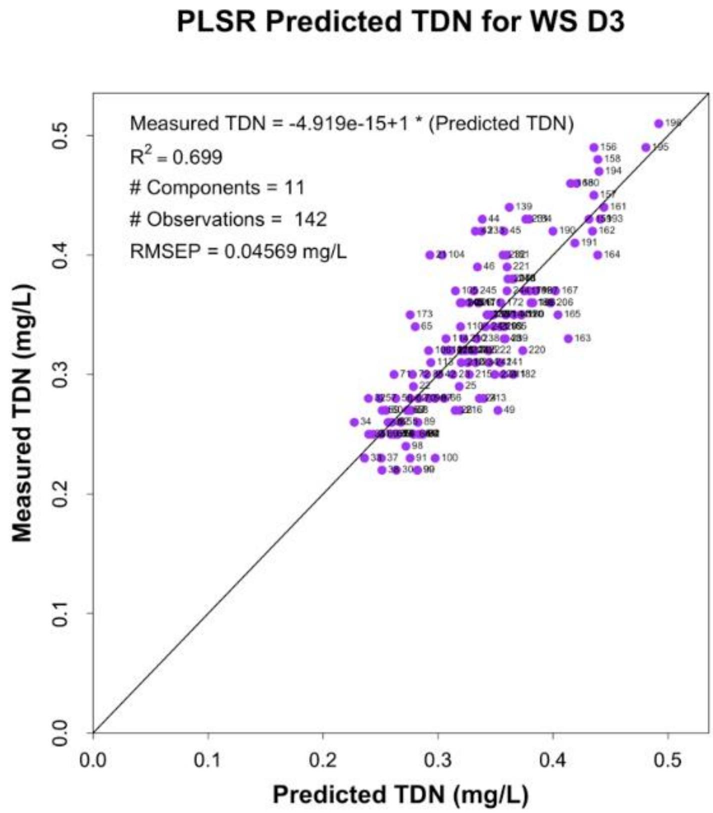

Figure B.170. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 11 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (142 measured samples).

```
Data: 	X dimension: 116 205
	Y dimension: 116 1
Fit method: kernelpls
Number of components considered: 20

VALIDATION: RMSEP
Cross-validated using 10 random segments.
       (Intercept)  1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
CV         0.04623  0.04342  0.04282  0.04205  0.04054  0.03562  0.03290  0.03233  0.03215  0.03443   0.03481   0.03563
adjCV      0.04623  0.04339  0.04277  0.04214  0.04040  0.03547  0.03278  0.03218  0.03198  0.03400   0.03444   0.03515
       12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
CV      0.03715   0.03886   0.03905   0.04115   0.04257   0.04365   0.04553   0.04627   0.04698
adjCV   0.03639   0.03817   0.03794   0.03997   0.04120   0.04196   0.04375   0.04433   0.04492

TRAINING: % variance explained
                      1 comps  2 comps  3 comps  4 comps  5 comps  6 comps  7 comps  8 comps  9 comps  10 comps  11 comps
X                       82.48    99.51    99.91    99.97    99.98    99.99   100.00   100.00   100.00    100.00    100.00
as.vector(samp.conc)    13.47    16.54    19.47    30.93    47.94    56.37    59.53    61.27    65.79     67.79     71.89
                      12 comps  13 comps  14 comps  15 comps  16 comps  17 comps  18 comps  19 comps  20 comps
X                       100.00    100.00     100.0    100.00    100.00    100.00    100.00    100.00    100.00
as.vector(samp.conc)     75.97     78.22      82.6     84.04     86.31     89.39     90.79     92.53     93.71
```

Figure B.171. R output of root mean square error of prediction (RMSEP, mg L^{-1}) for 20 components from partial least squares regression for total dissolved nitrogen (TDN) in watershed D3, used to select the number of components (removed data points>0.4 mg L^{-1}).

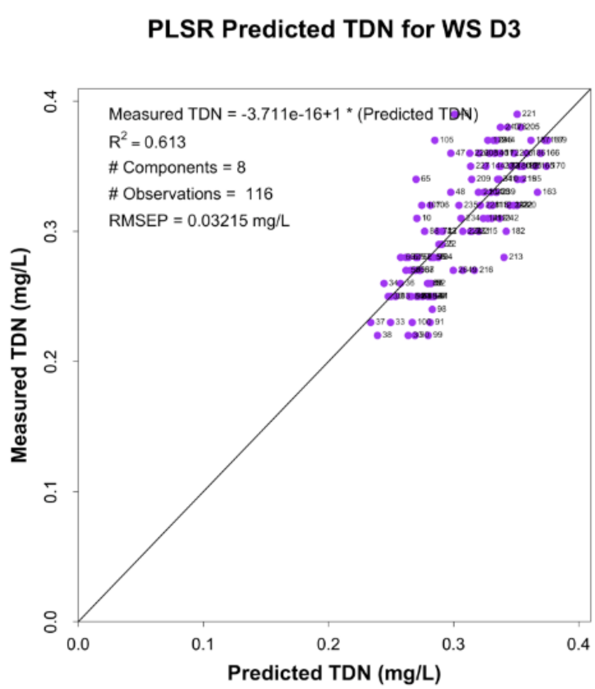

Figure B.172. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 8 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (116 measured samples after removing data points>0.4 mg L^{-1}).

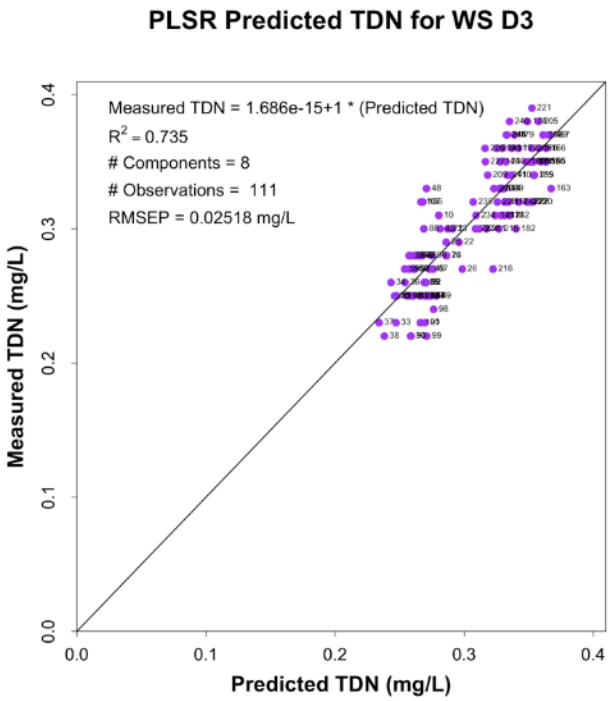

Figure B.173. Measured versus predicted total dissolved nitrogen (TDN) values using partial least squares regression (PLSR) with 8 components for watershed D3 in Carteret County, North Carolina using data from Nov 2013 to Nov 2014 (111 measured samples).

APPENDIX C: Detailed analysis of continuous chemographs

C.1 Typical patterns

The figures shown below illustrate the typical patterns of DOC dilution and NO_3^--N increases observed during relatively normal flow conditions. Figure C.1 shows the two smaller events and one large event that occurred between April 6 and 20 2014 and the three following figures zoom in on each of these events. With the smaller events that occurred before fertilization on April 8 (Figure C.2) and April 16 (Figure C.3) there were decreases in TDN indicating a dilution effect; however, there was no increase in NO_3^--N concentration during these small events.

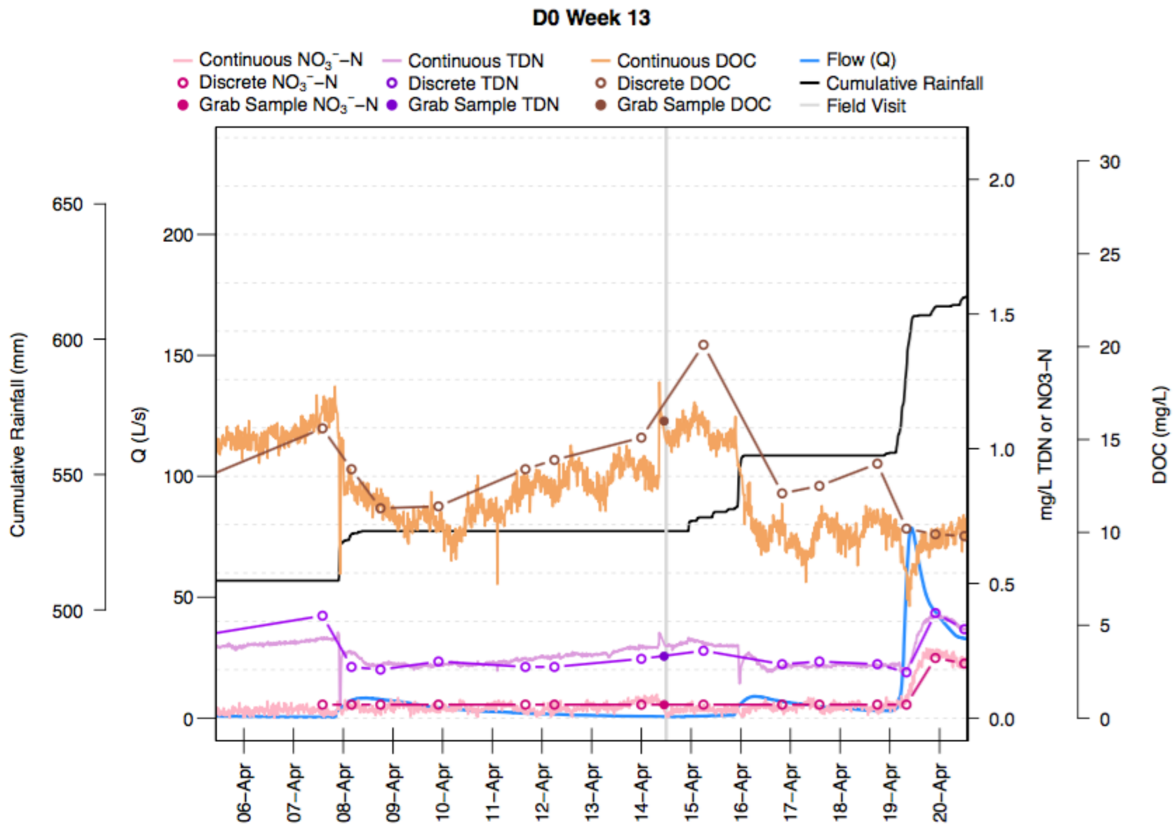

Figure C.1. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Apr 06 to 20).

With the larger event (April 19-20, Figure C.4), flow rates peaked at 80 L/s, i.e., about 10 times those of the previous two events. There was a slight decrease in TDN at the beginning of the event, but then an increase in TDN that also corresponded to a NO_3^--N increase from about 0.05 to about 0.2 mg/L (Figure C.4).

Similar to the TDN trend, the dilution effect was observed for DOC during the first two events, but not as much for the third, larger event. There is some dissonance between the discrete values of DOC concentration and the predicted continuous values around the April

16th event, with the discrete values showing a decrease from 20.1 to 12.1 mg L^{-1} (Figure C.1), followed by an increase to ~14 mg L^{-1}following the second event and, while the continuous values show a clear decrease from ~15 mg L^{-1} to the equilibrium concentration ~10 mg L^{-1}, remaining there until the next event (April 19). At the beginning of the large event (April 19 05:00, Figure C.4), the continuous data shows a brief dilution to around 6 mg L^{-1}, but the concentration quickly (after ~8 hours) returns to an apparent baseline concentration of ~10 mg L^{-1}. The discrete data also show a dilution effect, but the values are shifted higher, starting ~14 mg L^{-1} and decreasing to ~10 mg L^{-1} at the beginning of the event.

For both small events, the small TDN troughs occur at the end of rainfall, and as flow rates are calculated to be at 4-5 L s^{-1}, at the early stages of the rise of the hydrograph. This water thus likely corresponds to a volume of previously stagnant water that has been diluted by the rainfall. In both small events, the TDN troughs are followed by a small peak that lasts about one hour. This peak is possibly an indication that water previously present in the ditches is being pushed out by new water draining from the soil profile, as one would expect it to be rich in DOC and DON. The DOC data follow the same trend for the April 07-08 event, but not for the April 15 event and shows no response that day, which is surprising.

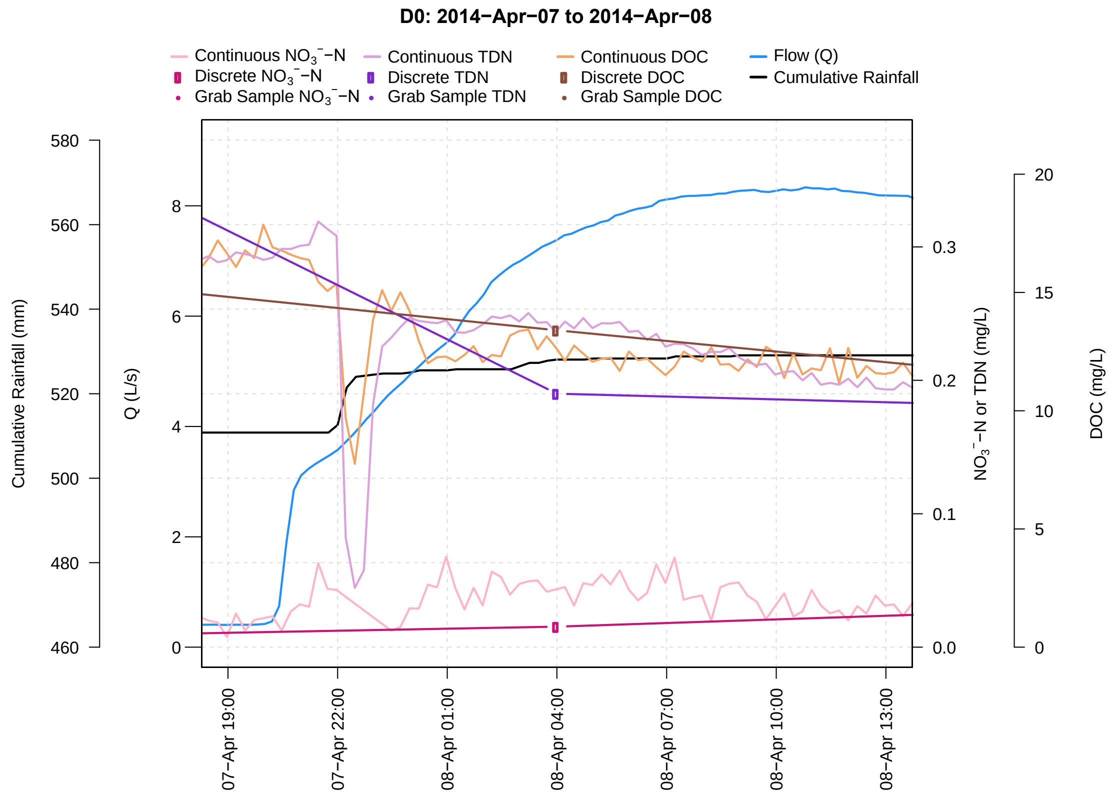

Figure C.2. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Apr 07 to 08).

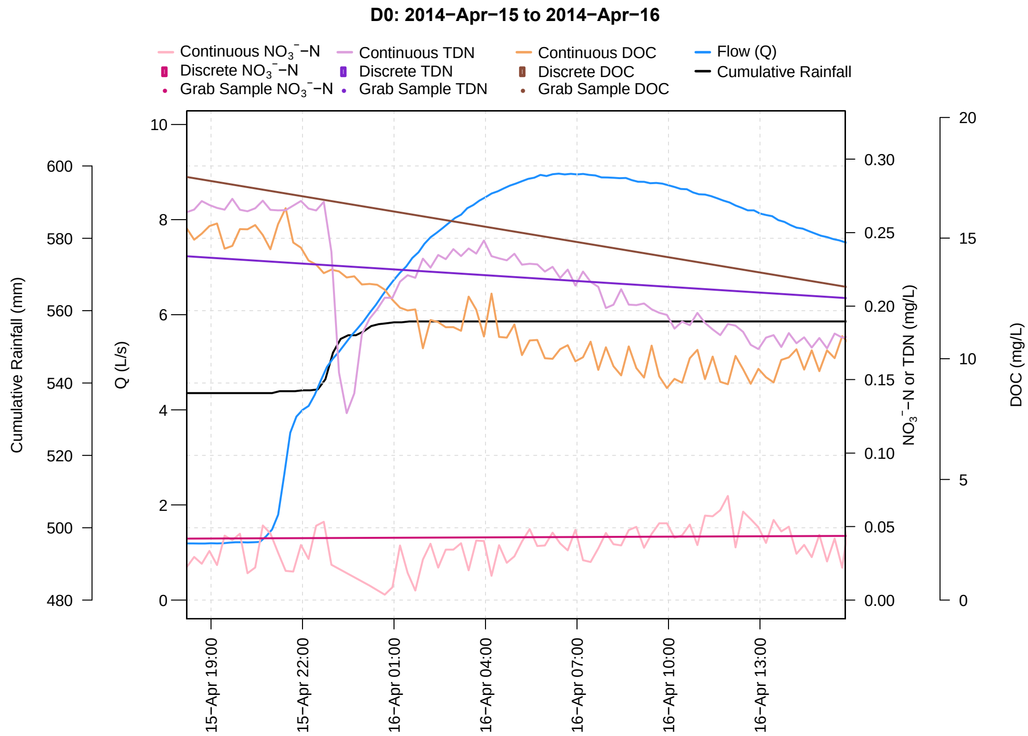

Figure C.3. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Apr 15 to 16).

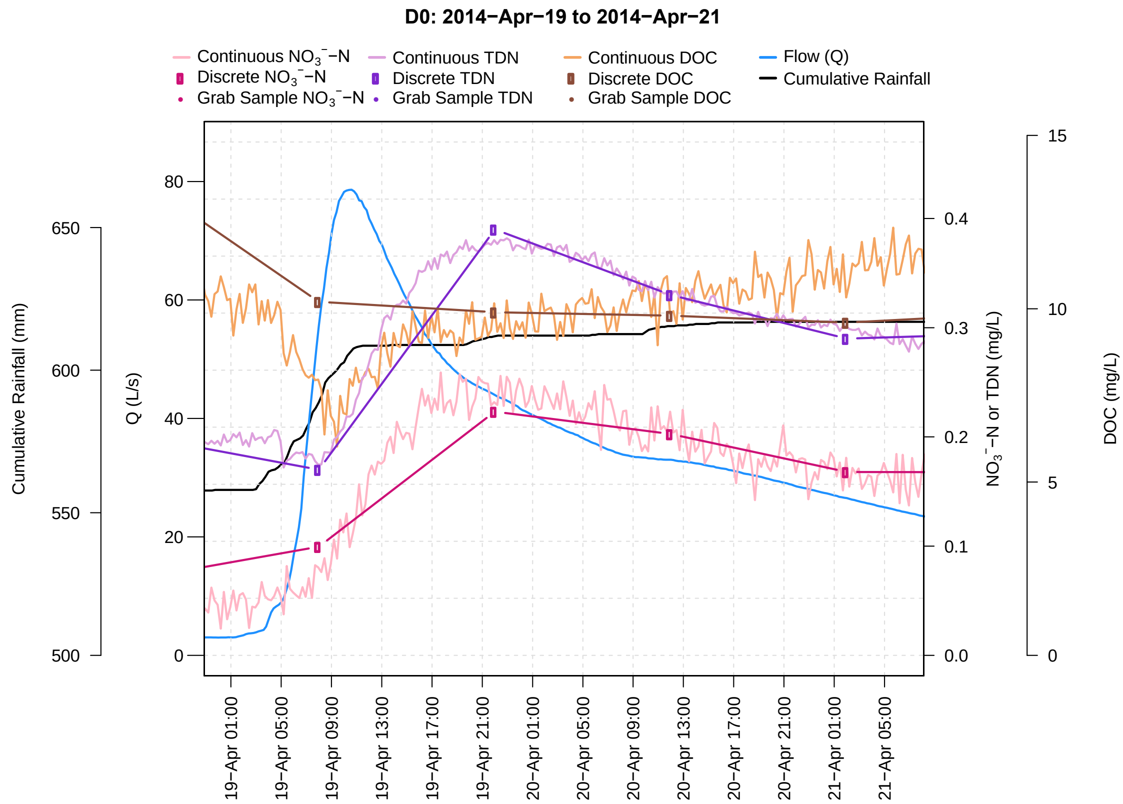

Figure C.4. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Apr 19 to 21).

The April 19 event, yielding a lot more water gives hint about the processes not only in the ditches but in the soil profile too. The DOC concentration trough appears in synchrony with the flow peak. In other words, the processes generating the flow peaks go through areas in the watershed where DOC is relatively poor. Drainage hydraulics tell us that the shape of the water table, directly following rainfall is not elliptical and that a large portion of the flow volume leaches through the near-ditch soil profile (Paris, 2004). This zone of the soil, being drier and being leached, in relative terms, with higher volumes than the rest of the soil profile, is expected to contain less leachable material, including DOC and NO_3-N. The nitrate concentration peak lags after the flow peak, most likely corresponding to water which infiltrated vertically in the soil, away from the near ditch area, where it would be enriched in leachable nitrate in the soil, and then moved laterally until it reached the ditches.

The 66.3 mm rainfall event that occurred over 10.5 hours after a relatively dry period of summer 2014 (July 4-5) generated flow that peaked at 20 L/s (Figure C.5). This event was chosen as it illustrates long and short term dynamics, but also that the calculated concentrations have to be taken with caution. Prior to the event, there is a build-up of TDN and DOC in the water upstream the weir. Calculated concentrations suggest that DOC may have increased by more than 5 mg/L in less than three days, while TDN may have increased by 0.1 mg/L over during the same preceding dry period. These increasing concentrations occurred in an essentially stagnant water upstream the weir and are likely indicative of the sediment diagenetic processes at this location.

Approximately halfway along the rising limb of the hydrograph, the TDN concentration decreases, evident in both the continuous and discrete data. The same reasons presented above could be invoked (less nutrient rich water coming directly from the rain, or surface runoff from the road, rain, or leaching from the nutrient deficient banks). The continuous data indicates a slight decrease in NO_3-N, although that effect is not captured by the discrete data. The initial TDN and NO_3-N concentration troughs are followed by previously described increase in NO_3-N and TDN concentrations during the falling limb of the hydrograph. Both

TDN and NO_3-N concentrations peak after the flow peak. Since TDN includes dissolved organic nitrogen (DON), NO_3-N, and NH_4-N, the TDN dilution effect is likely due to the dilution of the DON (as is observed with DOC) as NH_4-N concentrations were below MDL; this also suggests that the proceeding rise in TDN is due to the rise in NO_3-N.

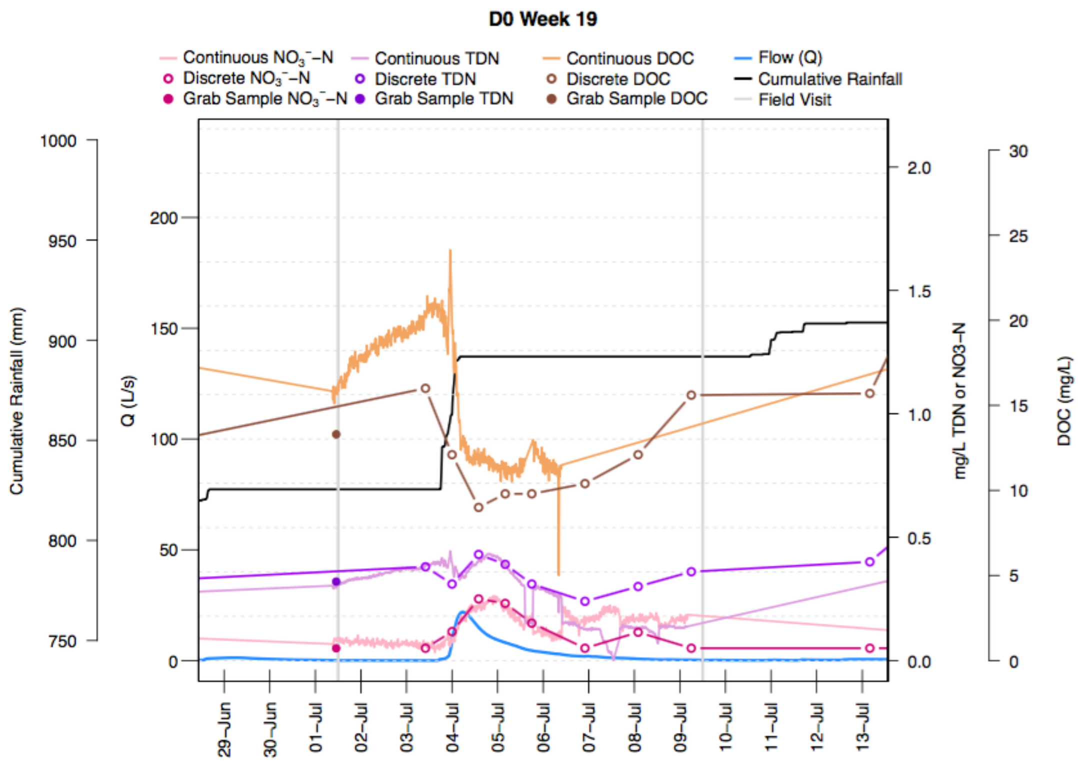

Figure C.5. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 June 29 to July 13).

With DOC concentration, there is a gradual buildup during the dry period and a decrease following an event. The continuous data indicates that there is an initial drop, followed by a rapid, sharp increase, followed by a sharp decrease to an equilibrium or average level of 12 mg L^{-1}, which is not captured by the 14-hour discrete data. It is likely that there are complicated in-stream dynamics occurring at the start of an event, due to new inputs from the incoming rainfall and the release of nutrients that have been bound to substrate in the sediment or entering the stream from surface runoff. In the coastal plain watersheds, it is not likely to be released from the banks given that these areas are typically dry and nutrient deficient.

It should be noted however that, although the calculated concentrations seem to follow the discrete concentration value trends, the calculated concentrations failed to match the discrete values, particularly for DOC. It would be tempting to correct for this using an offset value. This suggests, however, that the PLS chemometric technique used here using samples spanning 12 months, was unable to adjust for the variable fouling observed for different seasons, and, to predict the likely season-variable co-variability of the concentrations with the water 'color-matrix'.

During week 22 (2014 Aug 10 to 24, Figure C.6), there are two events (peak ~25 L s^{-1}) that occur within a 5-day period. Figure C.7 zooms in on these two events. As observed during week 19, there is a buildup of TDN preceding the first event which is not attributed to NO_3^--N or NH_4^+-N, but the DON, given that NO_3^--N concentration remains relatively stable preceding the event and NH_4^+-N concentrations are near or below MDL (0.1 mg L^{-1}) throughout the entire study period. There is an initial drop in TDN due to the dilution effect, followed by a peak attributed to the corresponding NO_3^--N increase. The TDN trend beyond the first peak corresponds to the trend of the NO_3^--N, with the chemical peaks following the flow peaks.

Given that the baseline NO_3^--N concentration is consistently low, but increases with flow events, indicates that NO_3^--N was being added to the canal from an outside source during events or being leached shortly after. Two potential outside sources are surface runoff or leachate from the banks, which are hypothesized to be areas of high mineralization given that these areas are well drained (water table asymptotically approaching the ground surface further away from the canal, leaving the canal banks dry except during events and lacking organic matter).

With DOC, as observed previously, there is a buildup of DOC (similar, but more pronounced than the DON buildup) over the preceding dry period, peaking at 25 mg L^{-1} (discrete) and ~21 mg L^{-1} (continuous), The continuous data indicates a sudden drop in concentration to ~12 mg L^{-1}, with the initial rainfall, followed by a subtle increase to ~15 mg L^{-1}, then a decrease to a relatively stable concentration ~ 11 mg L^{-1}. At the beginning of the second event, there is a slight decrease to ~10 mg L^{-1}, but the equilibrium concentration remains ~11 mg L^{-1}. The continuous and discrete concentrations are similar, although the continuous data reveals much more detail, particularly just at the onset of an event, which is missed by the discrete samples. DOC remaining relatively stable with the second event further supports the hypothesis that the DOC source is mainly attributed to diagenetic processes occurring in the sediment, releasing DOC during low flow conditions and indicates that this canal has an equilibrium background DOC level (~11 mg L^{-1}) under steady flow conditions.

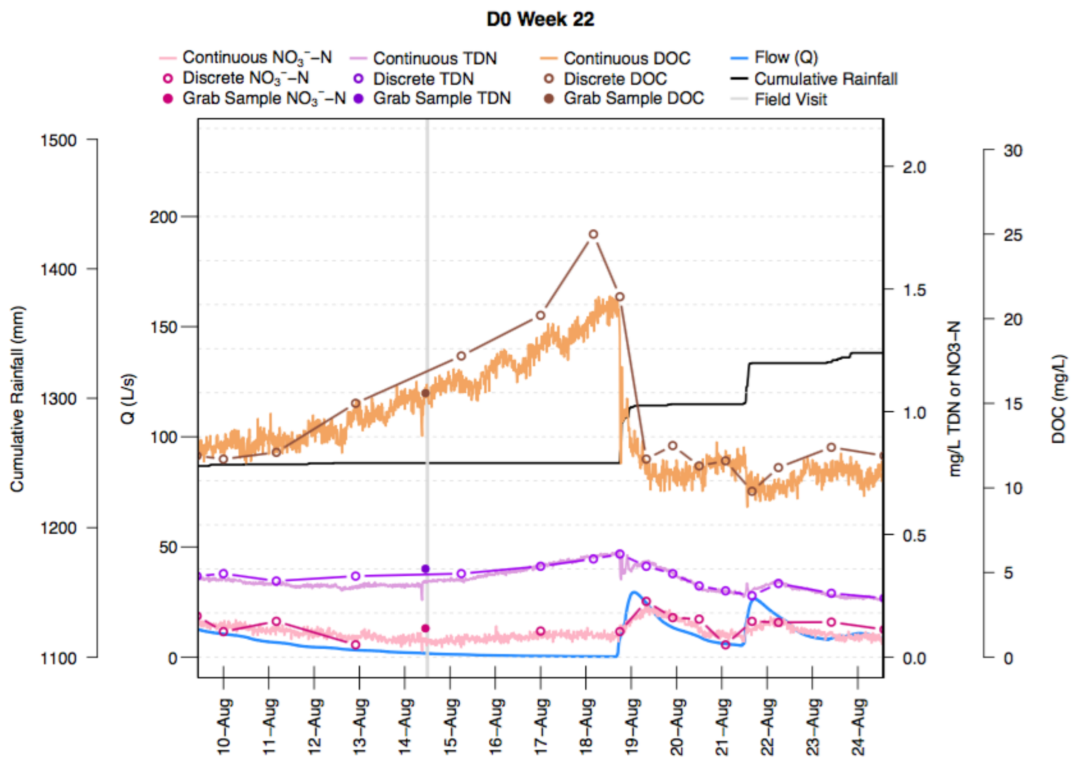

Figure C.6. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Aug 10 to 24).

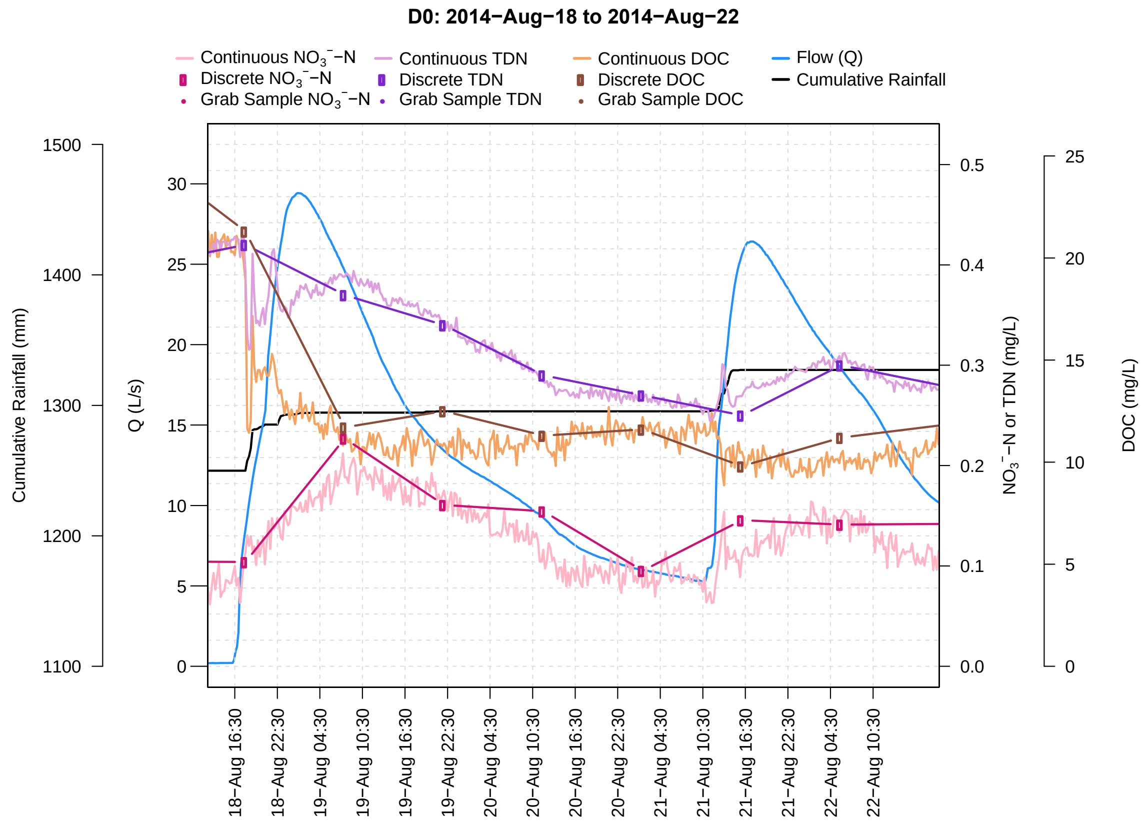

Figure C.7. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Aug 18 to 22).

C.2 Dry antecedent conditions and seasonal variation in nutrient dynamics

There are two different reactions to dry (no-flow) antecedent conditions, one example in spring (Figure C.8) and one in the fall of 2014 (Figure C.10). Figure C.9 zooms in on the small event that occurs on May 16 2014. With this event in May, there is a dilution of both DOC and TDN at the beginning of the event, with a quick return to near average concentrations. There is also a slight increase in NO_3-N following the dilution of DOC and TDN that gradually decreases with receding flow. For the small event in fall, DOC, TDN, and NO_3-N react differently. Figure C.10 captures the dramatic dynamics that occur from a relatively small event after a period of no flow from Oct 5 to Oct 19 2014. Figure C.11 zooms in on this small event Oct 16 and shows that there is stepwise dilution of DOC; there is an initial increase in DOC at the start of the event, followed by a short period of dilution, then a return to peak concentration, another dilution (not as great as the first), followed by an increase (not as high as the first two pulses, but of longer duration), and then a final dilution to around equilibrium DOC concentration which remains steady for about three days before beginning to build up again during no-flow conditions. The pulses of DOC may be from the sediment, i.e., the DOC that has been accumulating during low flow conditions which is then flushed at the onset of the event. The sudden drop in DOC may be a dilution effect from water leached from the banks where there is little organic matter, but potentially high mineralization rates. This hypothesis is further supported by simultaneous increases in TDN and NO_3-N, which could be present in the pore water of the mineralized zone. The increase in the TDN in the fall would then be attributed to the NO_3-N increase, rather than the DON, which is consistent with other events. Typically, at the beginning of an event, there is a decrease in TDN that corresponds to a DOC decrease, followed by an increase in TDN that corresponds to the NO_3-N increase. In the spring event, the TDN closely mimics the DOC trend; whereas, in the fall, the TDN closely mimics the NO_3-N trend. These observations could indicate that DON is the more dominant form in the spring, whereas inorganic nitrogen is the more dominant form in the fall.

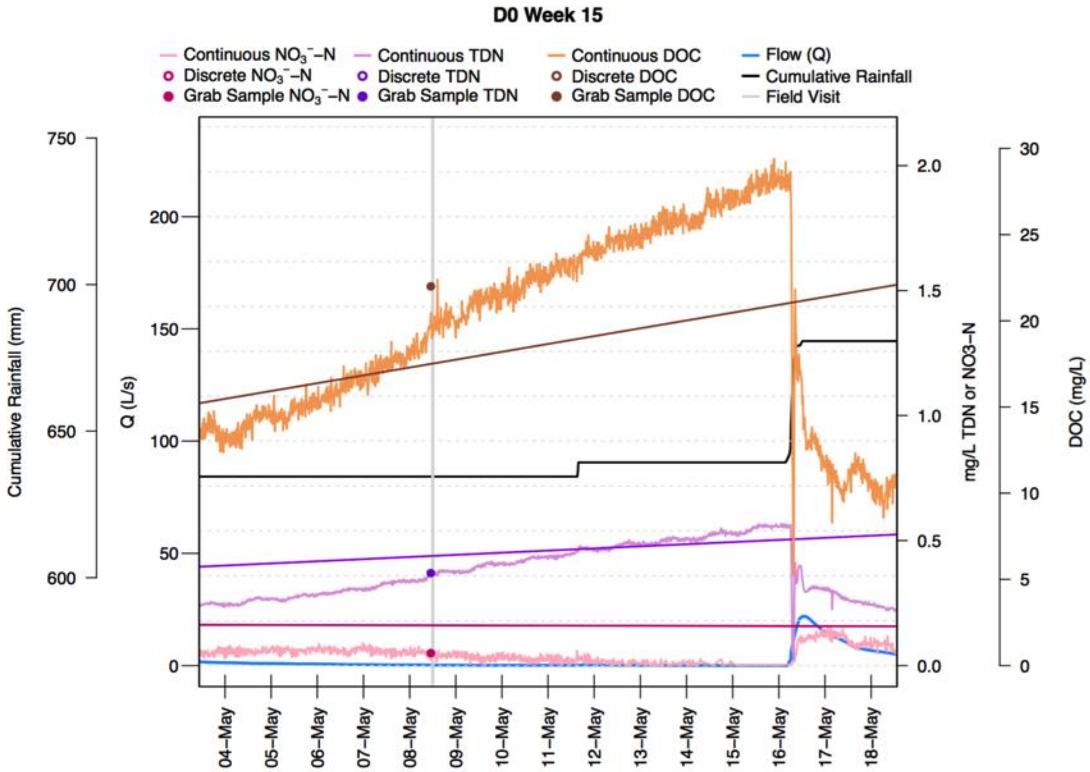

Figure C.8. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 May 04 to 18).

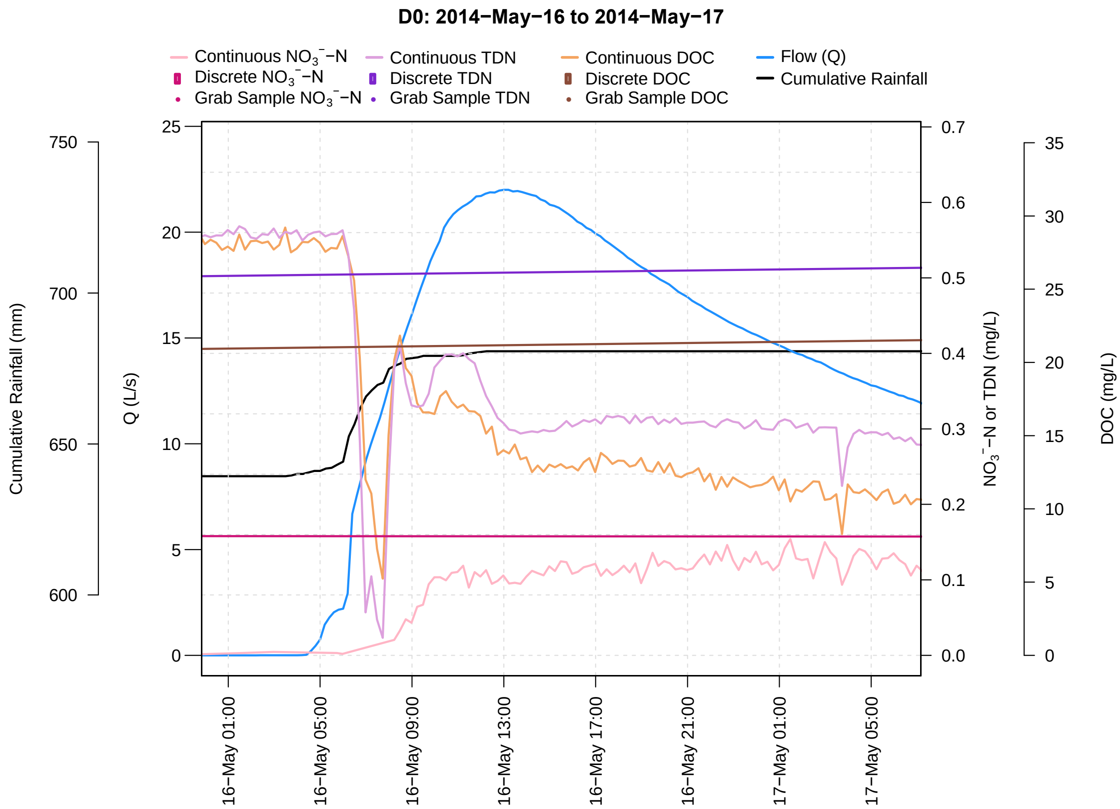

Figure C.9. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 May 16 to 17).

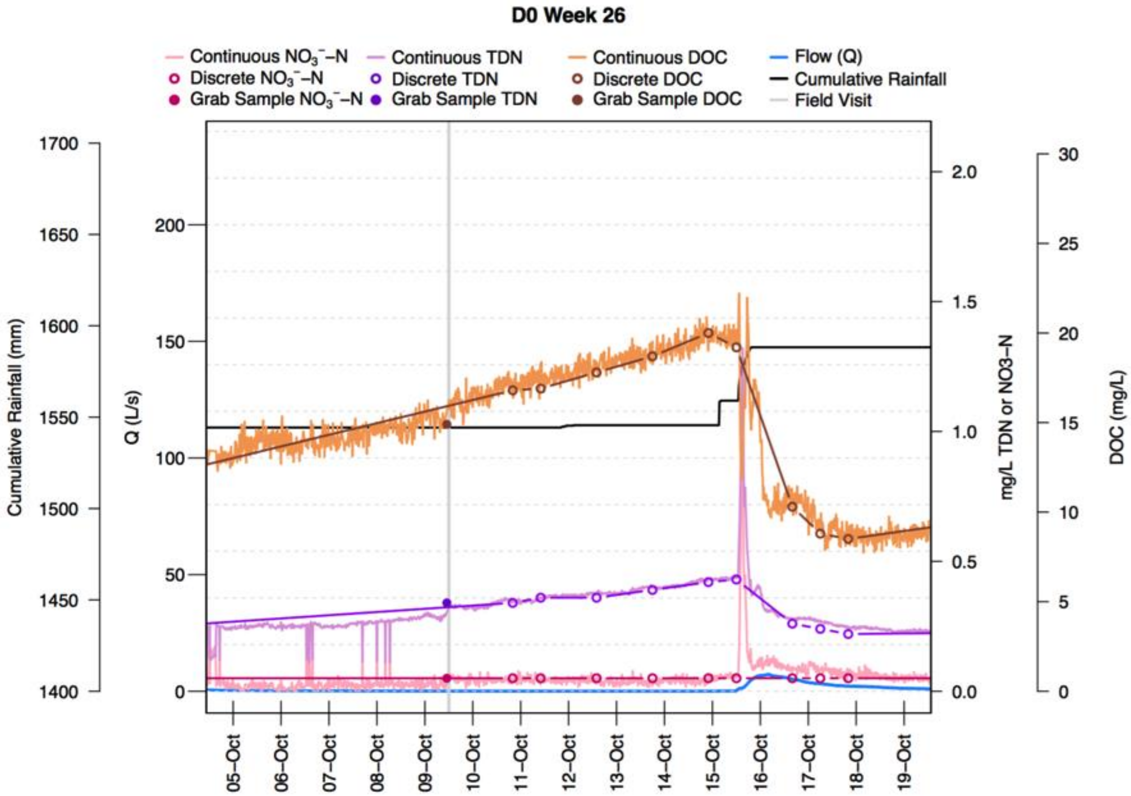

Figure C.10. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Oct 05 to 19).

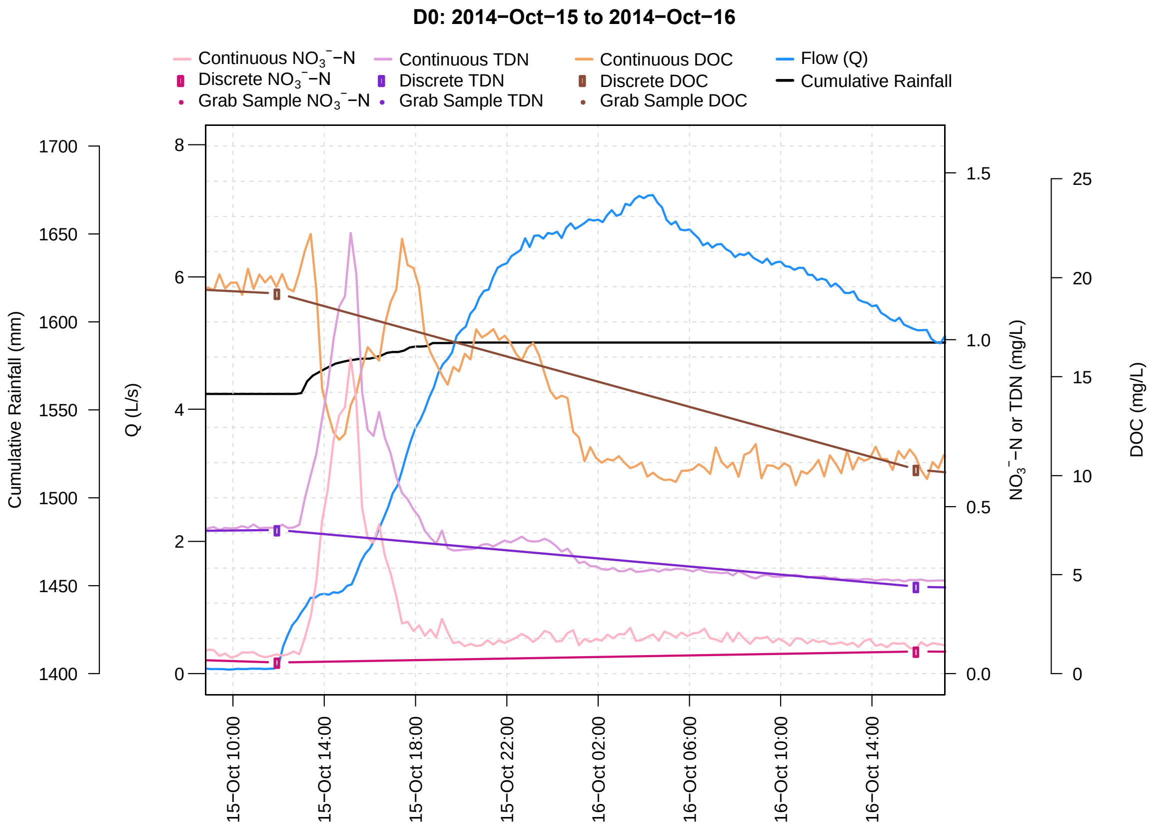

Figure C.11. Continuous concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Oct 15 to 16).

Another event took place on March 6 to 7 2014, following no-flow conditions (Figure C.12). Similar to the event in May, there was no initial pulse of DOC, but only a dilution effect where you have a decrease in DOC corresponding to the increase in flow (Mar 06 22:00 to Mar 07 10:00); however, there is no additional DOC dilution associated with the second flow peak (Mar 07 20:00), with the DOC continuous concentration remaining steady ~8 mg L^{-1}. Similarly, there is also a dilution of the TDN at the onset of the event, with the TDN peak corresponding to the NO_3^--N peak. The NO_3^--N steadily increases with the increasing flow, but the chemical peaks (TDN and NO_3^--N) were slightly delayed compared with the flow peak. The relatively short delay in chemical peaks following the flow peak supports the hypothesis of NO_3-N being leached into the canal from mineralized portions of the soil profile rather than coming directly from the rainfall or surface runoff, particularly since this was before fertilizer was applied.

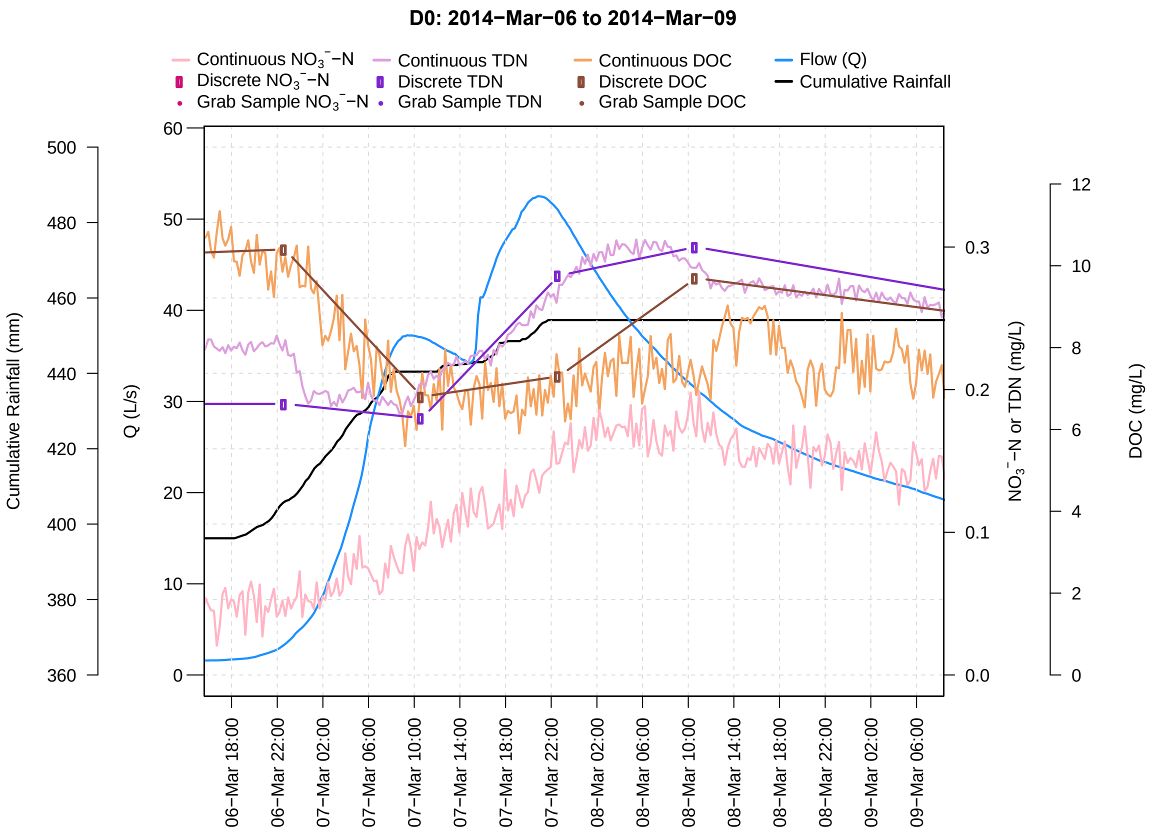

Figure C.12. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 Mar 6 to 9).

In the event on July 3 to 4 2014 (Figure C.13) with dry antecedent conditions, we have the initial pulse in both DOC and TDN, followed by a decrease in both, and an increase in NO_3^--N and TDN, similar to the trend observed in the small event in October (Figure C.11). Again, the initial pulse in organic matter is likely from the sediment buildup, given the dry conditions, followed by a dilution effect. The TDN increase is then driven by the NO_3^--N, which again peaks shortly after the flow peak.

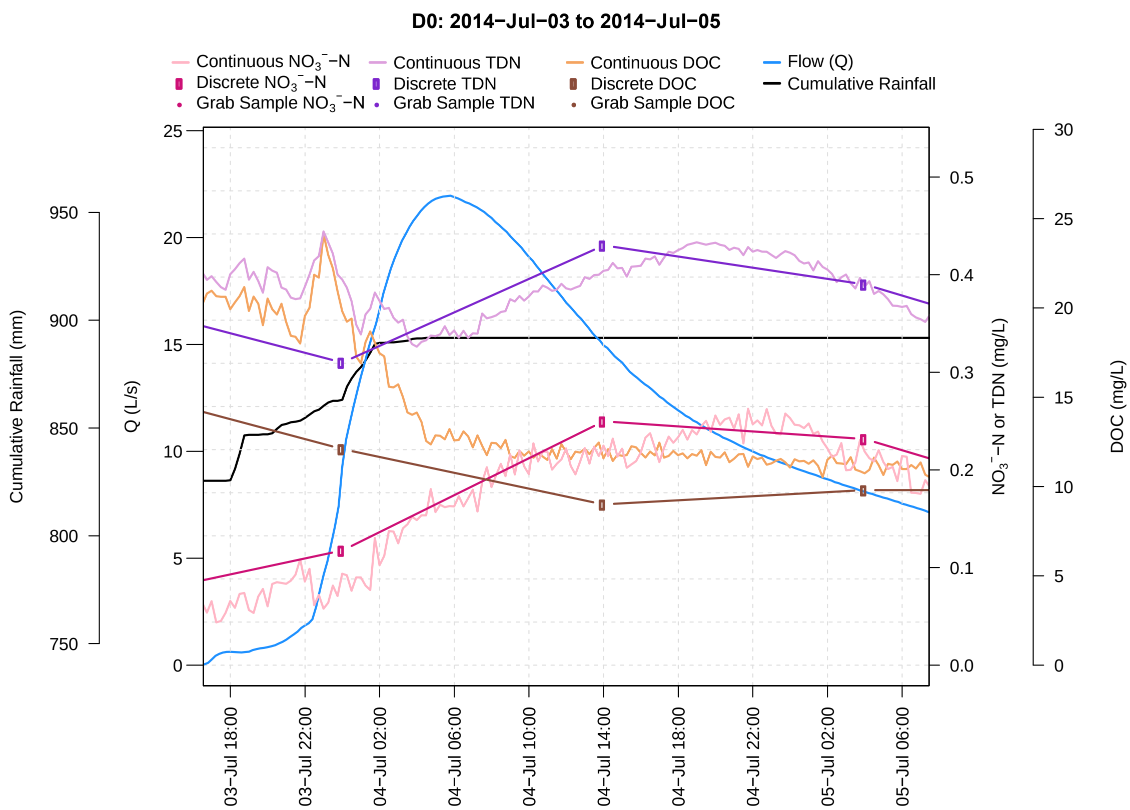

Figure C.13. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 July 03 to 05).

C.3 Prolonged wet conditions and elevated water table

Between July 24 and August 8 2014, there were several substantial flow events, which caused the water table elevation to remain relatively high for an extended period of time (Figure C.14). Because of this extended period of high water table conditions, trends in DOC concentration behaved differently than under typical conditions, i.e., increasing rather than decreasing during an event (Figure C.18, Figure C.20). There was a large event that began July 24 12:00 (Figure C.15, Figure C.16). There were no discrete measurements taken, but the continuous data showed an increase in both NO_3^--N and TDN, consistent with the trends of other events and proportional to the size of this large event. At the start of the event on July 24, the DOC dipped briefly from ~10 to ~6 mg L^{-1} (Figure C.16), but returned to ~8 mg L^{-1} and steadily increased until another large event occurred Aug 01 10:00, at which point the DOC concentration rapidly increased with the onset of another large event (Figure C.18). As the DOC concentration steadily increases between 24 July and 01 Aug, there are sharp and brief dips in DOC along the way, e.g., the event that began around 16:00 July 28 (Figure C.17). For the NO_3^--N and TDN during the July 28 event, there are subtle dips at the start, followed by corresponding increases to a max of 0.57 and 0.72 mg L^{-1} for NO_3-N and TDN, respectively, following the flow peak.

With the first of the two back-to-back large events, beginning at 10:00 August 01 2014 (Figure C.18, Figure C.19, Figure C.20), the DOC dramatically increases (both discrete and continuous data) to around 20 mg L^{-1}, remaining there until Aug 05 (~4 days later) when the DOC began to decrease and eventually returned to a stable concentration around 12 mg L^{-1}

after August 06. Both the NO_3^--N and TDN increase with the August 01 event (both peaking at 22:45 Aug 01) at 0.74 and 1.08 mg L^{-1}, respectively, and then decrease to 0.42 (14:15 Aug 02) and 0.83 mg L^{-1} (12:15 Aug 02), respectively, when more rainfall occurs. There is another increase in TDN and NO_3^--N with the second large event (23:00 Aug 02), although not as great as the first peak. There is another event on Aug 07 12:00 for which there is no detectable DOC response, but slight increases in NO_3-N and TDN, peaking at 0.22 (08/08/2014 4:45) and 0.40 mg L^{-1} (08/08/2014 1:00), respectively.

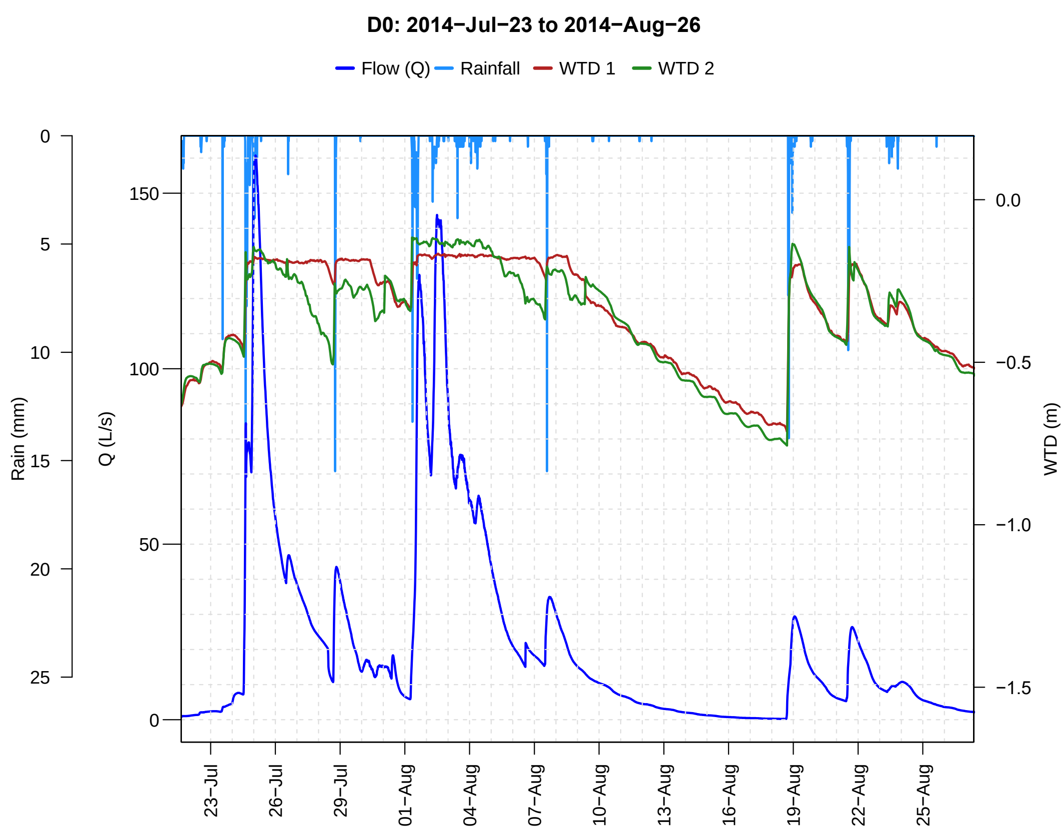

Figure C.14. Hydrology including flow (L s^{-1}), rainfall (mm), and water table depth (m) in two locations (WTD 1 and 2) in watershed D0 during July 23 to August 26.

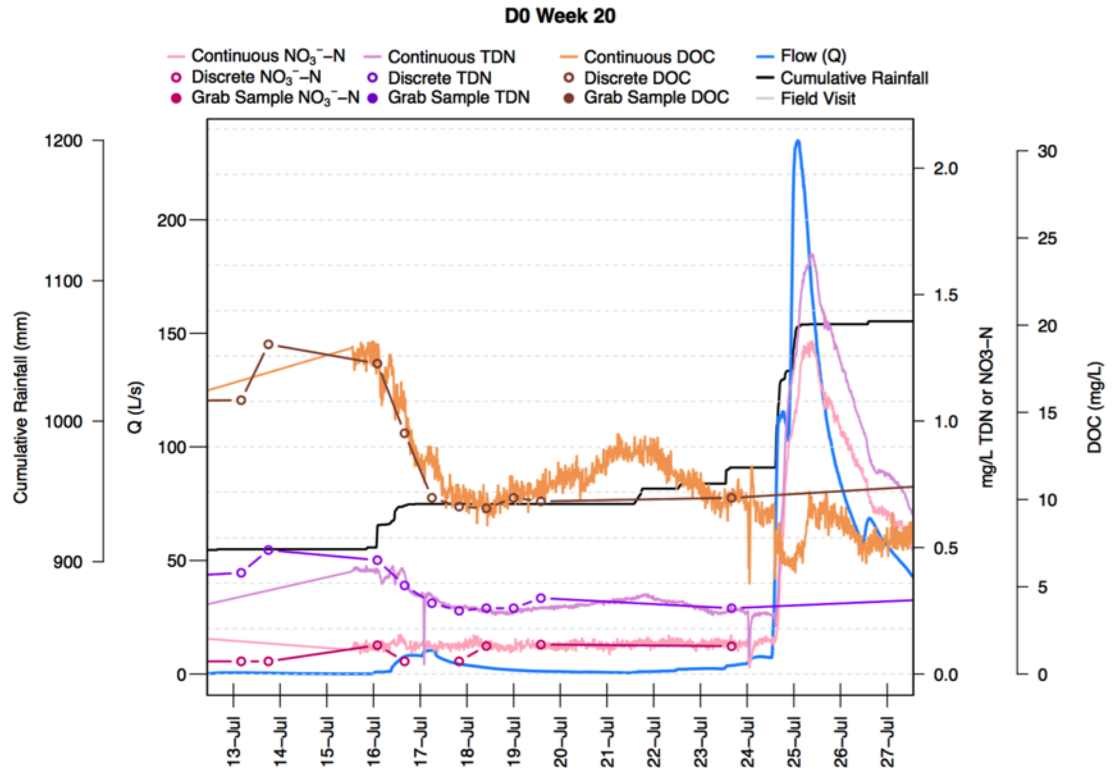

Figure C.15. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 July 13 to 27).

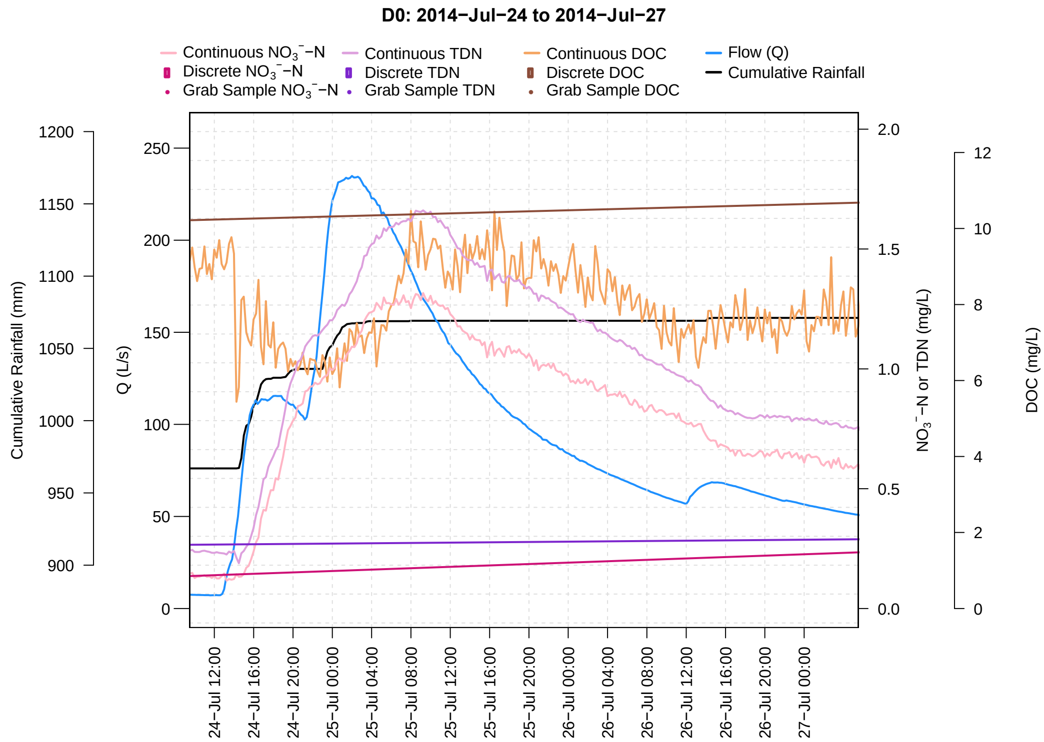

Figure C.16. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 July 24 to 27).

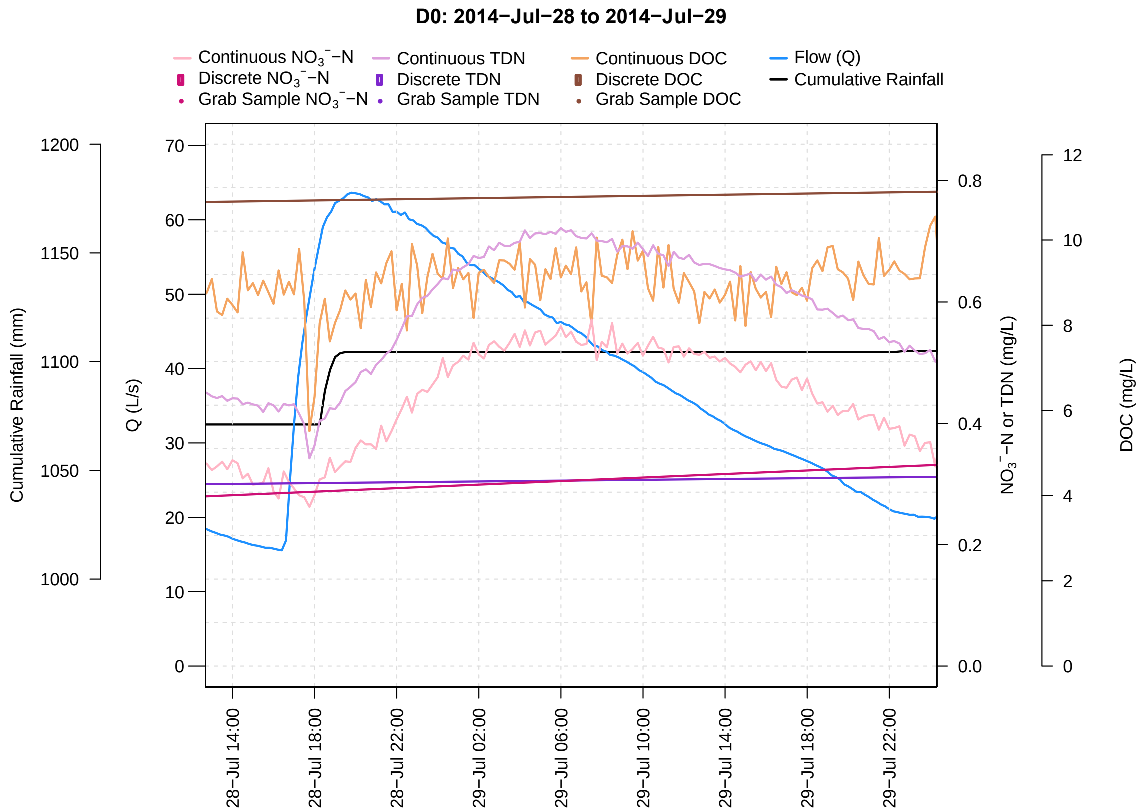

Figure C.17. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 July 28 to 29).

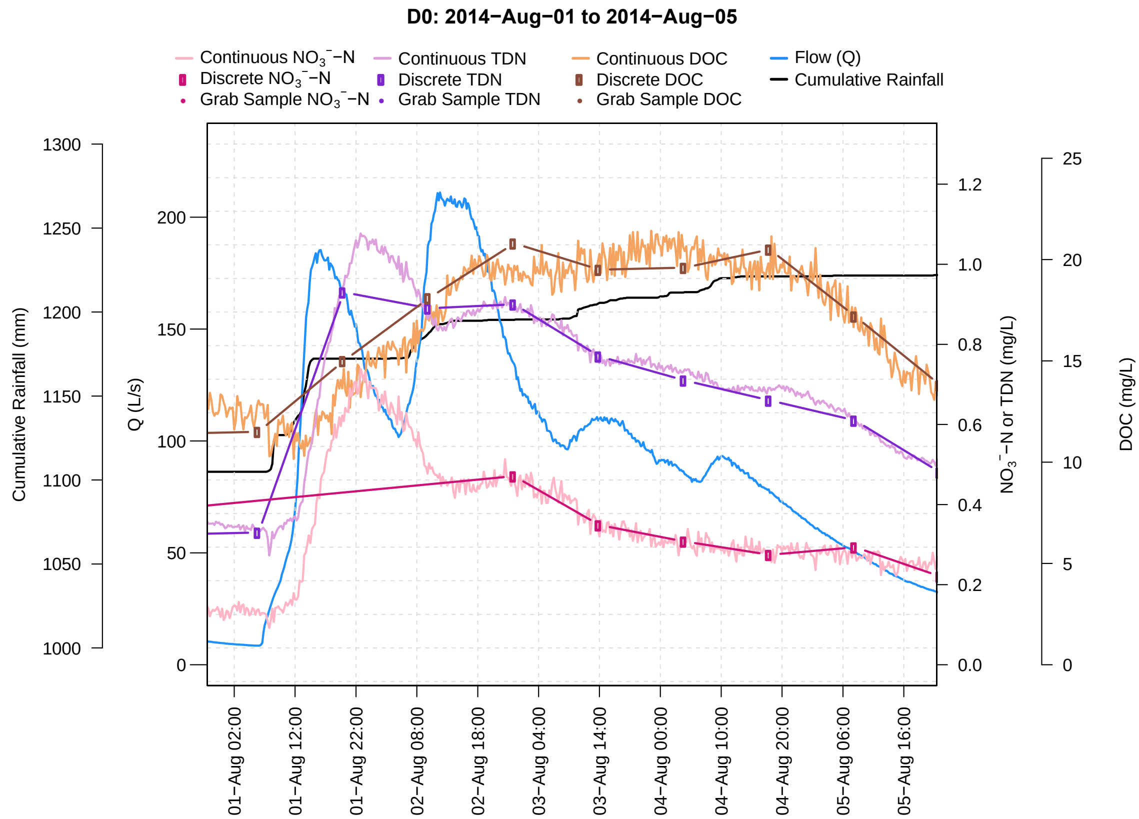

Figure C.18. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 August 01 to 05).

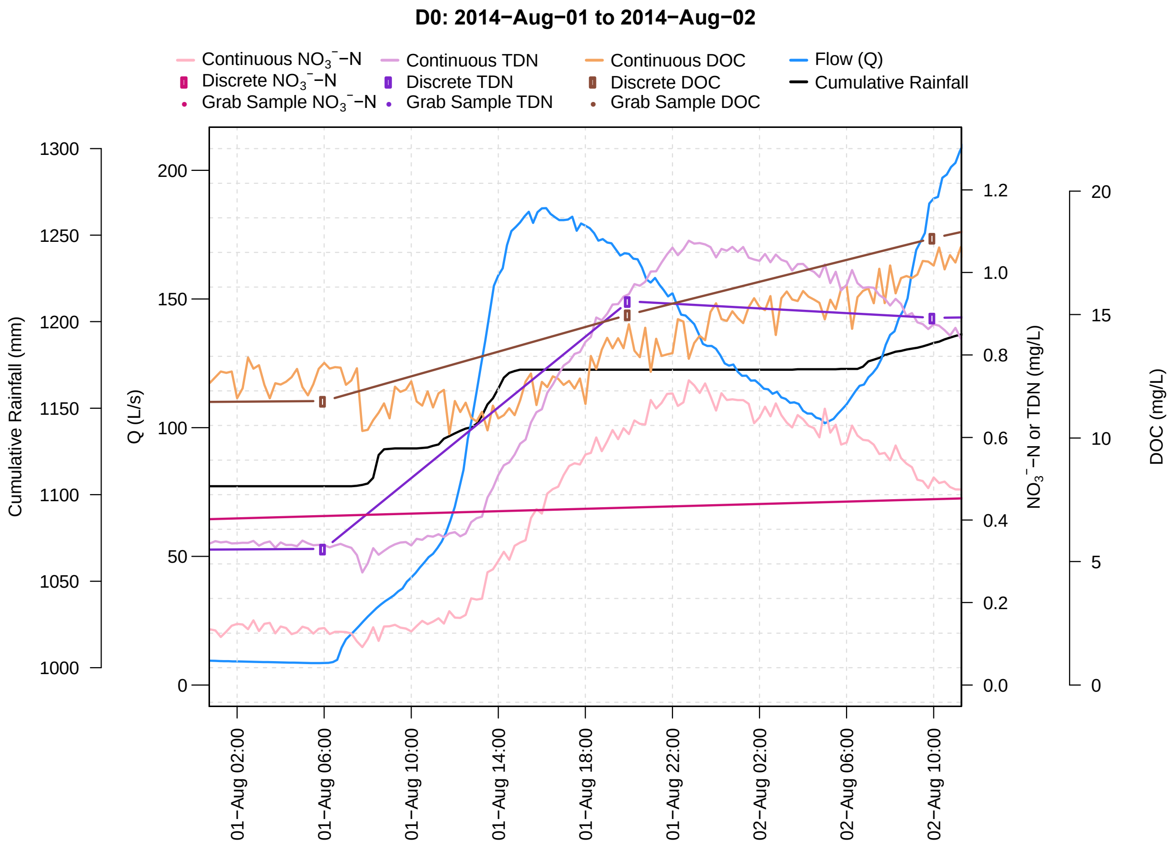

Figure C.19. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 August 01 to 02).

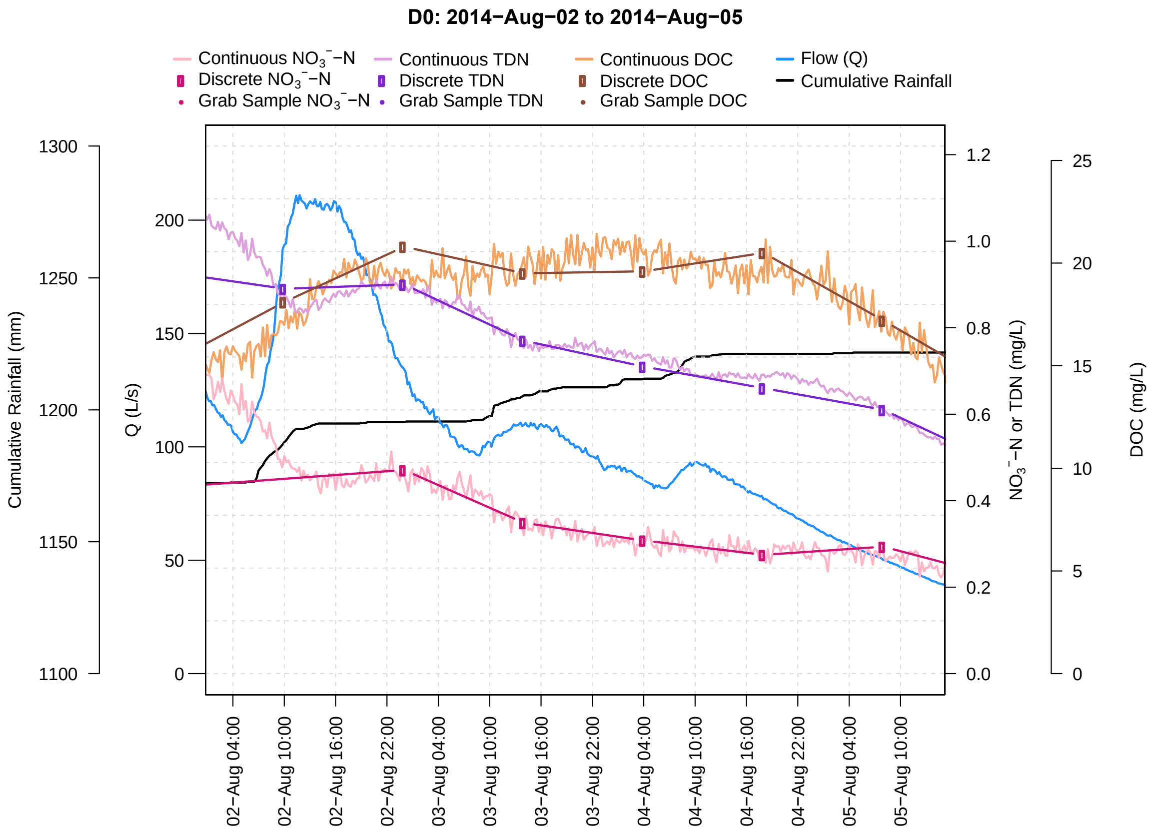

Figure C.20. Continuous, discrete, and grab sample concentrations (mg L^{-1}) of dissolved organic carbon (DOC), nitrate (NO_3^--N), and total dissolved nitrogen (TDN), continuous flow (L s^{-1}), and cumulative rainfall (mm) for D0 watershed (2014 August 02 to 05).

APPENDIX D: Filling in Flow Data Gaps in Greene County, Alabama

D.1 Filling in data gaps: ISCO-HOBO relationships

There were missing stage data for all watersheds from 2014-05-01 00:02 until 2014-05-17 23:58 and additional missing data for watershed GR3 from 2014-03-14 12:56 until 2014-04-10 12:48. The following techniques were used to fill in this missing data with the surrogate data.

GR1

For filling in large gaps of missing ISCO stage data for GR1 watershed, relationships between HOBO and ISCO stage data of nearby events were obtained. Only low flow and small events occurred during these data gaps. To fill in the small gaps, a linear regression between ISCO and HOBO stage of nearby small events was used. Overall, HOBO stage trends (i.e., peaks) occur 14 minutes earlier than ISCO, so that this time difference was included when calculating the missing ISCO data. For filling in data during low flow conditions, the difference in medians of nearby low flow was used. For filling in missing low flow data between 4/3/2014 8:38 and 4/6/2014 2:10, the difference in ISCO and HOBO medians from nearby low stage occurring between 3/30/2014 12:44 and 4/2/2014 9:00 (ISCO median = 0.064 m and HOBO median = 0.263 m; difference = 0.199 m) was subtracted from the HOBO stage occurring 14 minutes earlier. To replace the small event occurring between 4/4/2014 5:36 and 4/4/2014 15:14, a linear relationship was obtained from a similar sized event occurring between 4/6/2014 20:00 and 4/7/2014 0:26 (see Table D.1 for equation).

For the second gap, different small event and median relationships were obtained. For the missing low flow between 4/19/2014 3:18 and 5/20/2014 10:18 the median difference of 0.125 m obtained from nearby low stage data occurring between 5/26/2014 23:08 and 5/28/2014 3:00 was subtracted from HOBO stage occurring 14 minutes earlier (ISCO median = 0.010 m and HOBO median = 0.135 m). To replace the small events occurring between 4/27/2014 9:58 and 4/27/2014 15:44, 4/28/2014 20:26 and 4/29/2014 3:14, 4/29/2014 18:16 and 4/30/2014 15:14, 5/14/2014 16:28 and 5/14/2014 19:14, a linear relationship (rising and falling limb combined) was applied using a similar sized event from 4/14/2014 18:32 to 4/15/2014 3:00.

GR3

For filling in large gaps of missing ISCO stage data, HOBO data was used to predict ISCO stage based on relationships for the following scenarios: base flow, the rising and falling limbs of small events, and the rising and falling limbs and top of large events (>50 cm peak). Base flow was considered anything <10 cm; for these data, the difference in medians (2 cm) was subtracted from the HOBO value. The following equations were used for the rising and falling limbs, as well as the top of large events (Table D.1).

GR2, GR4, GRREF

For these watersheds, the missing data occurred during low flow conditions so that the HOBO stage could be directly inserted into to the ISCO stage data, drift corrected to align with the ISCO stage, and resampled at a 2-minute rate using AQUARIUS software.

Table D.1. Relationships for filling in missing ISCO stage data with HOBO stage data during various hydrological scenarios.

WS	**Hydrological scenario**	**Comparison data dates**	**Equation for calculating missing ISCO stage**
GR1	Small event	4/6/2014 to 4/7/2014	$y = 0.4349x - 0.0416$
	Small event	4/14/2014 to 4/15/2014	$y = 0.4728x - 0.0081$
	Low flow	4/3/2014 to 4/6/2014	$y = x - 0.199$
	Low flow	4/19/2014 to 5/20/2014	$y = x - 0.125$
GR3	Rising limb, small event		$y = 0.5553x + 0.018$
	Falling limb, small event		$y = 0.4896x + 0.0274$
	Rising limb, large event		$y = 0.7762x^2 - 0.1406x + 0.1573$
	Top portion of large event		$y = 1.2267x + 0.4232$
	Falling limb, large event		$y = 02.5919x^3 - 2.7674x^2 + 1.2333x - 0.0124$

APPENDIX E: Hydrology Plots for Greene County, Alabama

E.1 Cumulative Flow: Treatment versus Control (GR1)

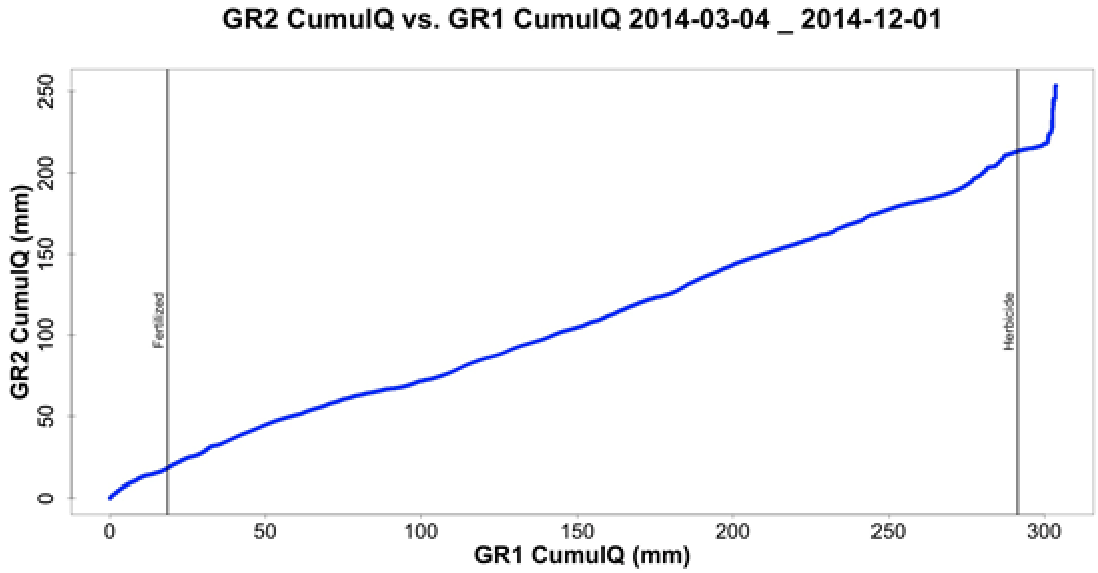

Figure E.1. Cumulative flow relationship of GR2 as a function of GR1 during year 5 (2014-03-04 to 2014-12-01). Vertical lines represent operations (fertilizer and herbicide application).

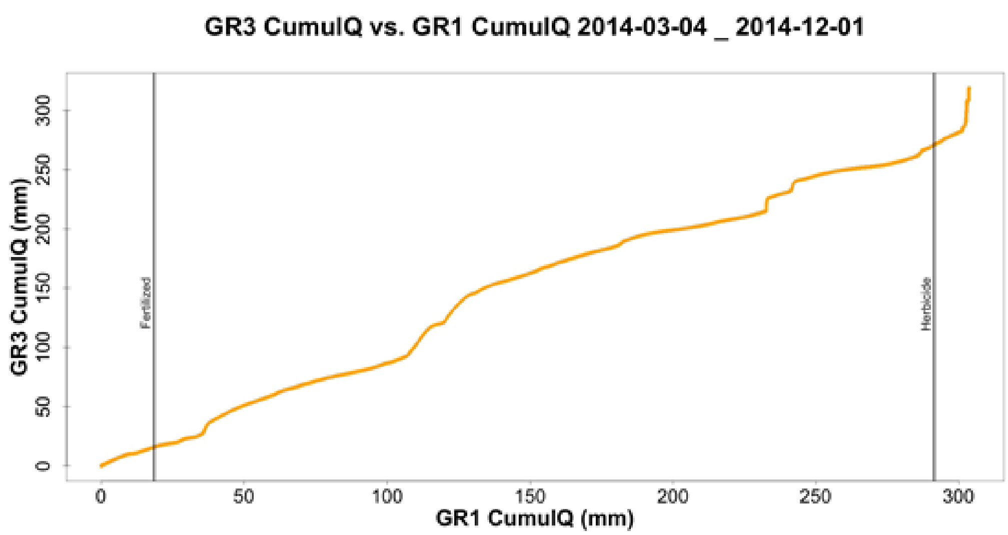

Figure E.2. Cumulative flow relationship of GR3 as a function of GR1 during year 5 (2014-03-04 to 2014-12-01). Vertical lines represent operations (fertilizer and herbicide application).

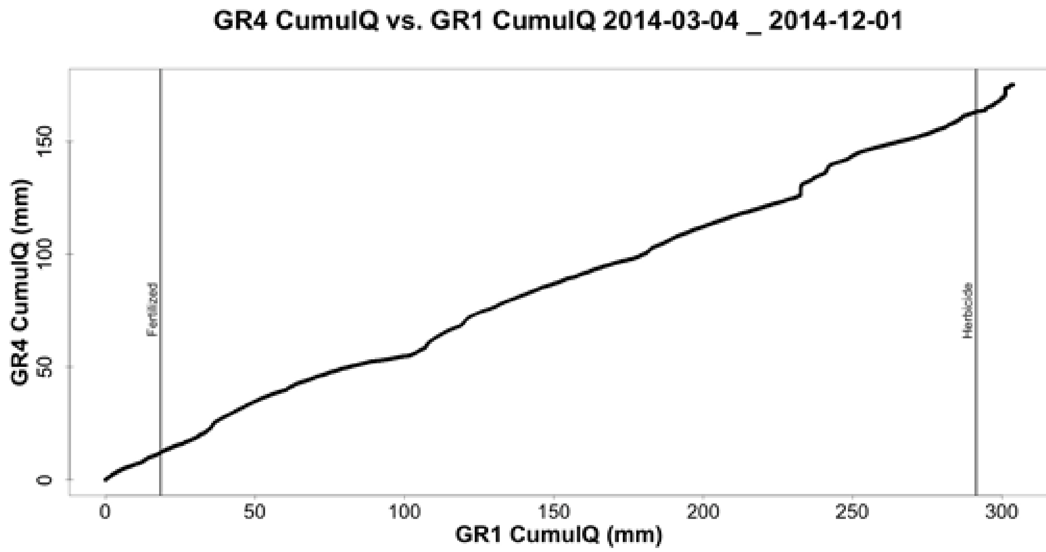

Figure E.3. Cumulative flow relationship of GR4 as a function of GR1 during year 5 (2014-03-04 to 2014-12-01). Vertical lines represent operations (fertilizer and herbicide application).

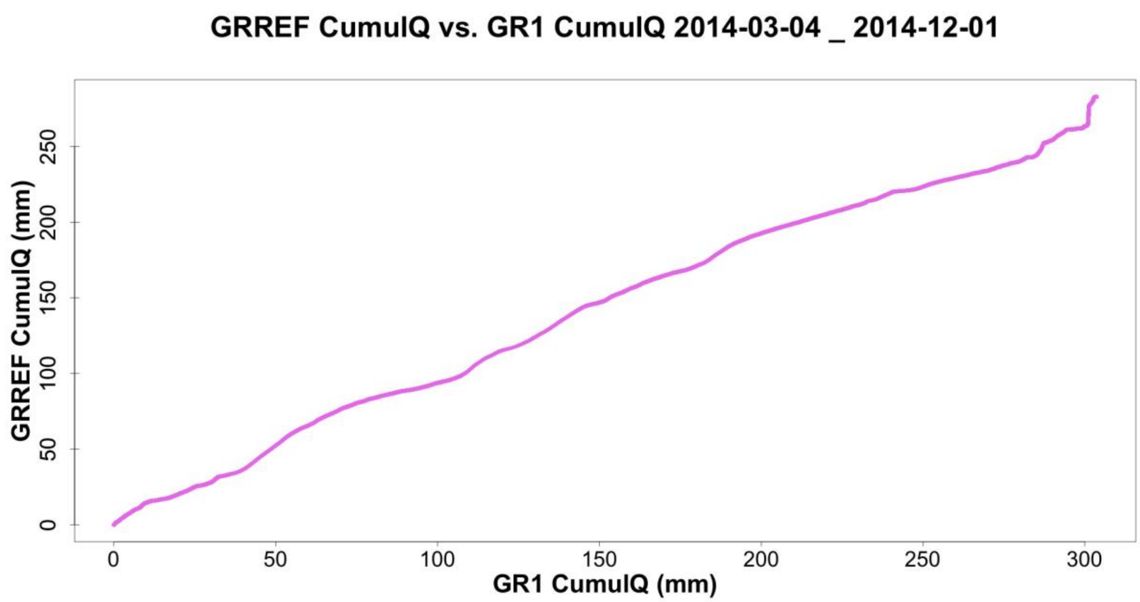

Figure E.4. Cumulative flow relationship of GRREF as a function of GR1 during year 5 (2014-03-04 to 2014-12-01). Vertical lines represent operations (fertilizer and herbicide application).

APPENDIX F: Water Balance in Greene County, Alabama

F.1 Water Balance

The water balance for each watershed was evaluated cumulatively on a yearly basis. Reference ET (ET_0) was calculated as follows (Equation A.1); however, this was only used as a rough comparison given that ET_0 is location specific and will be equal for the same location and only differ based on crop height input. PET is species specific, but we do not know crop coefficients for either loblolly pine or switchgrass.

$$P = Q + \Delta S + ET_0 \qquad \text{(F.1)}$$

where P is precipitation, Q is the outflow from the watershed, ET_0 is reference evapotranspiration, and ΔS is the change in storage in the soil or bedrock that may also represent bypass flow or error in ET_0 estimation (all quantities in mm).

Weather data

A single weather station located at the site in Greene County, Alabama supplied 15-minute weather data including precipitation (mm), atmospheric pressure (mbar), outgoing solar radiation (OSolarRad, W m^{-2}), incoming solar radiation (ISolarRad, W m^{-2}), wind speed (m s^{-1}), gust speed (m s^{-1}), temperature (°C), and relative humidity (%). Weather data was missing from 9/19/13 12:45 to 10/10/13 13:15 and was filled in using hourly data (resampled to 15 minutes) from a nearby weather station in Starkville, Mississippi. The missing atmospheric pressure data for September was filled in with a constant value from the last available atmospheric pressure value in September and the missing October data was filled in with a constant value from the first available October data.

ET calculations

The Penman-Monteith combination equation (Allen et al., 1989) was used to estimate reference ET (ET_0) (mm d^{-1}): (taken out of book, p 144: Evapotranspiration and Irrigation Water Requirements. 1990. ASCE, Edited by Jensen, M.E., R.D. Burman, and R.G. Allen).

$$ET_0 = \frac{\Delta}{\Delta+\gamma^*}(R_n - G) + \frac{\gamma}{\Delta+\gamma^*} K_1 \frac{0.622 / r_a}{P} \frac{1}{r_a}(e_s - e_a) \qquad \text{(F.2)}$$

Where, Δ is the slope of the saturation vapor pressure curve (kPa °C^{-1}); R_n is the net radiation flux density to the plant canopy (MJ m^{-2} d^{-1}); G is soil head flux density (MJ m^{-2} d^{-1}) which was taken to equal 0; K_1 is a unit conversion of 86,400 s d^{-1} for ET_0 in mm d^{-1}; ρ_a is the density of air (kg m^{-3}), equal to 1.23 kg m^{-3}; P is atmospheric pressure (kPa); e_s is the saturation vapor pressure of air (kPa); e_a is the actual vapor pressure of air (kPa); r_a is the bulk aerodynamic resistance for water vapor (s m^{-1}); γ is the psychrometric constant (kPa °C^{-1}). Aerodynamic resistance (r_a, s m^{-1}) was calculated as follows:

Aerodynamic resistance (r_a, s m^{-1}) was calculated as follows:

$$r_a = \frac{\ln\left[\frac{z_m - d}{z_{om}}\right]\ln\left[\frac{z_h - d}{z_{oh}}\right]}{k^2 u_z} \quad \text{(F.3)}$$

The von Karman's constant (k) is equal to 0.41. Because the wind speed was measured at a height other than 2 m (i.e., 3.35 m), the wind speed at height z (u_z) (m s^{-1}) must be correlated to a wind speed measured at 2 m (u_2) as follows:

$$u_2 = u_z \frac{4.87}{\ln(67.8h - 5.42)} \quad \text{(F.4)}$$

where h is the height of the wind measurement (3.35 m at the Greene County, AL site), and u_z is the measured average wind speed z m (i.e., 3.35 m) above the ground surface. After u_2 was found, a new u_z corresponding to 2 m above the canopy was calculated:

$$u_z = u_2 \frac{\ln(67.8z_m - 5.42)}{4.87} \quad \text{(F.5)}$$

z_m and z_h are the heights (m) of the wind and humidity measurements, respectively, corresponding to wind measurements 2 m above the canopy (i.e., crop height), and calculated as:

$$z_m = z_h = h_c + 2 \quad \text{(F.6)}$$

where h_c is crop height. The zero plane displacement height (d) (m) is calculated as:

$$d = \frac{2}{3} h_c \tag{F.7}$$

For crop height less than 2 m, the roughness length for momentum transfer (z_{om}) is:

$$z_{om} = 0.123 h_c \tag{F.8}$$

and for crop height greater than 2 m, z_{om} was calculated as:

$$z_{om} = 0.058 h_c^{1.19} \tag{F.9}$$

The roughness length governing transfer of heat and vapour was calculated as:

$$z_{oh} = 0.1 z_{om} \tag{F.10}$$

As shown in the table below, tree heights were estimated by adding 1.4 m to each successive year for GR1, GR2, and GR3. The tree height of the mature reference stand was kept at a constant 15.5 m, and the height of the switchgrass was estimated as 1 m for each year.

Table F.1. Crop heights (h_c, tree and switchgrass, m) for years 4 and 5.

	Year 4		Year 5		Years 4/5	Years 4/5
	GR1 & GR2 (pine)	GR3 (pine)	GR1 & GR2 (pine)	GR3 (pine)	GR4 (switchgrass)	GRREF (pine)
h_c (m)	8.4	1	9.8	2.4	1	15.5

$$\gamma^* = \gamma\left(1 + \frac{r_s}{r_a}\right) \quad \text{(F.11)}$$

where r_s is the bulk canopy surface resistance for a standard 12 cm grass reference, taken as 70 s m^{-1}.

The psychrometric constant (γ) (kPa °C^{-1}) was calculated as follows:

$$\gamma = \frac{C_p P}{0.622\lambda} = 0.0016286\frac{P}{\lambda} \quad \text{(F.12)}$$

where C_p is the specific heat of air (MJ kg^{-1} °C^{-1}), equal to 1.013e-3 MJ kg^{-1} °C^{-1}, 0.622 is the ratio of water vapor to air molecular weights, and the latent heat of vaporization (λ, MJ kg^{-1}) of water was calculated as:

$$\lambda = 2.501 - 0.002361T \text{ (Harrison, 1963)} \quad \text{(F.13)}$$

Vapor pressure deficit ($e_s - e_a$) (kPa) was calculated as follows:

$$e_s - e_a = 0.6108\left(\exp\left(\frac{17.27T}{T+273}\right)\right)\left(1-\frac{RH}{100}\right) \quad \text{(F.14)}$$

where T is average temperature (°C) and RH is relative humidity (%).

Slope of the saturation vapor pressure curve (Δ) (kPa °C^{-1}) was calculated as follows:

$$\Delta = \frac{4098\left[0.6108\exp\left(\frac{17.27T}{T+273}\right)\right]}{(T+273)^2} \quad \text{(F.15)}$$

ET_0 was calculated for each year, with varying crop heights by year and by treatment. To account for ET_0 on the intercropped sites (i.e., GR2 and GR3), the sum was taken of 50 percent of the value for the pine ET_0 at the particular site and 50 percent of the value of ET_0 for switchgrass as follows:

$$ET_{0,GR2} = 0.5(ET_{0,GR2-pine} + ET_{0,switchgrass}) \quad \text{(F.16)}$$

$$ET_{0,GR3} = 0.5(ET_{0,GR3-pine} + ET_{0,switchgrass}) \quad \text{(F.17)}$$

Stomatal conductance for pine was calculated using the following equation from Kirkham (2011):

$$g^m = 0.04g \tag{F.18}$$

where g^m is molar conductance (mol m^{-2} s^{-1}) and g is stomatal conductance (mm s^{-1}). Molar conductance for pine is 110 mmol m^{-2} s^{-1}. For switchgrass, a stomatal resistance of 70 s m^{-1} or stomatal conductance (reciprocal) of 0.014 m s^{-1} was used.

Net radiation (R_n, MJ m^{-2} d^{-1}) was calculated and converted to W m^{-2} as follows:

$$R_n = \frac{ISolarRad - OSolarRad}{11.574} \tag{F.19}$$

where ISolarRad (W m^{-2}) is incoming solar radiation and OSolarRad (W m^{-2}) is outgoing solar radiation.

For a more accurate representation of net radiation, a regression relationship between solar radiation and measured net radiation was obtained after removing outliers (Figure F.1, Figure F.2). That relationship was used to calculate net radiation (RN_{calc}) and a second regression between calculated and measured net radiation (RN_{meas}). Outliers were also removed from this relationship and the regression equation was used to obtain a better estimate of net radiation.

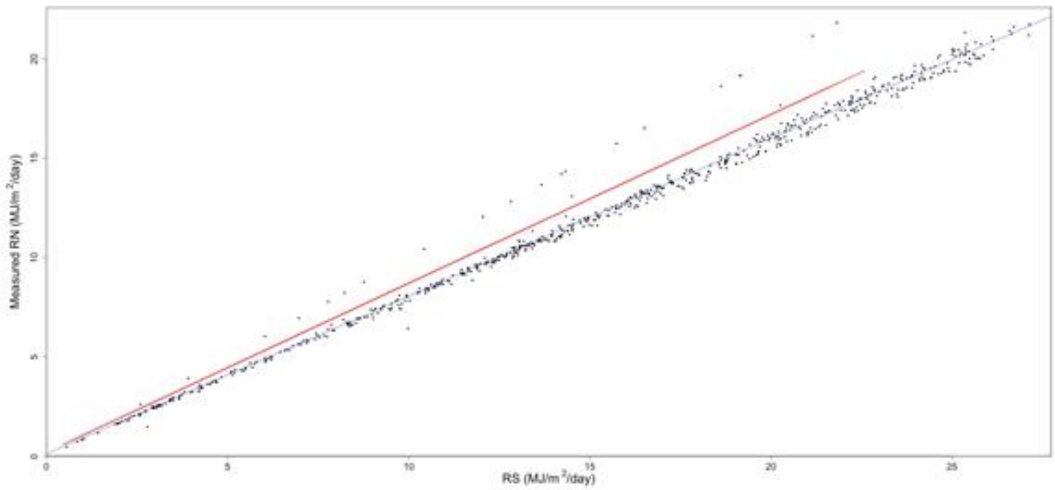

Figure F.1. Regression between measured solar radiation (RS) and net radiation (RN) (outliers above red line were removed).

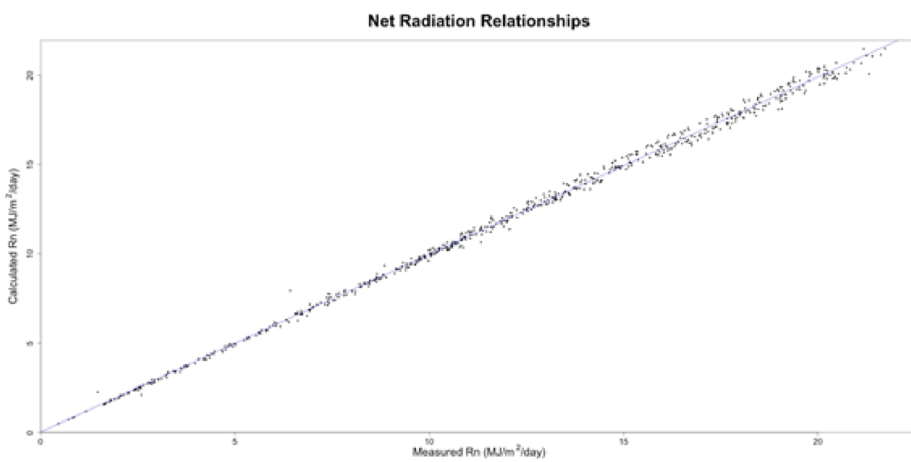

Figure F.2. Regression relationship between measured and calculated net radiation.

The regression equation between RN_{meas} and RN_{calc} used in the ET_0 calculation was:

$$RN_{calc} = 0.994RN_{meas} + 0.026 \qquad \text{(F.20)}$$

Higher residuals between calculated and measured net radiation occurred when missing weather data was filled in with supplemental data from Starkville weather station (9/19/13 12:45 to 10/10/13 13:15) (Figure F.3).

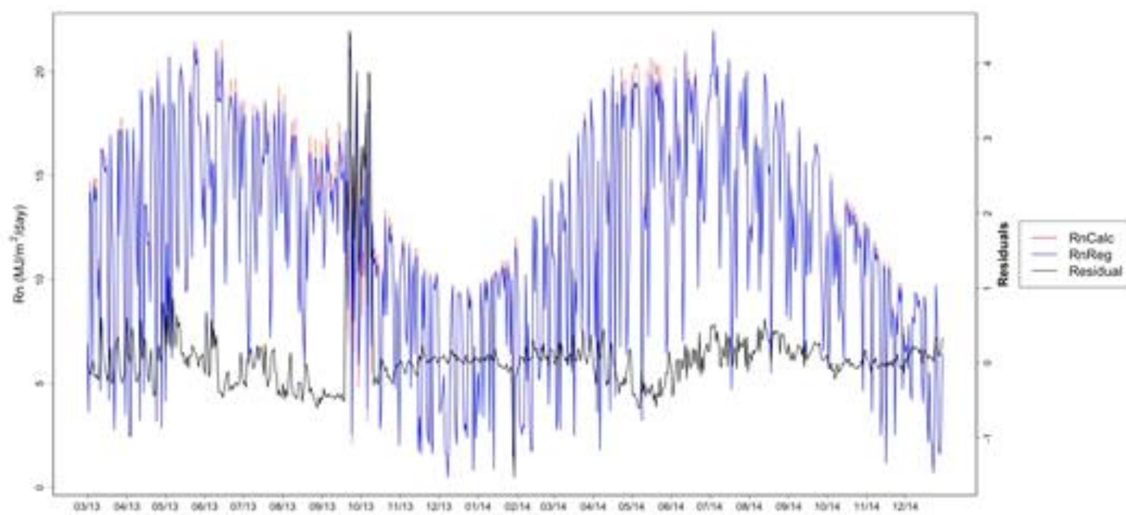

Figure F.3. Calculated (red) and measured (blue) net radiation and residual (black) between calculated and measured.

Table F.2. Cumulative evapotranspiration (ET_0) (mm) and flow (CQ) for each watershed in years 4 (2013) and 5 (2014) in Greene County, Alabama.

	Year 4		**Year 5**	
Cumulative Precipitation	1245		897	
	ET_0	**CQ**	**ET_0**	**CQ**
GR1	1152	494	1041	304
GR2	1115	425	1011	253
GR3	1078	510	986	319
GR4	1184	287	980	175
GRREF	1185	230	1086	283

APPENDIX G: Water Quality Plots for Greene County, Alabama

G.1 Total Suspended Solids (TSS)

Cumulative load over time with hydrograph (2011-2014)

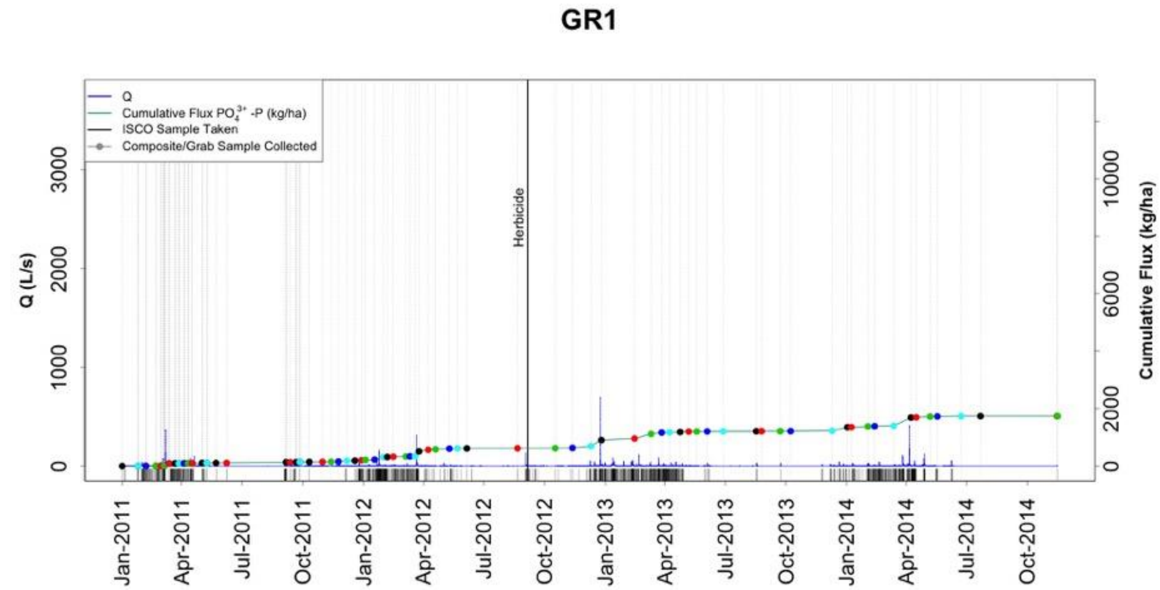

Figure G.1. Cumulative TSS flux over time (Jan 2011 to Nov 2014) in watershed GR1, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

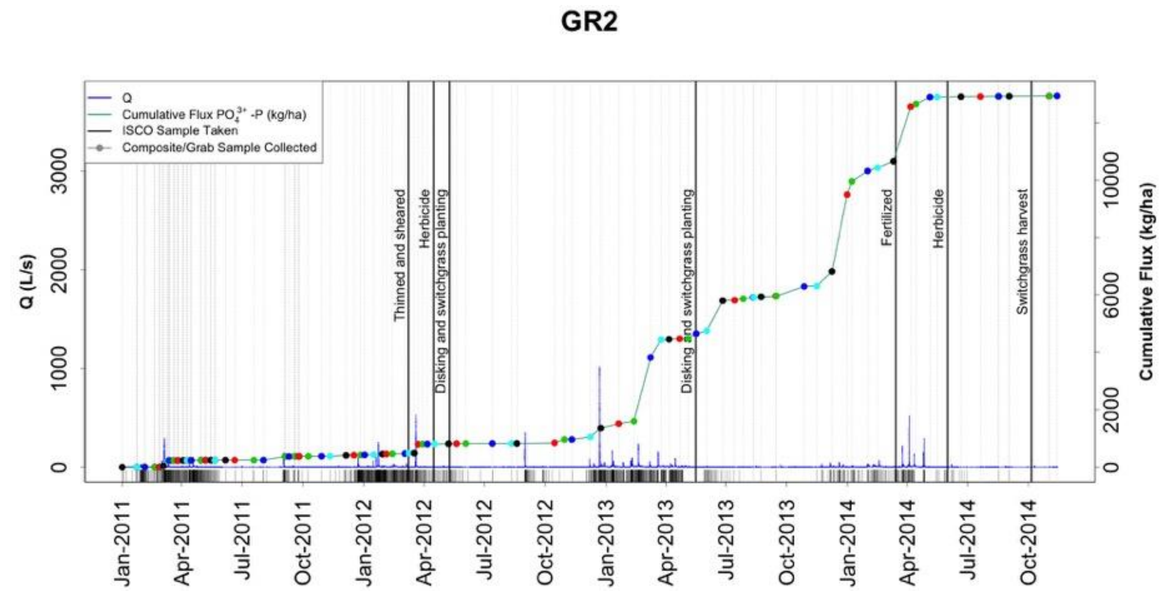

Figure G.2. Cumulative TSS flux over time (Jan 2011 to Nov 2014) in watershed GR2, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

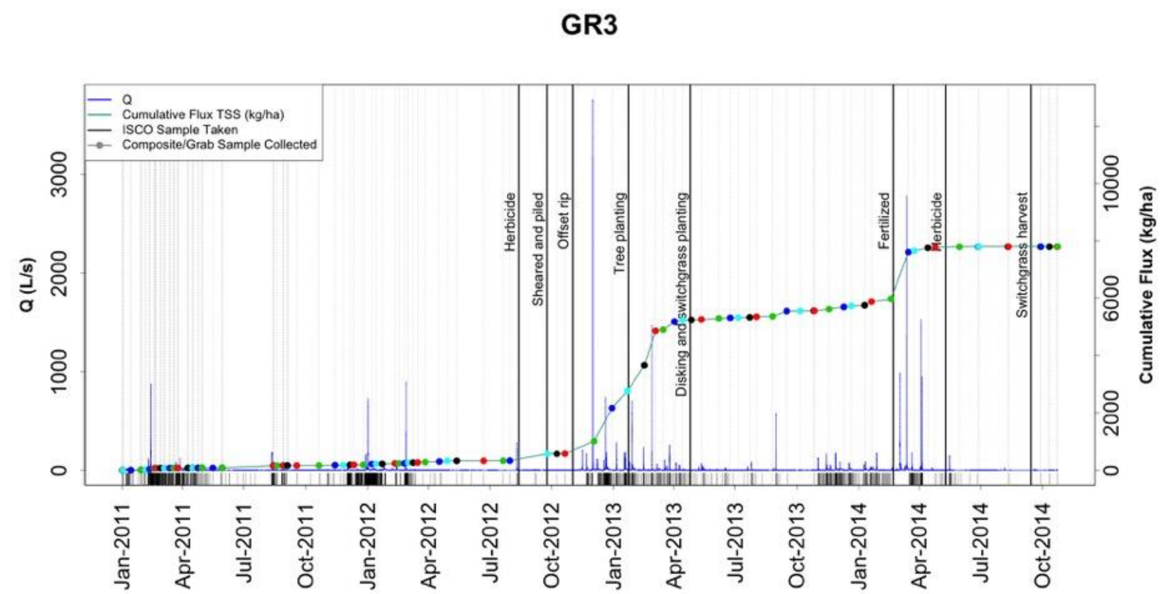

Figure G.3. Cumulative TSS flux over time (Jan 2011 to Nov 2014) in watershed GR3, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

GR4

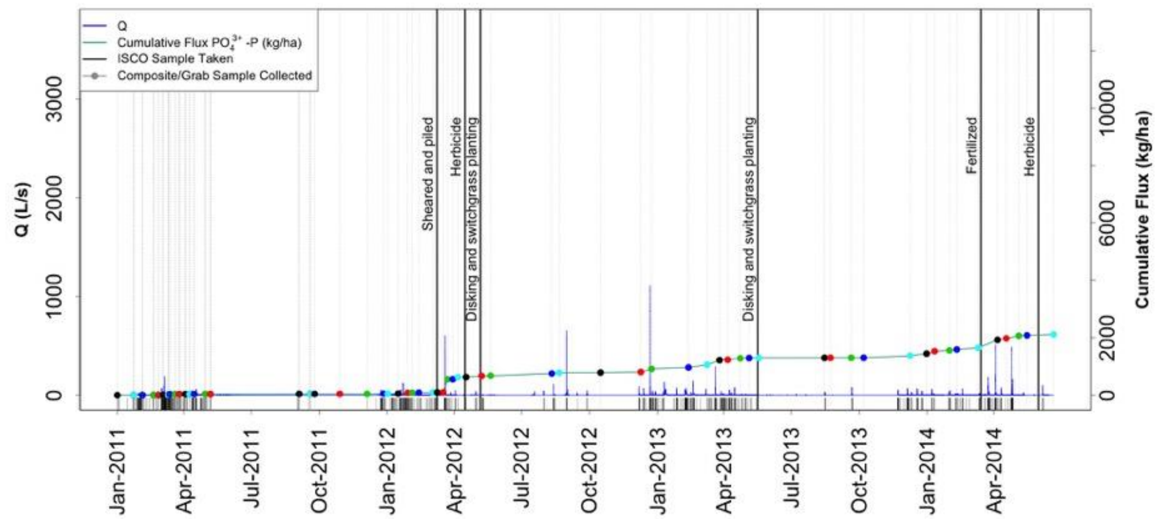

Figure G.4. Cumulative TSS flux over time (Jan 2011 to Nov 2014) in watershed GR4, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

GRREF

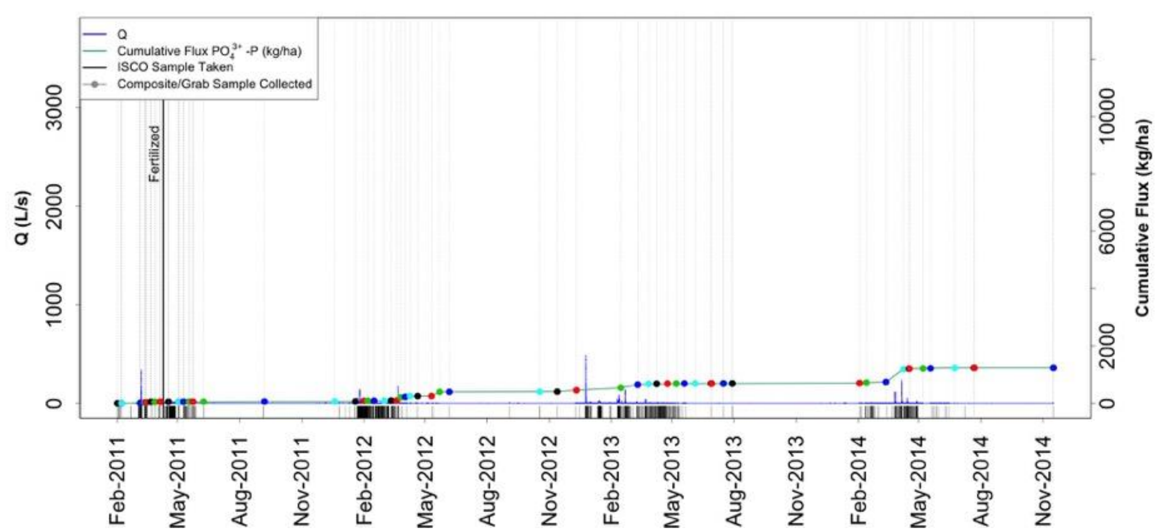

Figure G.5. Cumulative TSS flux over time (Jan 2011 to Nov 2014) in watershed GRREF, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

Cumulative load versus cumulative volume (2011-2014)

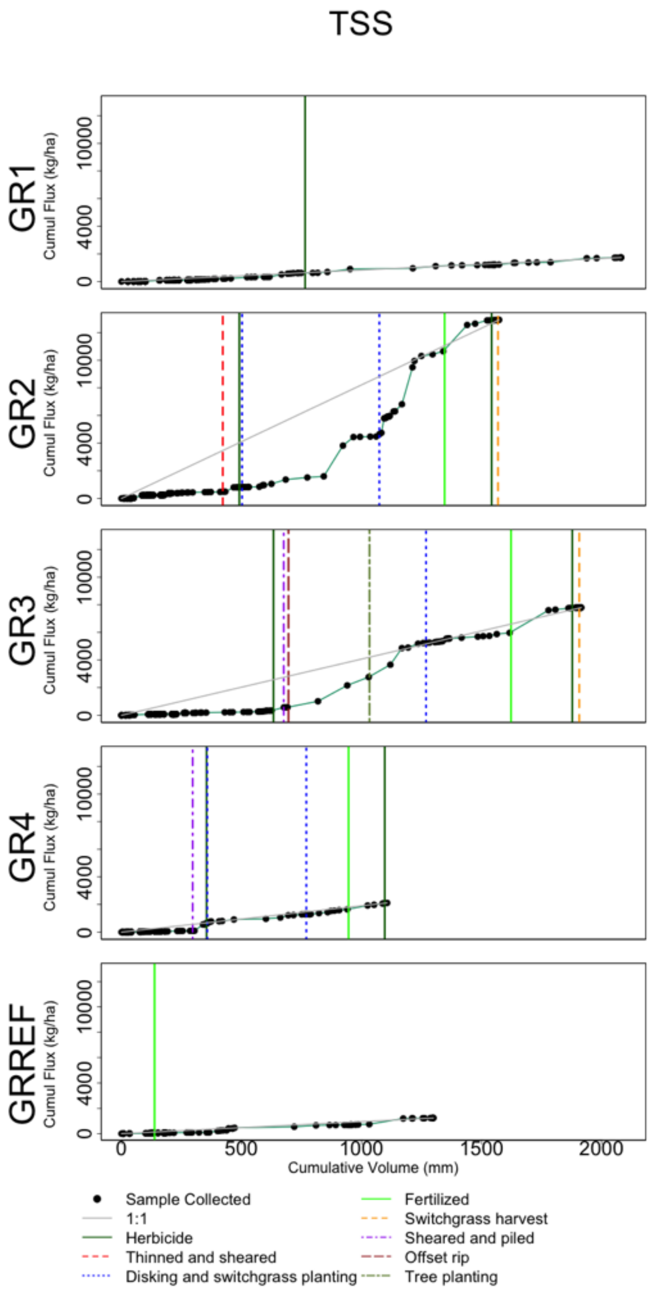

Figure G.6. Cumulative TSS flux (kg ha^{-1}) as a function of cumulative flow volume (mm) for all watersheds (GR1, GR2, GR3, GR4, GRREF) during Jan 2011 to Nov 2014.

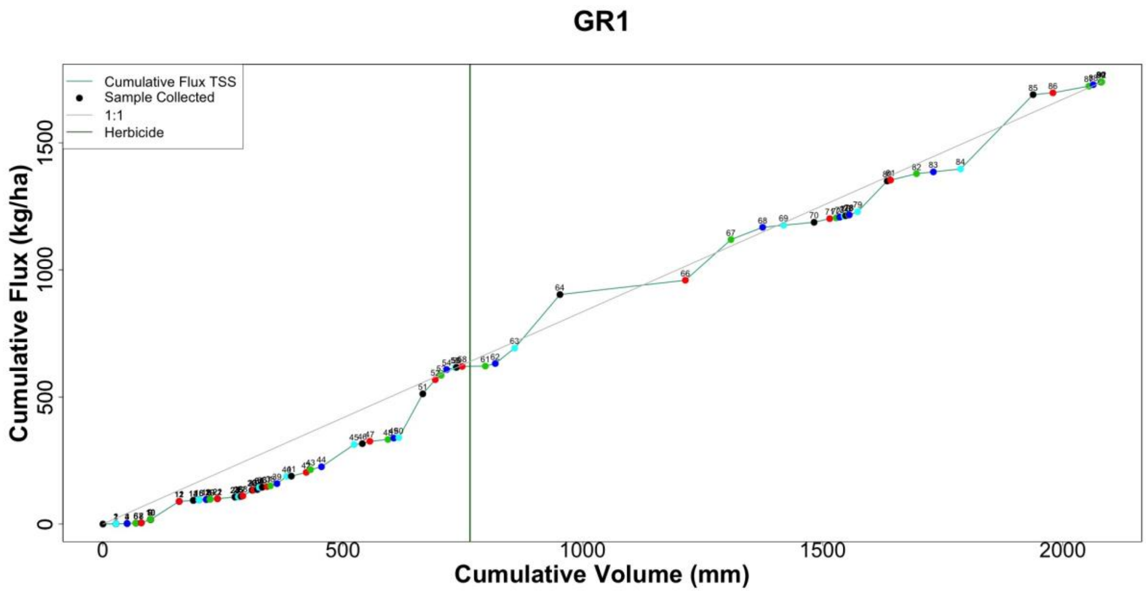

Figure G.7. Cumulative TSS flux (kg ha^{-1}) as a function of cumulative flow volume (mm) in watershed GR1 during Jan 2011 to Nov 2014.

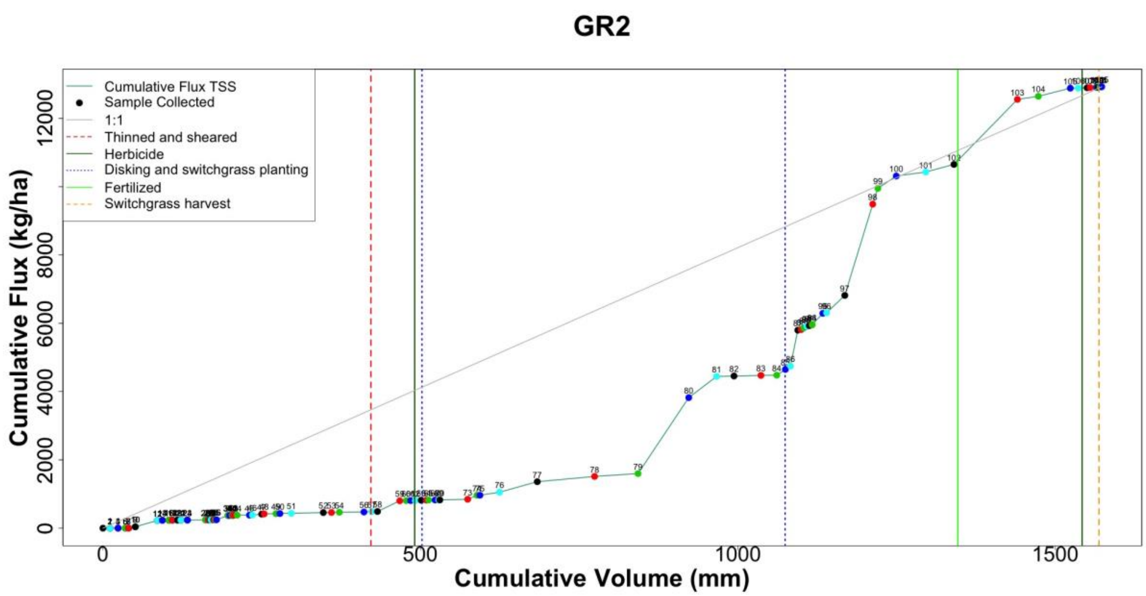

Figure G.8. Cumulative TSS flux (kg ha^{-1}) as a function of cumulative flow volume (mm) in watershed GR2 during Jan 2011 to Nov 2014.

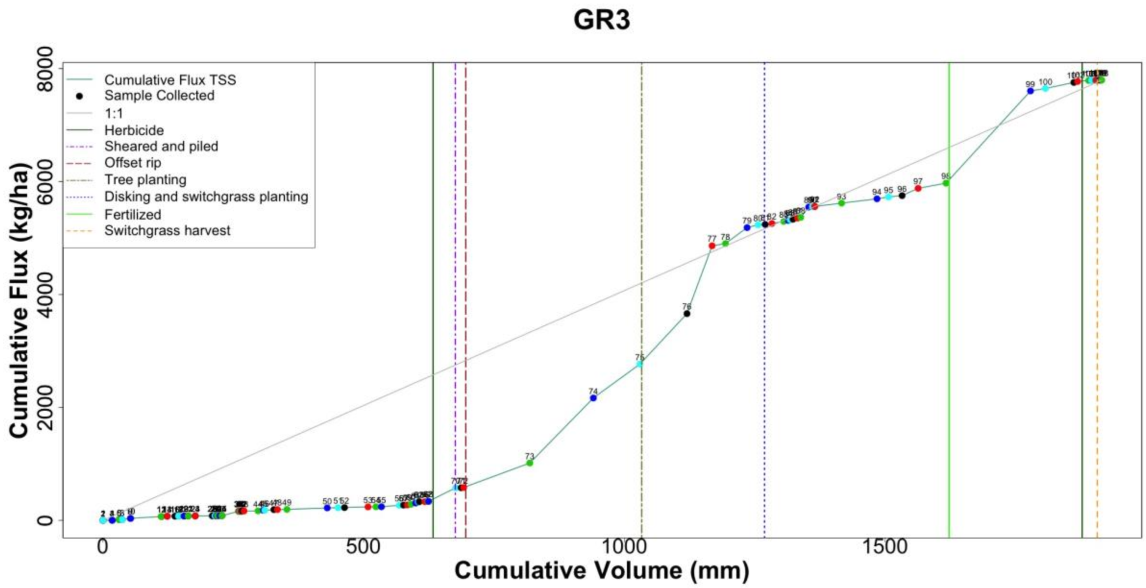

Figure G.9. Cumulative TSS flux (kg ha^{-1}) as a function of cumulative flow volume (mm) in watershed GR3 during Jan 2011 to Nov 2014.

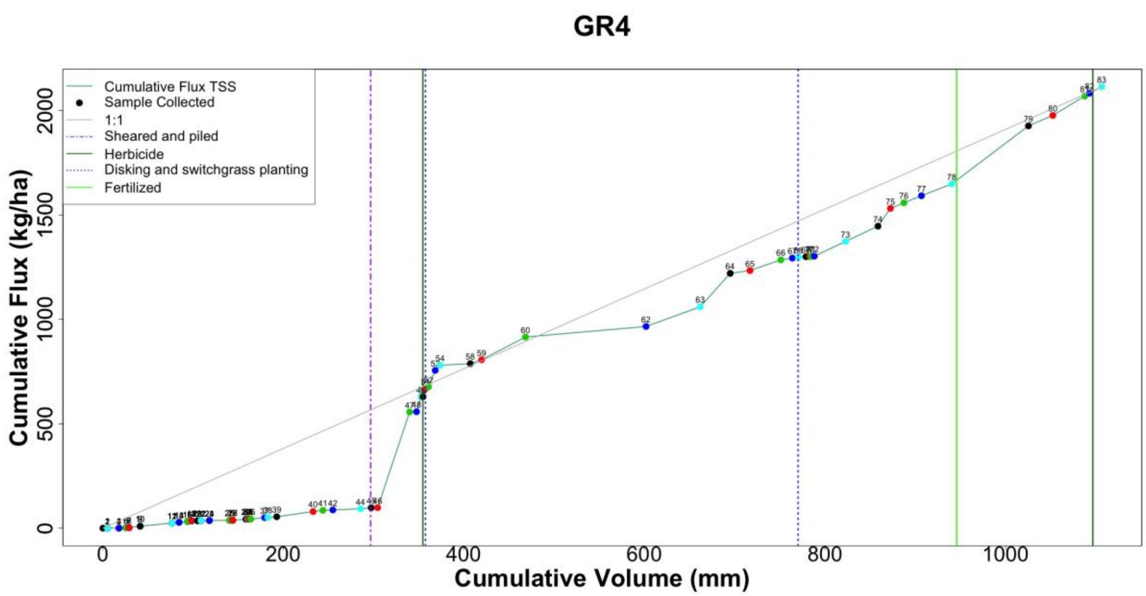

Figure G.10. Cumulative TSS flux (kg ha^{-1}) as a function of cumulative flow volume (mm) in watershed GR4 during Jan 2011 to Nov 2014.

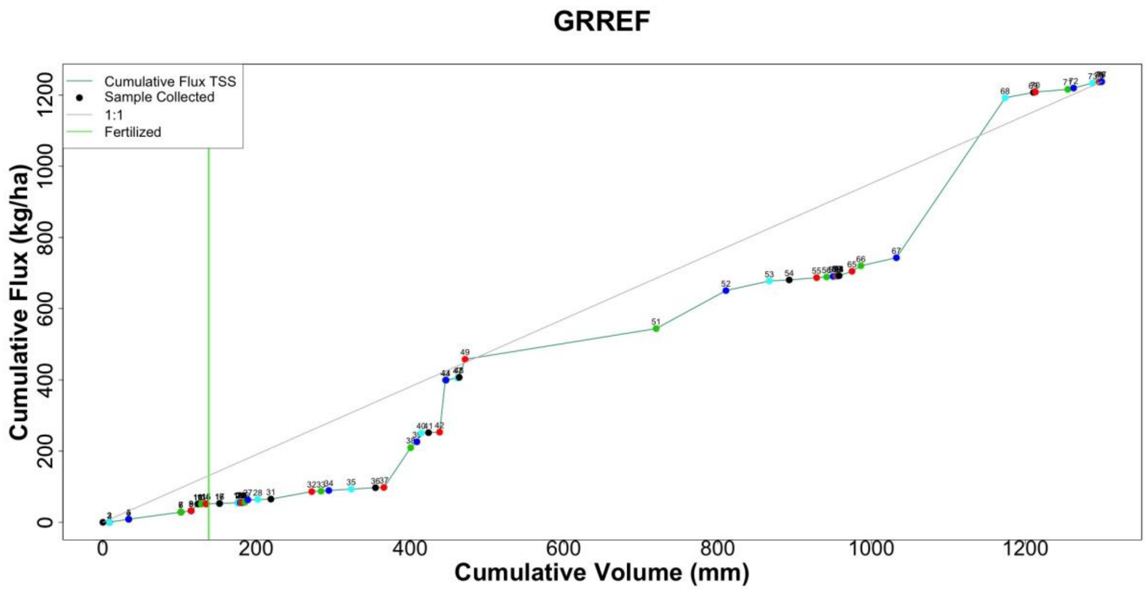

Figure G.11. Cumulative TSS flux (kg ha^{-1}) as a function of cumulative flow volume (mm) in watershed GRREF during Jan 2011 to Nov 2014.

Cumulative load: treatment versus control watershed (GR1) (2011 to 2014)

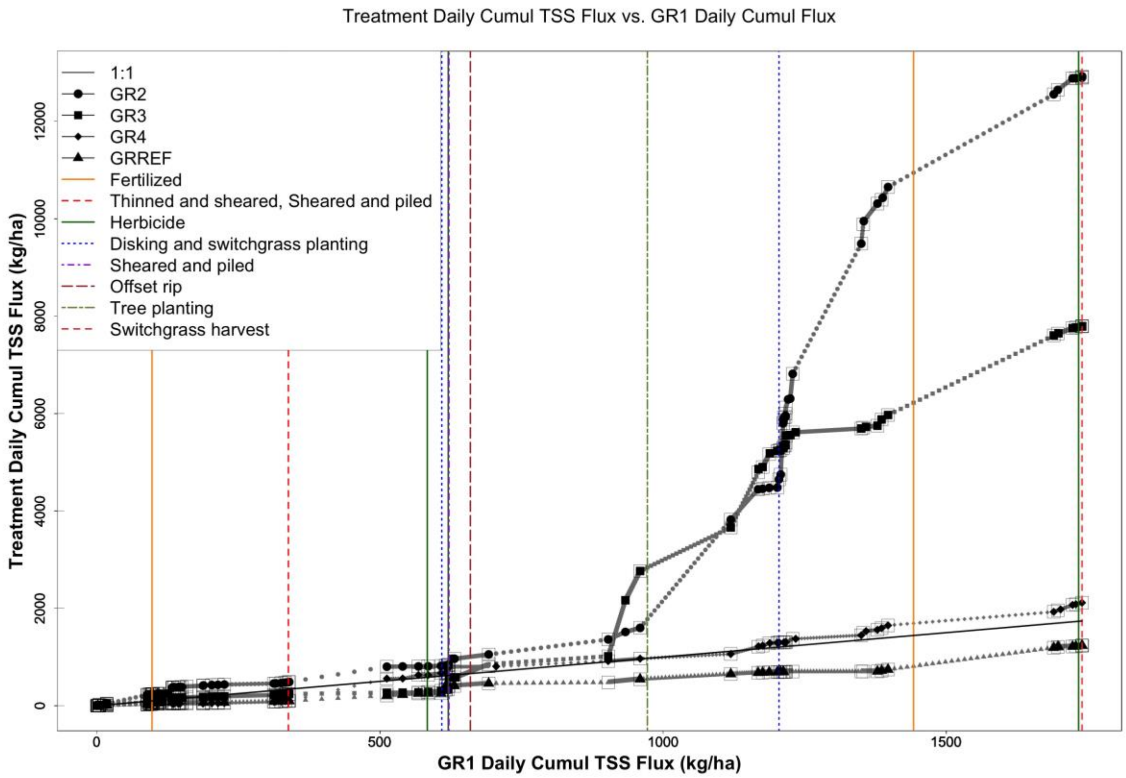

Figure G.12. Daily cumulative TSS load (kg ha^{-1}) of all watersheds (GR2, GR3, GR4, GRREF) as a function of daily cumulative TSS load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

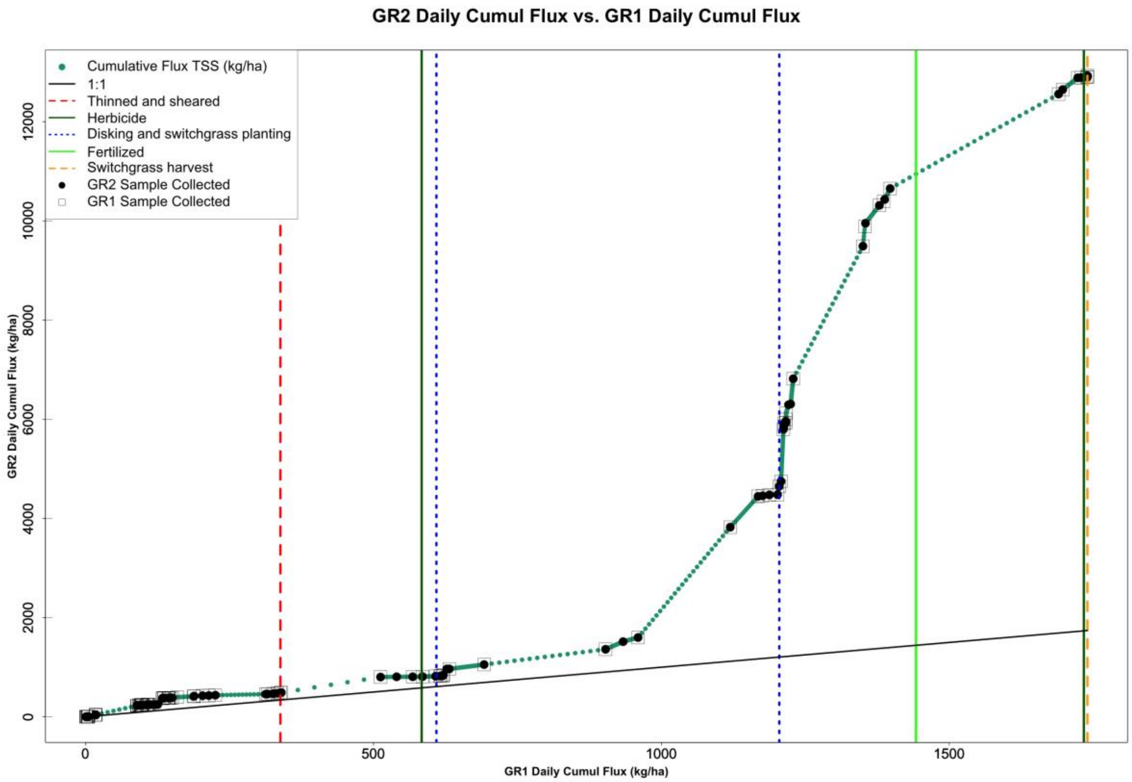

Figure G.13. Daily cumulative TSS load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative TSS load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

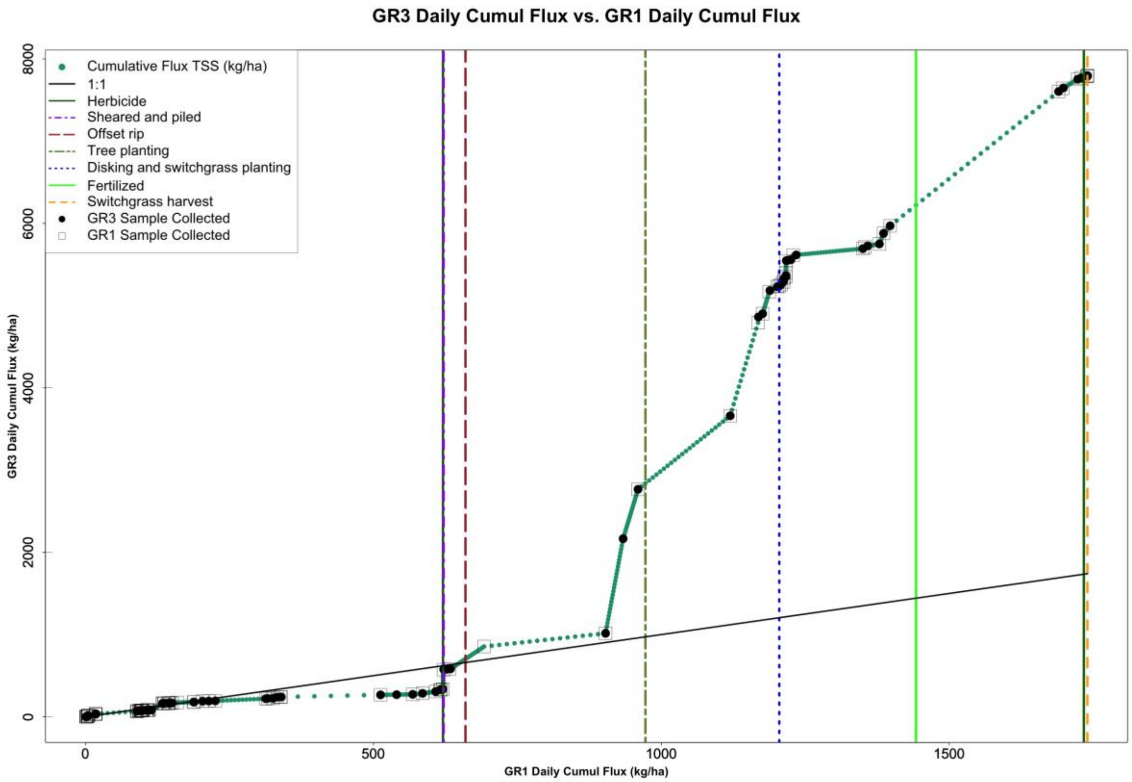

Figure G.14. Daily cumulative TSS load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative TSS load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

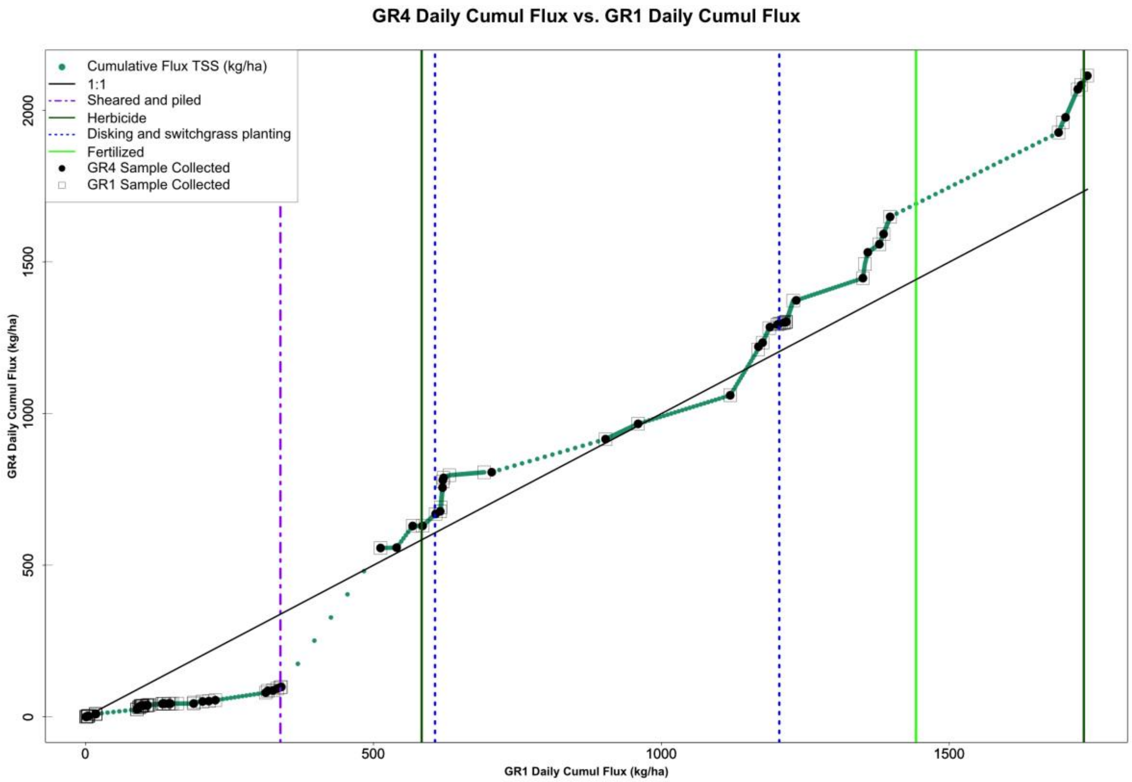

Figure G.15. Daily cumulative TSS load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative TSS load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

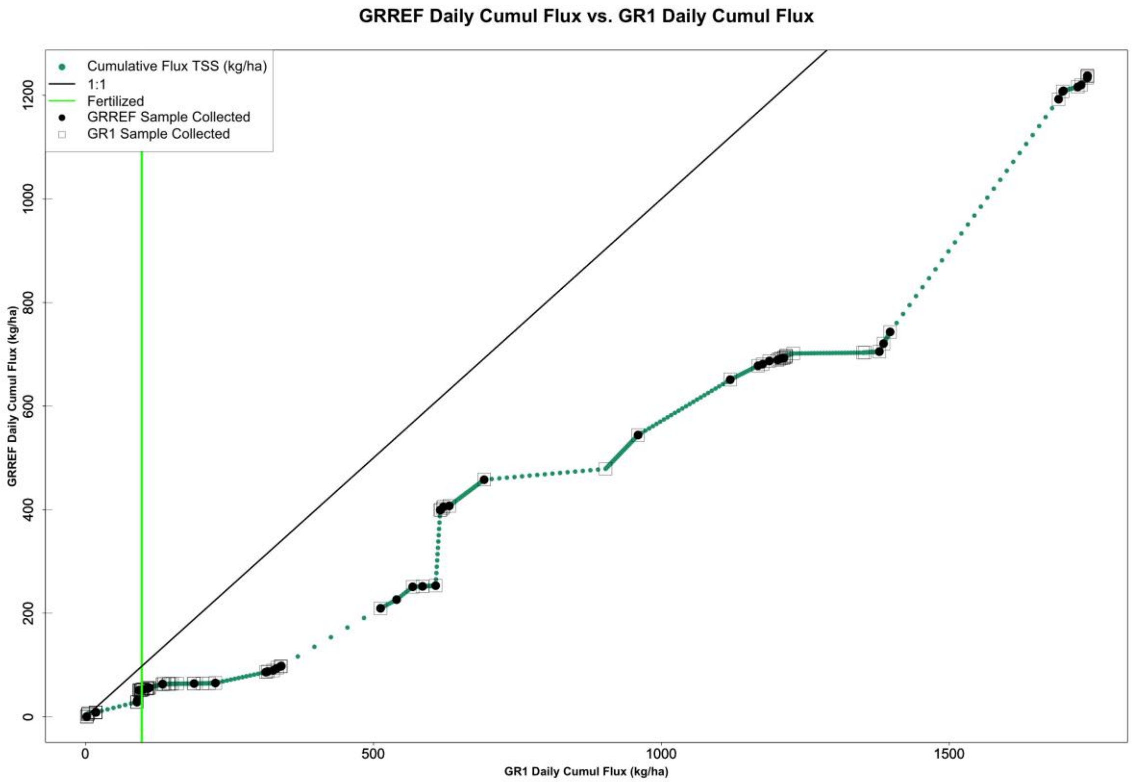

Figure G.16. Daily cumulative TSS load (kg ha^{-1}) of watershed GRREF as a function of daily cumulative TSS load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

Cumulative load: treatment versus mature reference watershed (GRREF) (2011 to 2014)

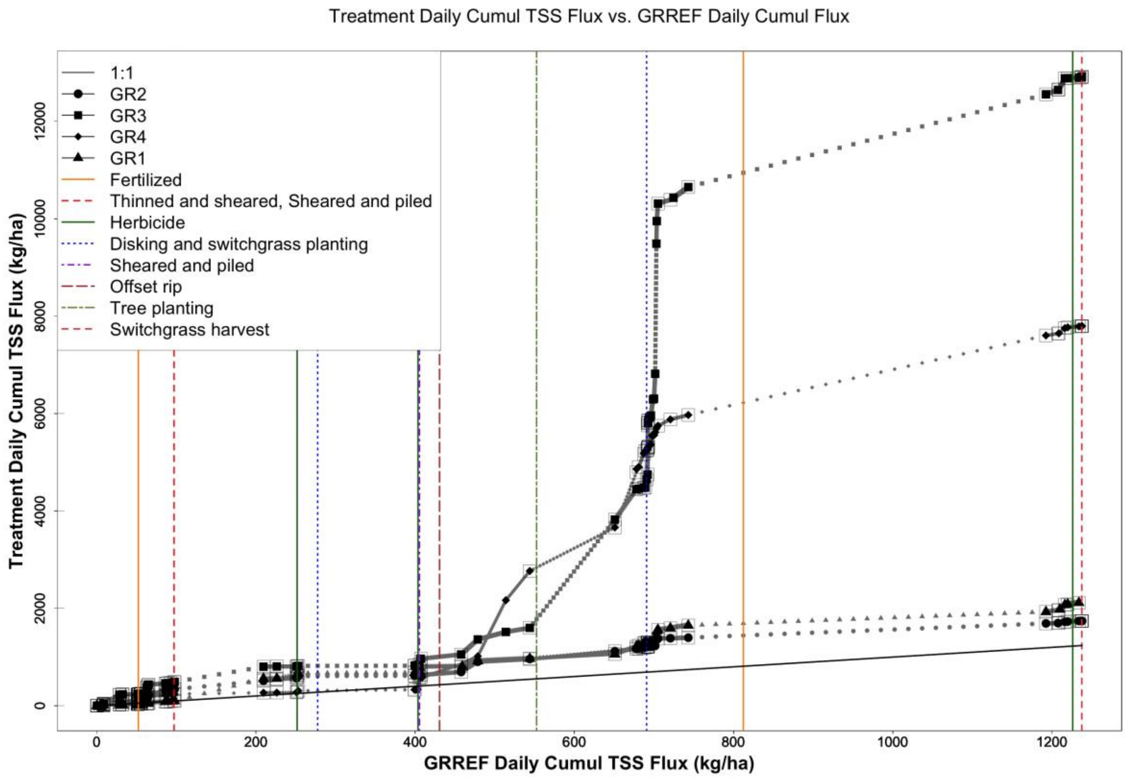

Figure G.17. Daily cumulative TSS load (kg ha^{-1}) of all watersheds (GR1, GR2, GR3, GR4) as a function of daily cumulative TSS load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

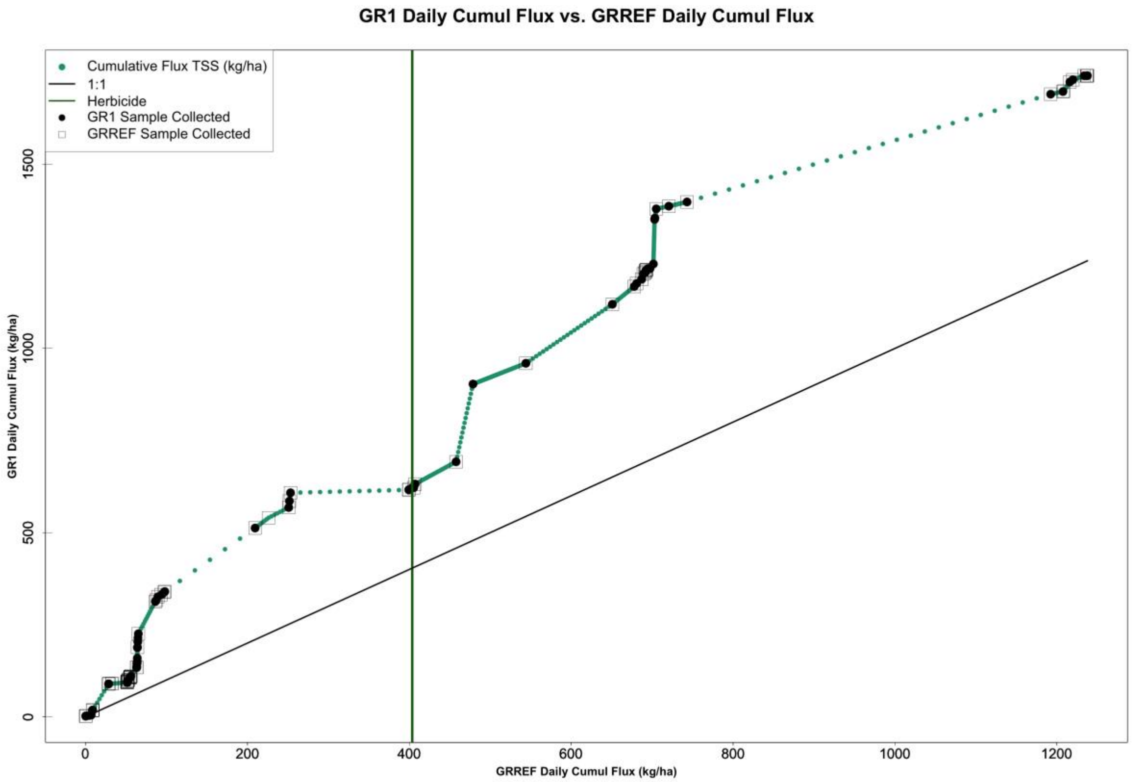

Figure G.18. Daily cumulative TSS load (kg ha^{-1}) of watershed GR1 as a function of daily cumulative TSS load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

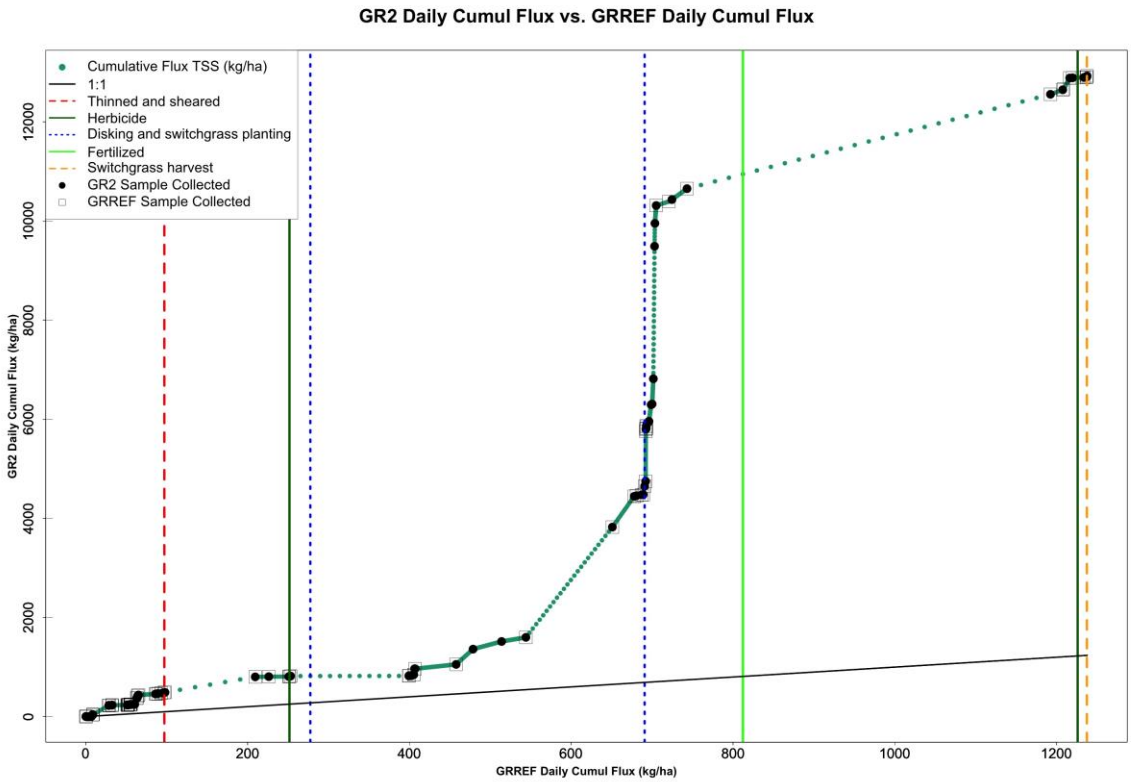

Figure G.19. Daily cumulative TSS load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative TSS load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

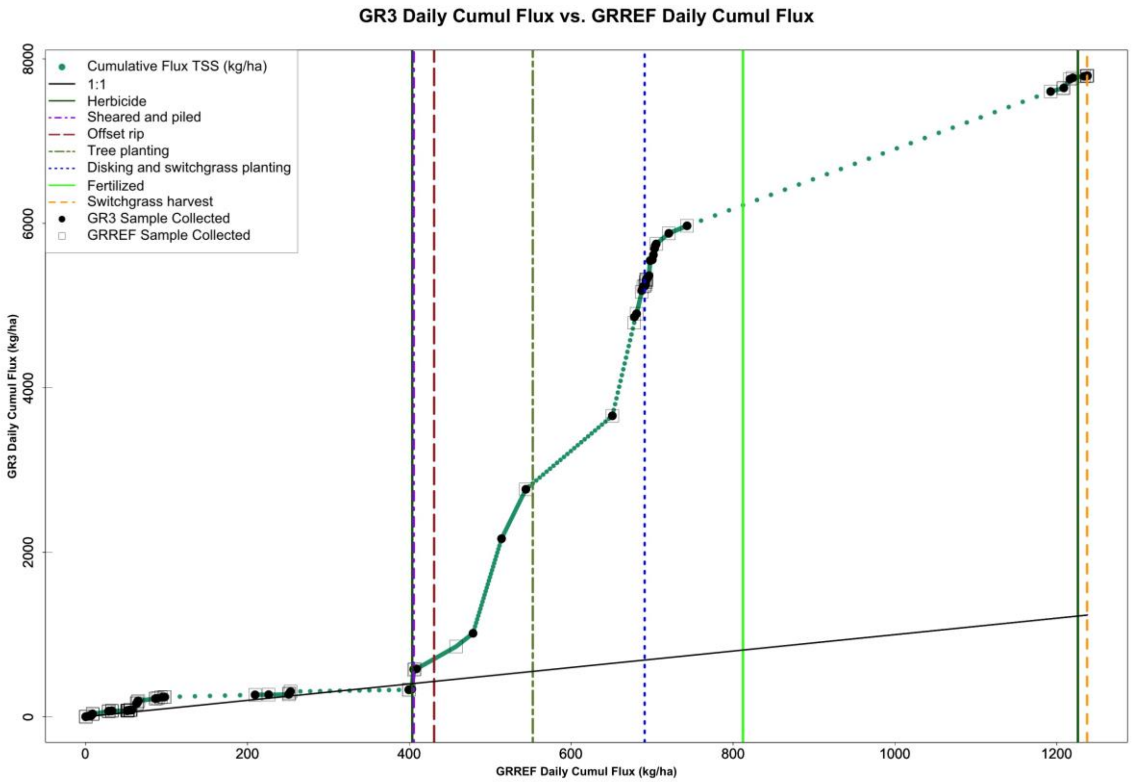

Figure G.20. Daily cumulative TSS load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative TSS load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

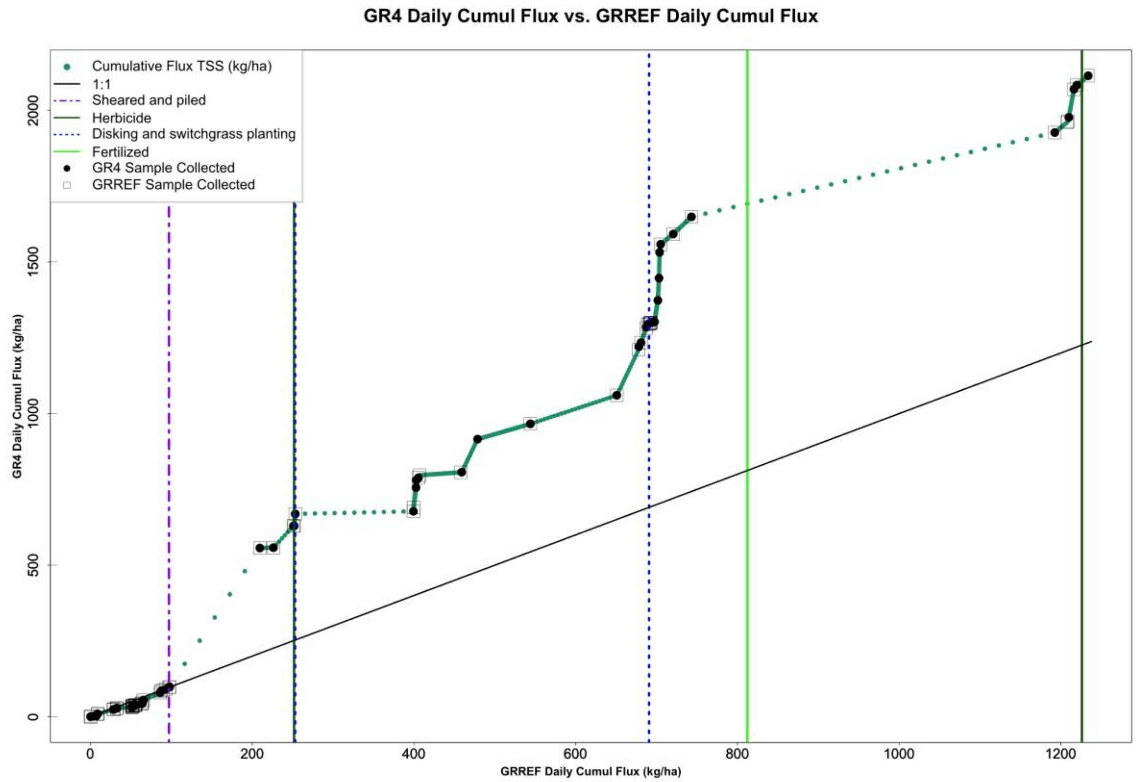

Figure G.21. Daily cumulative TSS load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative TSS load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

G.2 Dissolved organic carbon (DOC)

Cumulative flux over time with hydrograph (2011-2014)

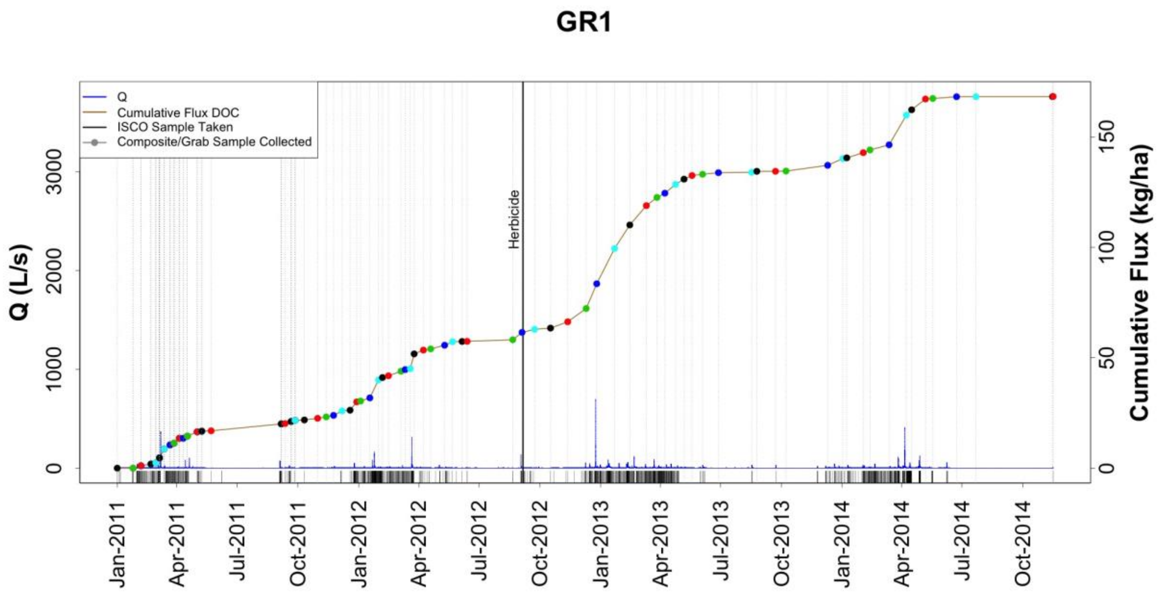

Figure G.22. Cumulative DOC flux over time (Jan 2011 to Nov 2014) in watershed GR1, Green County, Alabama, with hydrograph (L s^{-1}) and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

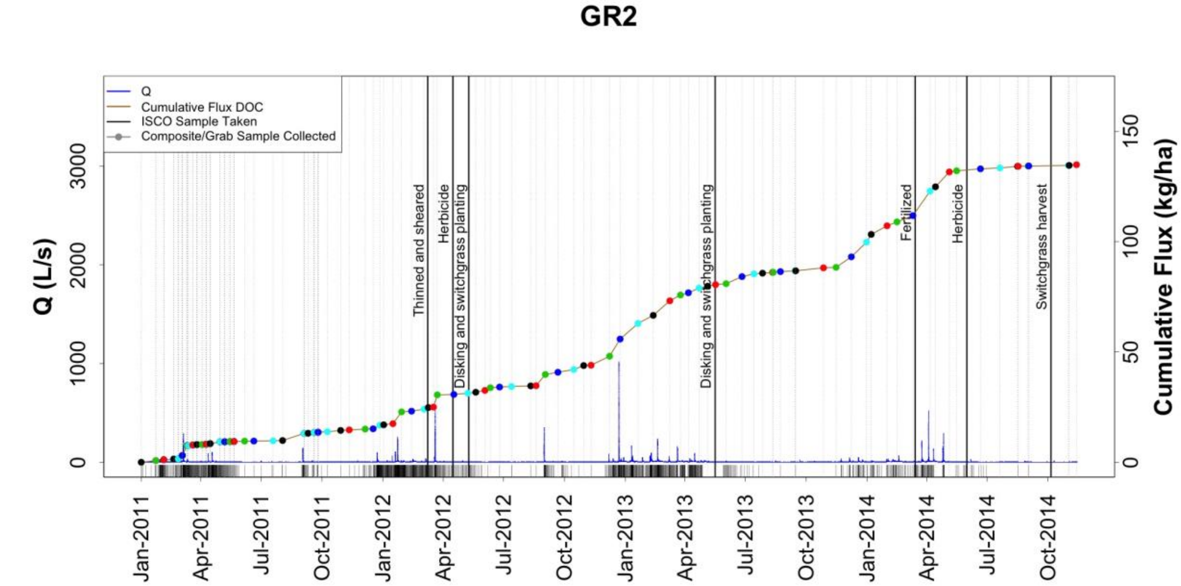

Figure G.23. Cumulative DOC flux over time (Jan 2011 to Nov 2014) in watershed GR2, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

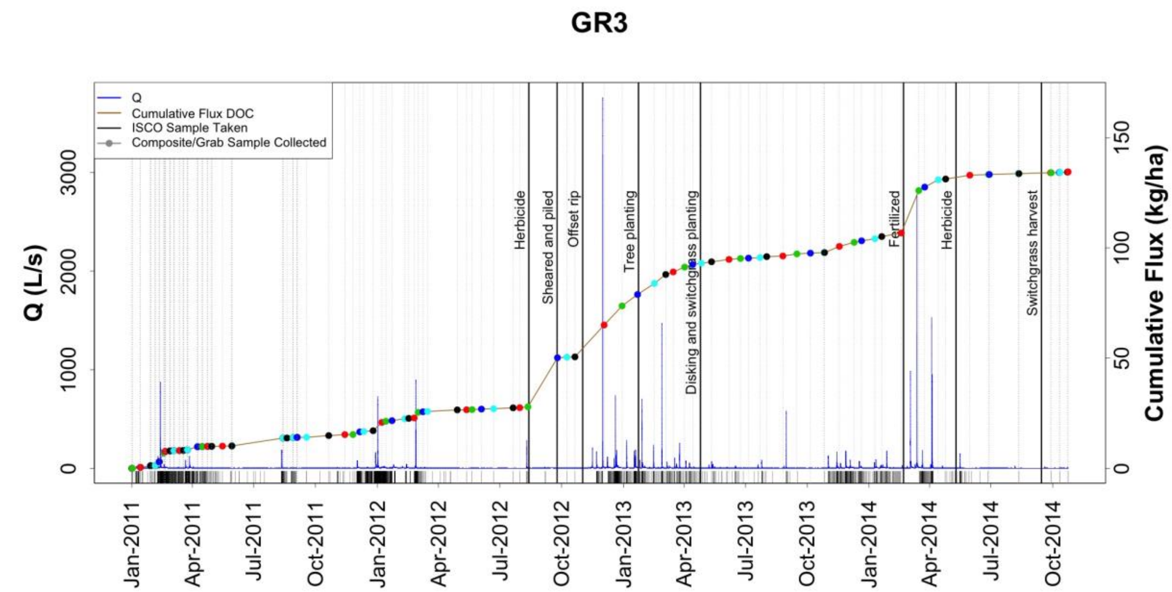

Figure G.24. Cumulative DOC flux over time (Jan 2011 to Nov 2014) in watershed GR3, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

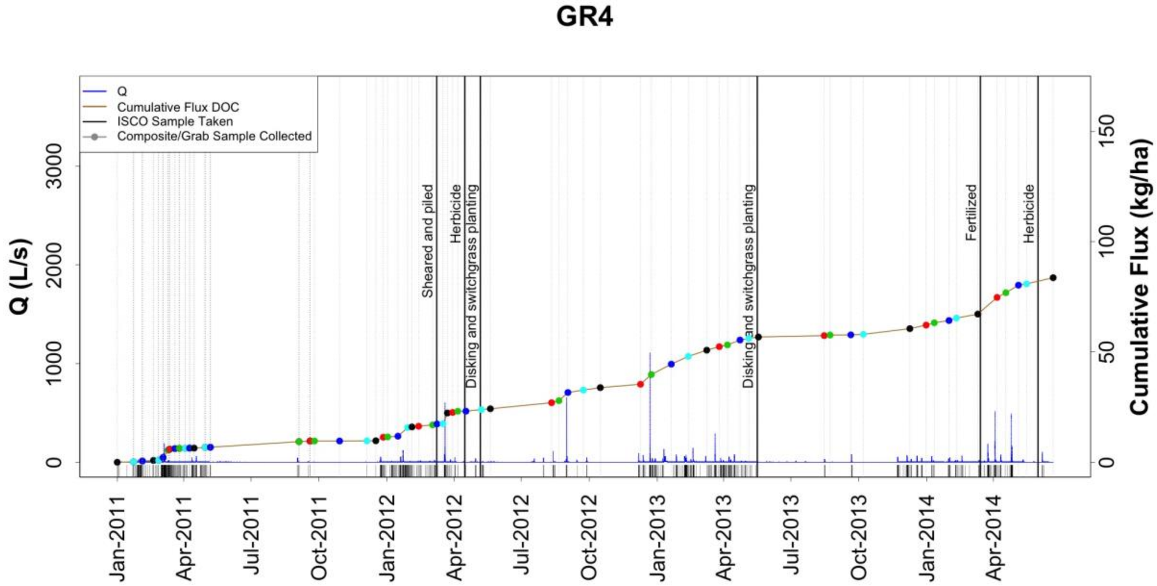

Figure G.25. Cumulative DOC flux over time (Jan 2011 to Nov 2014) in watershed GR4, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

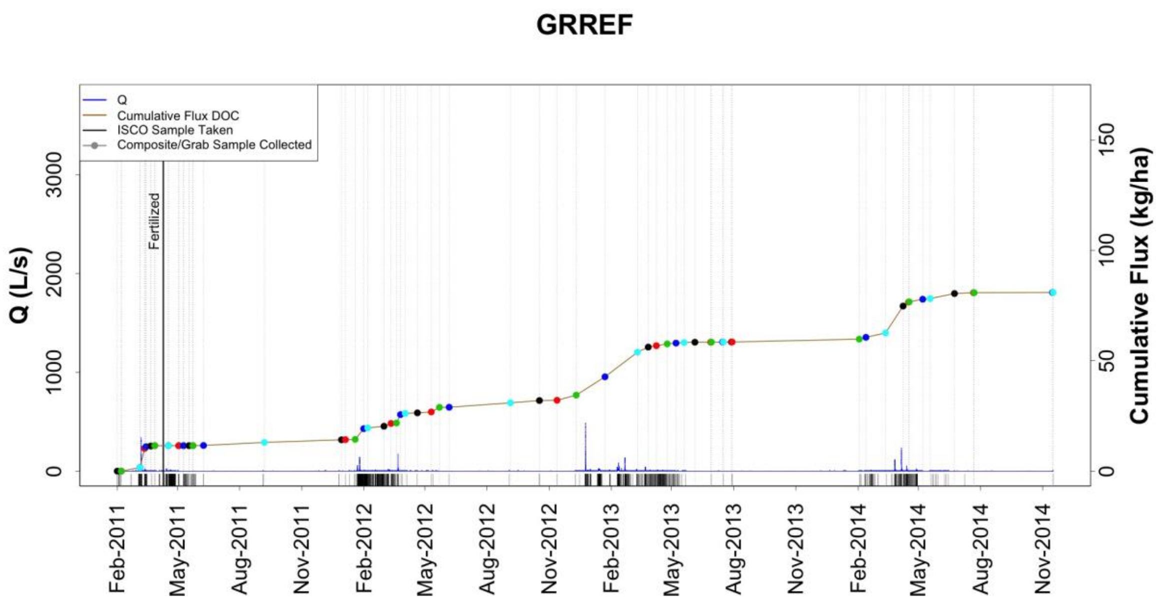

Figure G.26. Cumulative DOC flux over time (Feb 2011 to Nov 2014) in watershed GRREF, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

Cumulative flux versus cumulative volume (2011-2014)

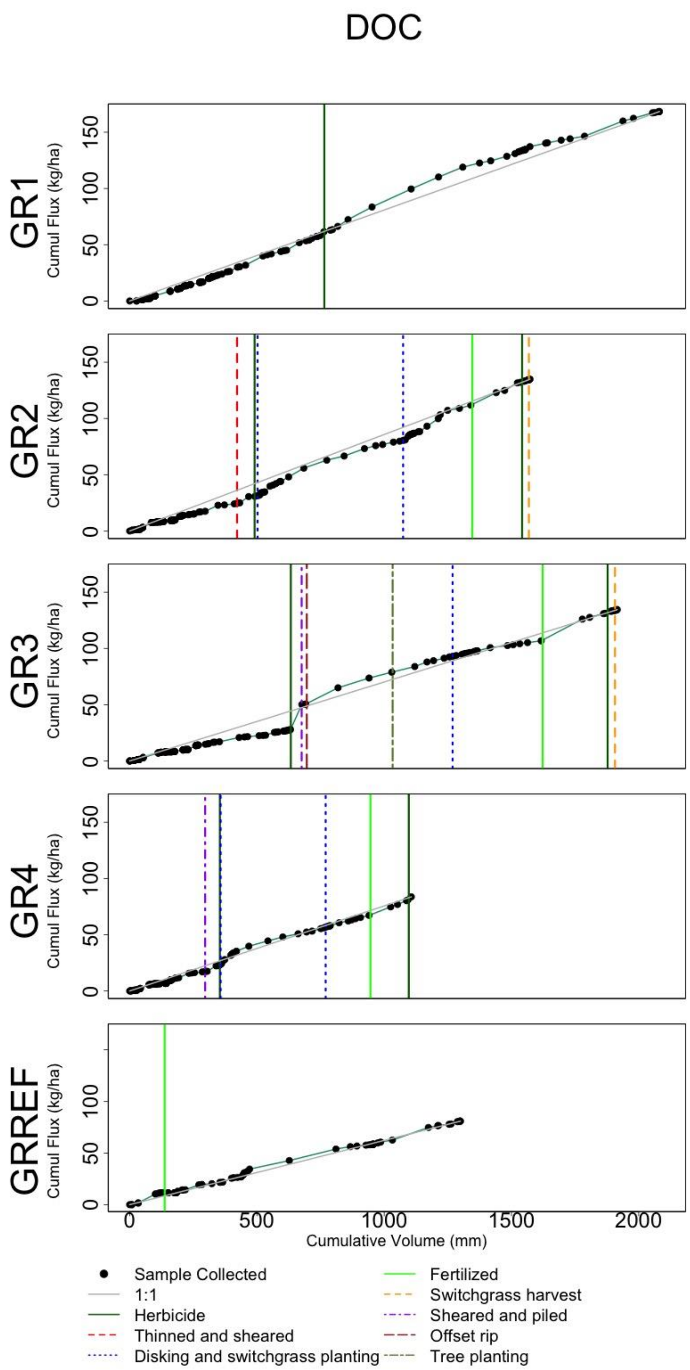

Figure G.27. Cumulative DOC load (kg ha^{-1}) as a function of cumulative flow volume (mm) from Jan 2011 to Nov 2014.

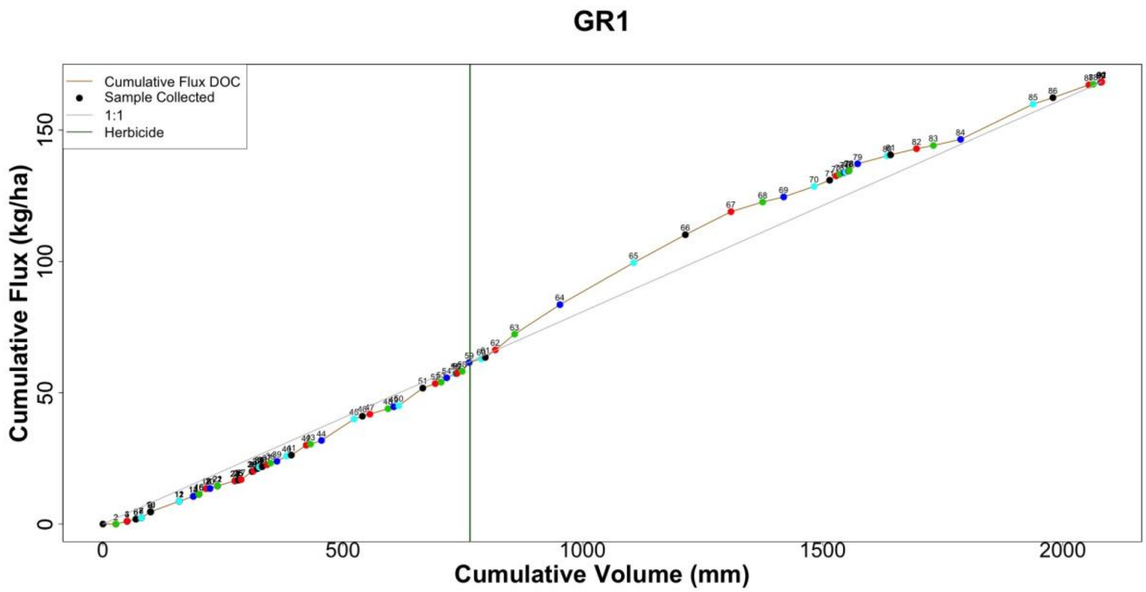

Figure G.28. Cumulative DOC load (kg ha^{-1}) of control watershed (GR1) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

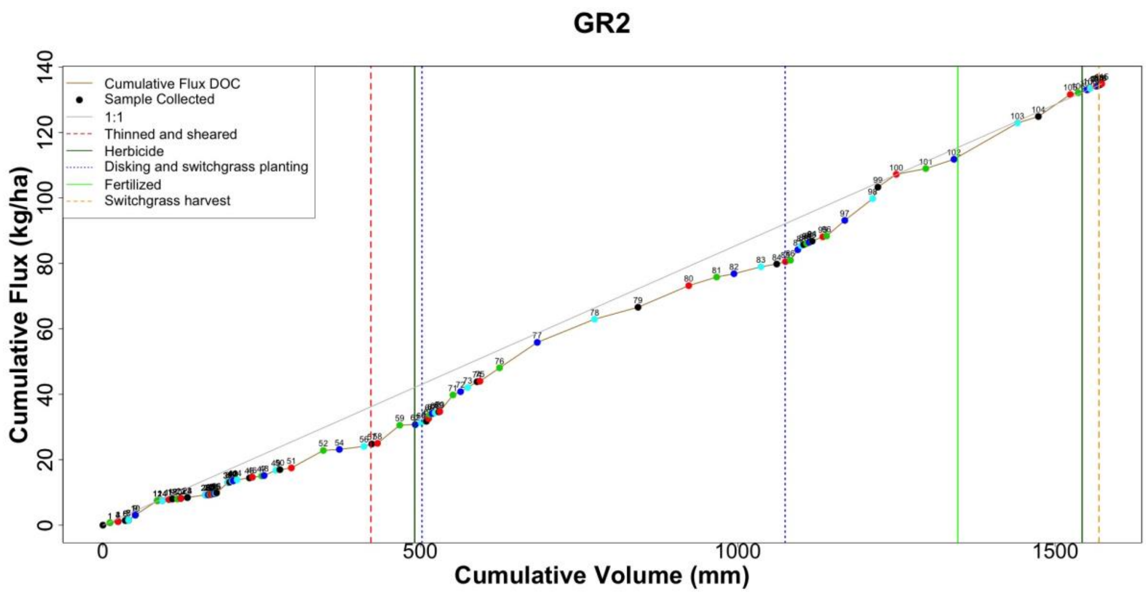

Figure G.29. Cumulative DOC load (kg ha^{-1}) of intercropped/thinned watershed (GR2) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

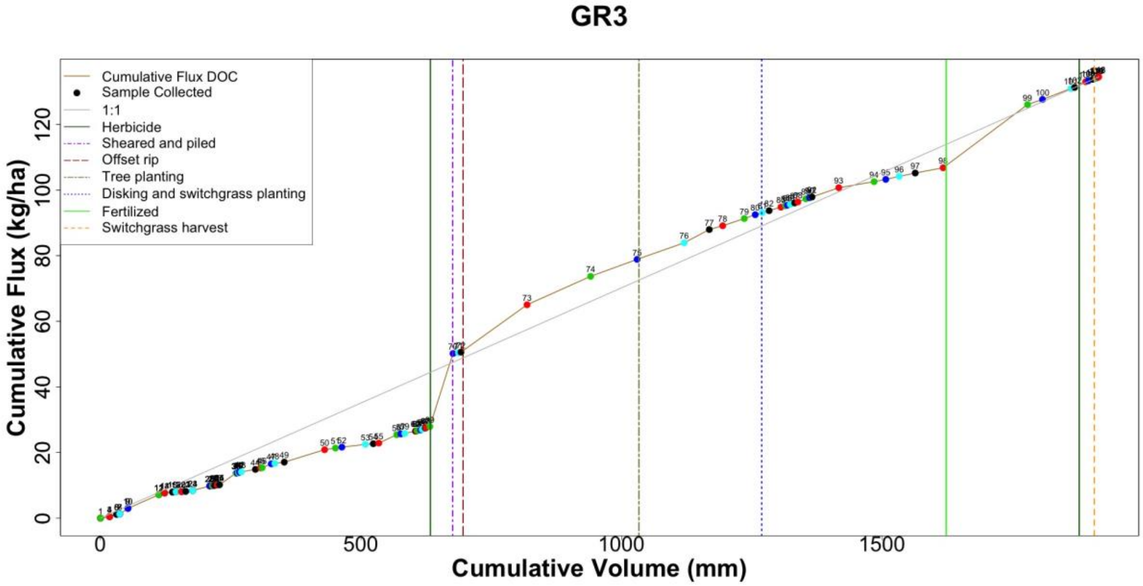

Figure G.30. Cumulative DOC load (kg ha^{-1}) of intercropped/replanted watershed (GR3) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

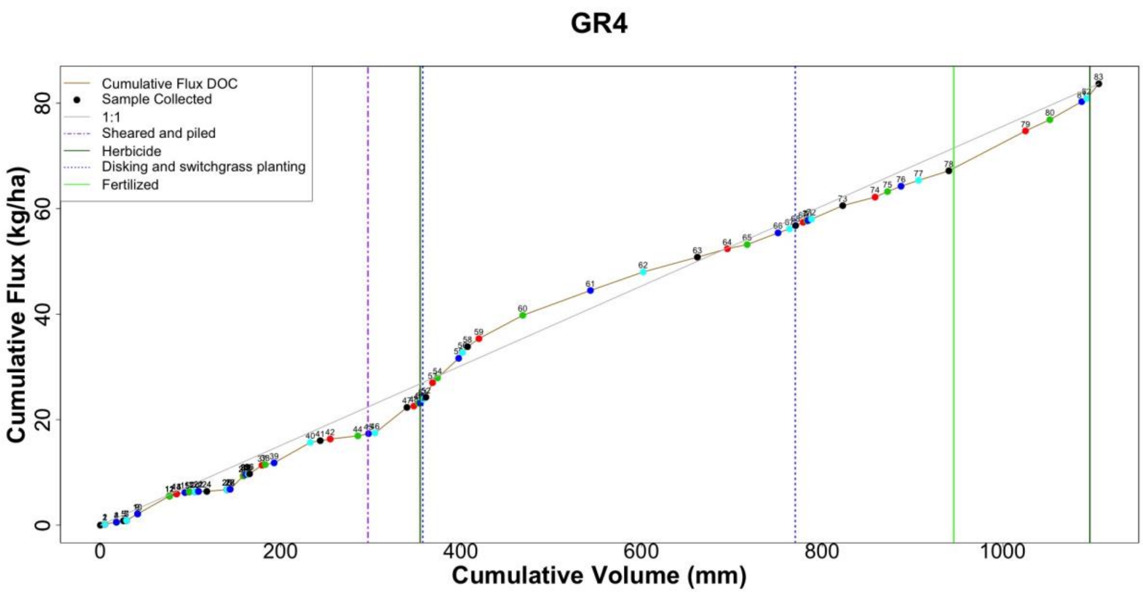

Figure G.31. Cumulative DOC load (kg ha^{-1}) of switchgrass watershed (GR4) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

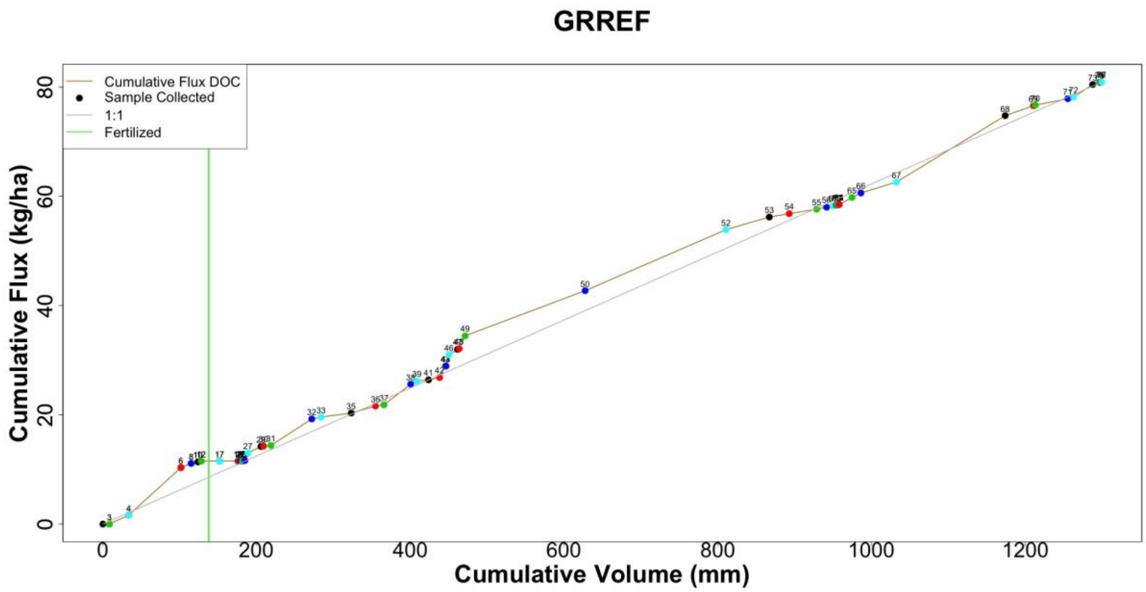

Figure G.32. Cumulative DOC load (kg ha^{-1}) of mature reference watershed (GRREF) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

Cumulative flux: treatment versus control watershed (GR1) (2011 to 2014)

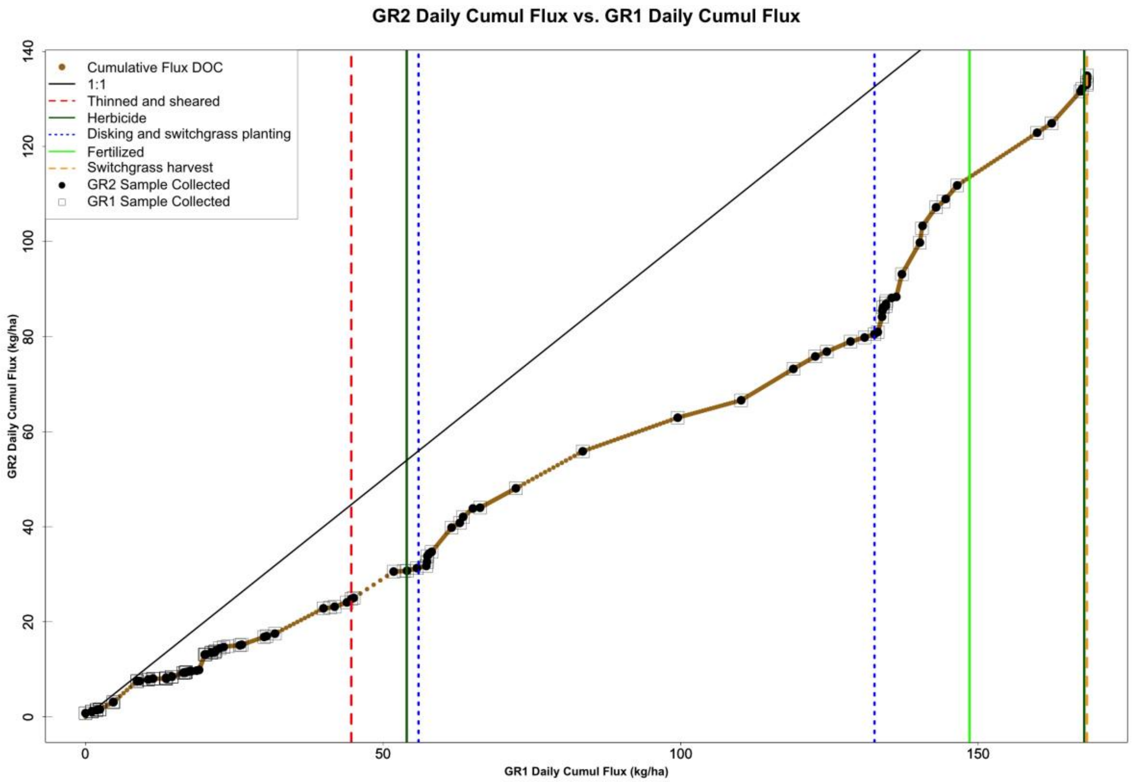

Figure G.33. Daily cumulative DOC load (kg ha^{-1}) of intercropped/thinned watershed (GR2) as a function of daily cumulative DOC load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

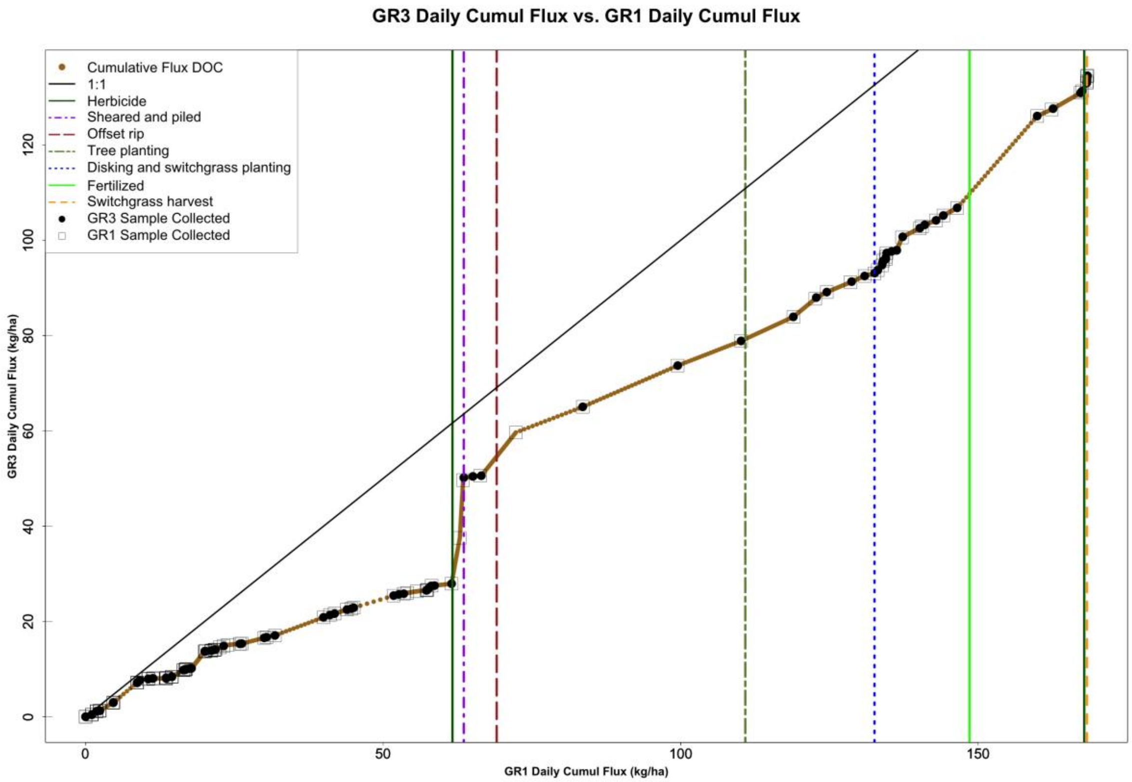

Figure G.34. Daily cumulative DOC load (kg ha^{-1}) of intercropped/replanted watershed (GR3) as a function of daily cumulative DOC load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

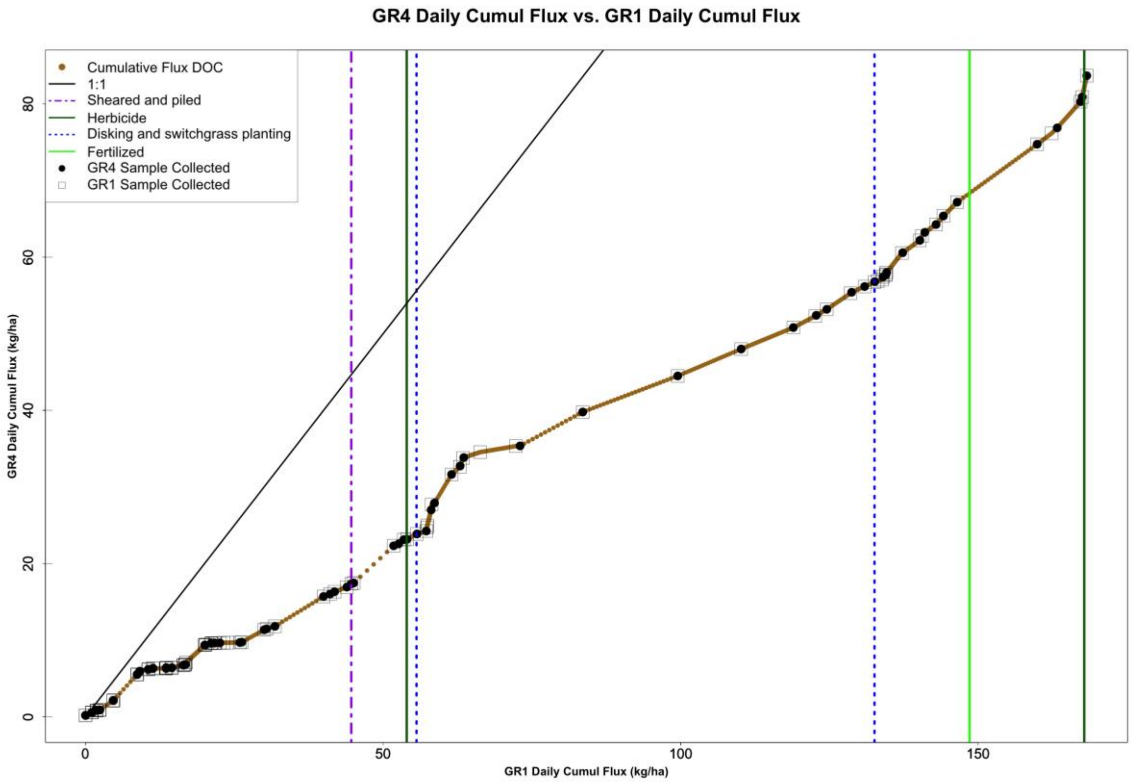

Figure G.35. Daily cumulative DOC load (kg ha^{-1}) of switchgrass watershed (GR4) as a function of daily cumulative DOC load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

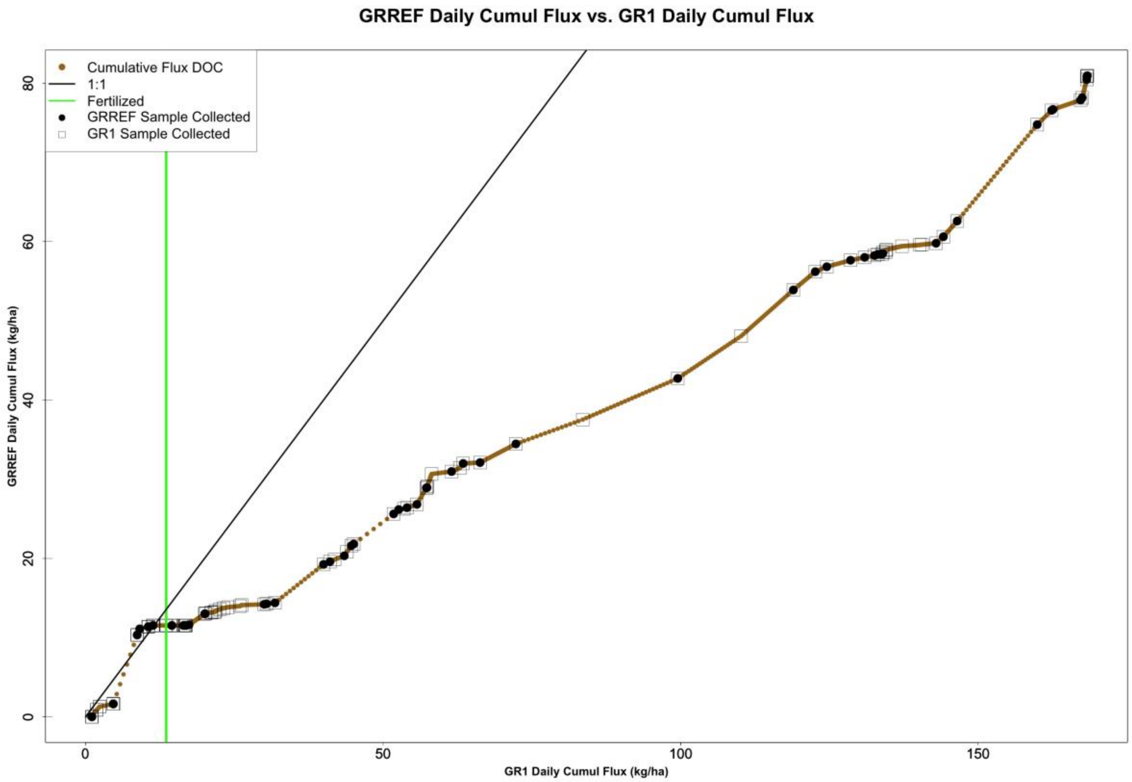

Figure G.36. Daily cumulative DOC load (kg ha^{-1}) of mature pine reference watershed (GRREF) as a function of daily cumulative DOC load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

Cumulative load: treatment versus mature reference watershed (GRREF) (2011 to 2014)

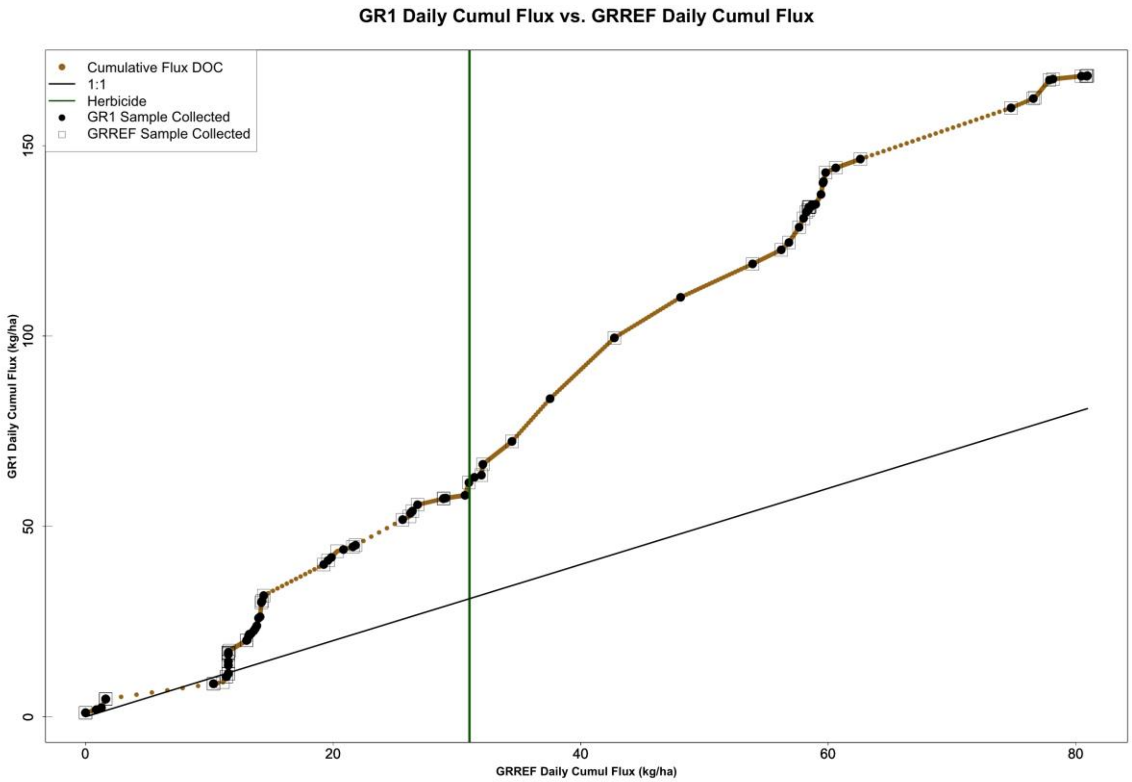

Figure G.37. Daily cumulative DOC load (kg ha^{-1}) of young pine control watershed (GR1) as a function of daily cumulative DOC load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

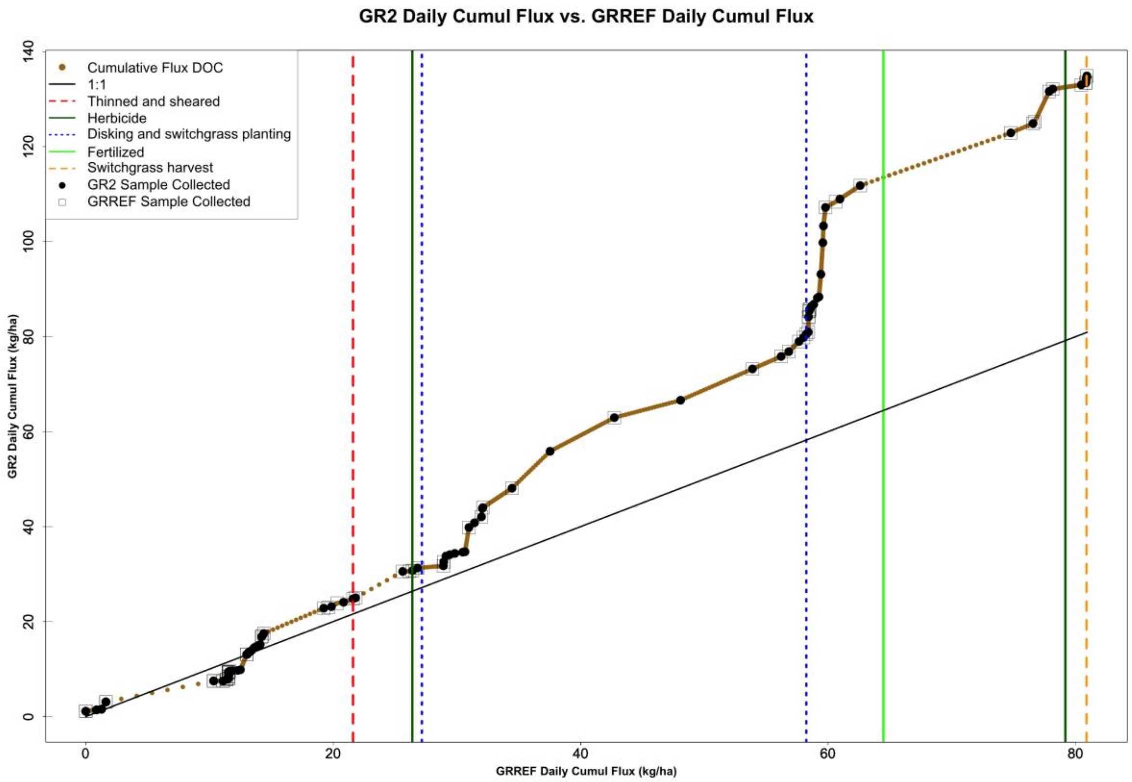

Figure G.38. Daily cumulative DOC load (kg ha^{-1}) of intercropped/thinned watershed (GR2) as a function of daily cumulative DOC load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

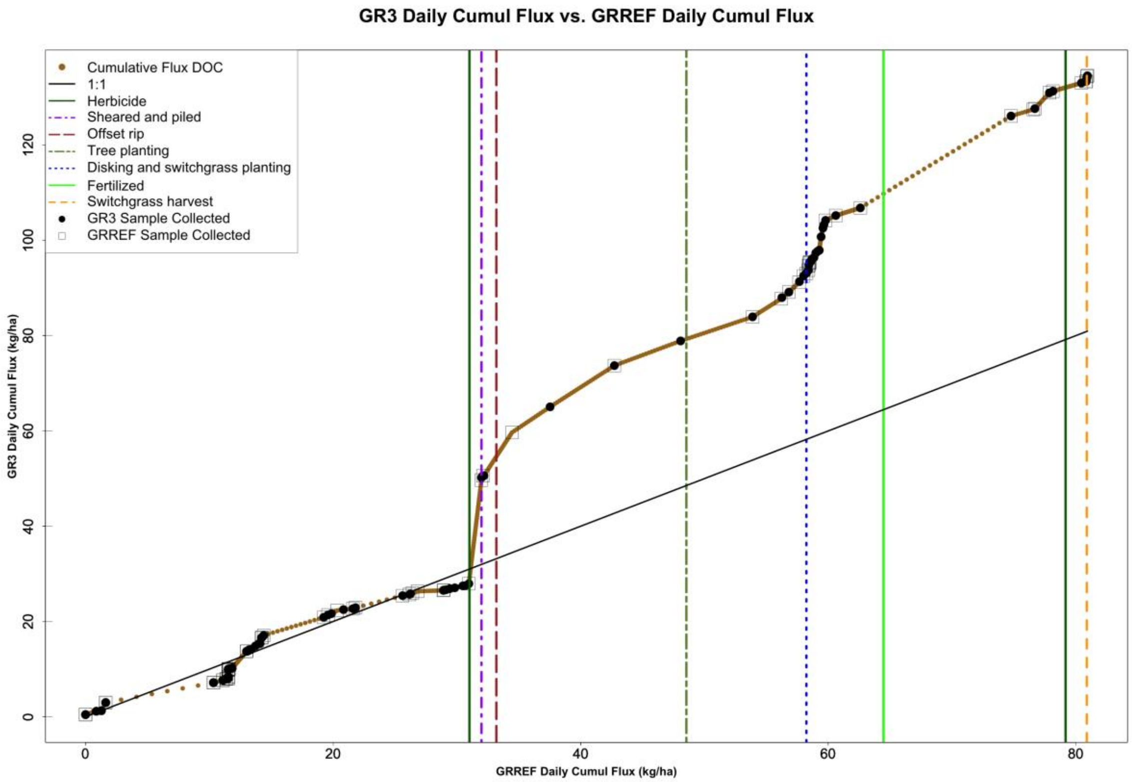

Figure G.39. Daily cumulative DOC load (kg ha^{-1}) of intercropped/replanted watershed (GR3) as a function of daily cumulative DOC load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

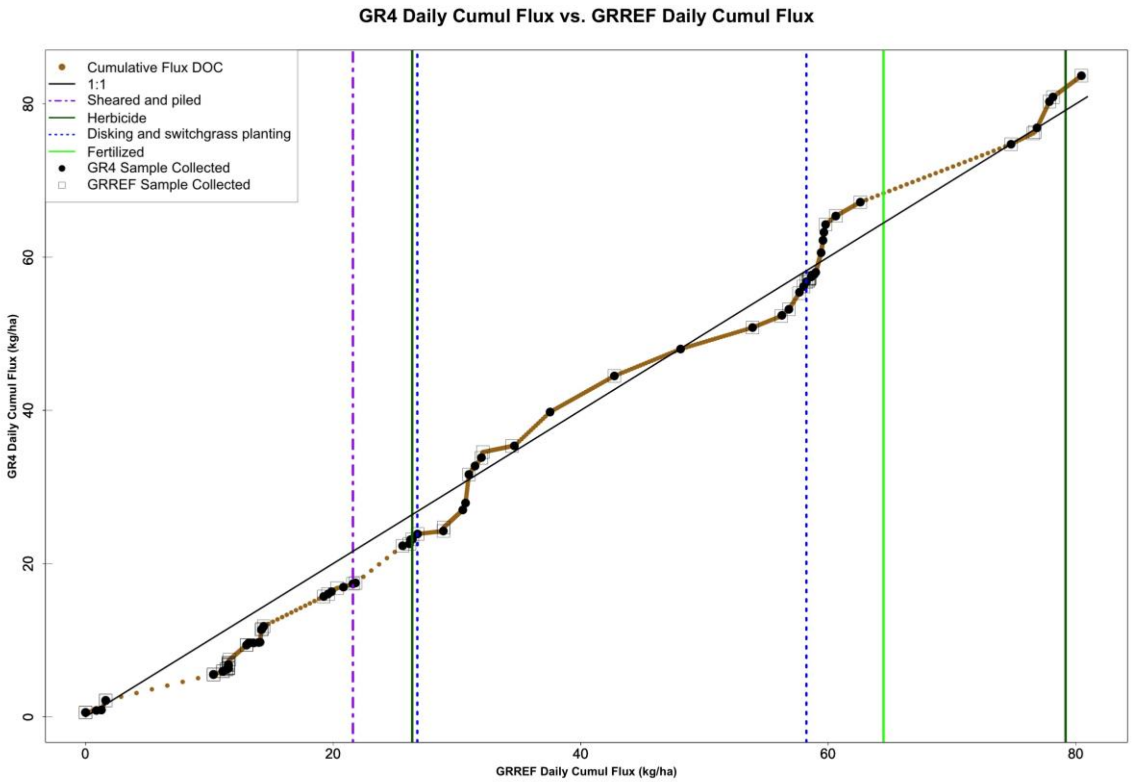

Figure G.40. Daily cumulative DOC load (kg ha^{-1}) of switchgrass watershed (GR4) as a function of daily cumulative DOC load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

G.3 Nitrate (NO_3^--N)

Cumulative load over time with hydrograph (2011-2014)

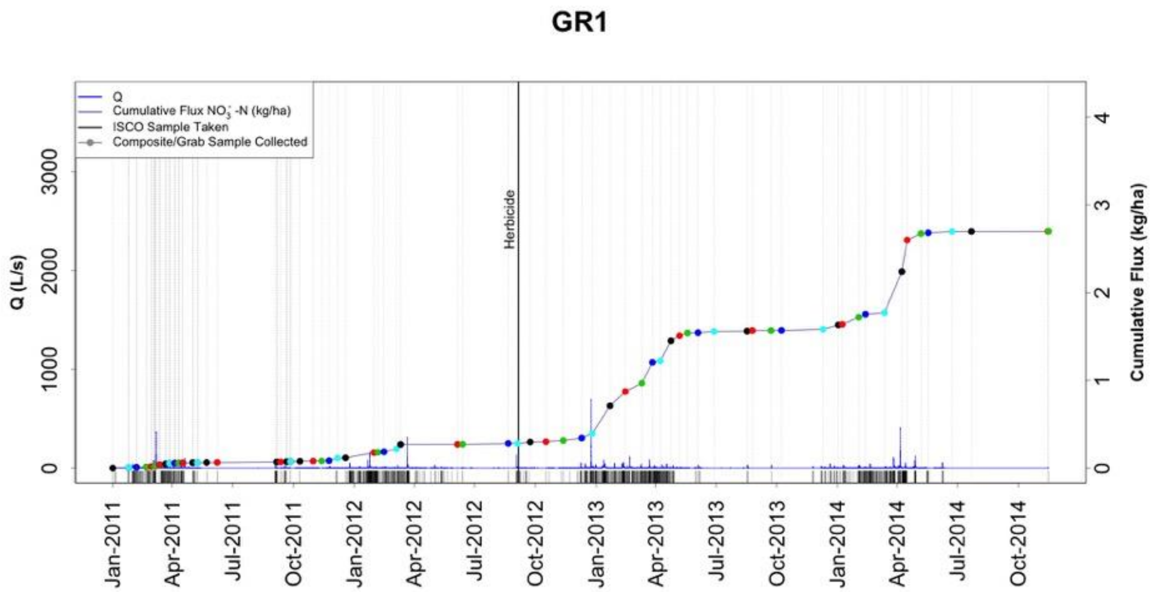

Figure G.41. Cumulative NO_3^--N flux over time (Jan 2011 to Nov 2014) in watershed GR1, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

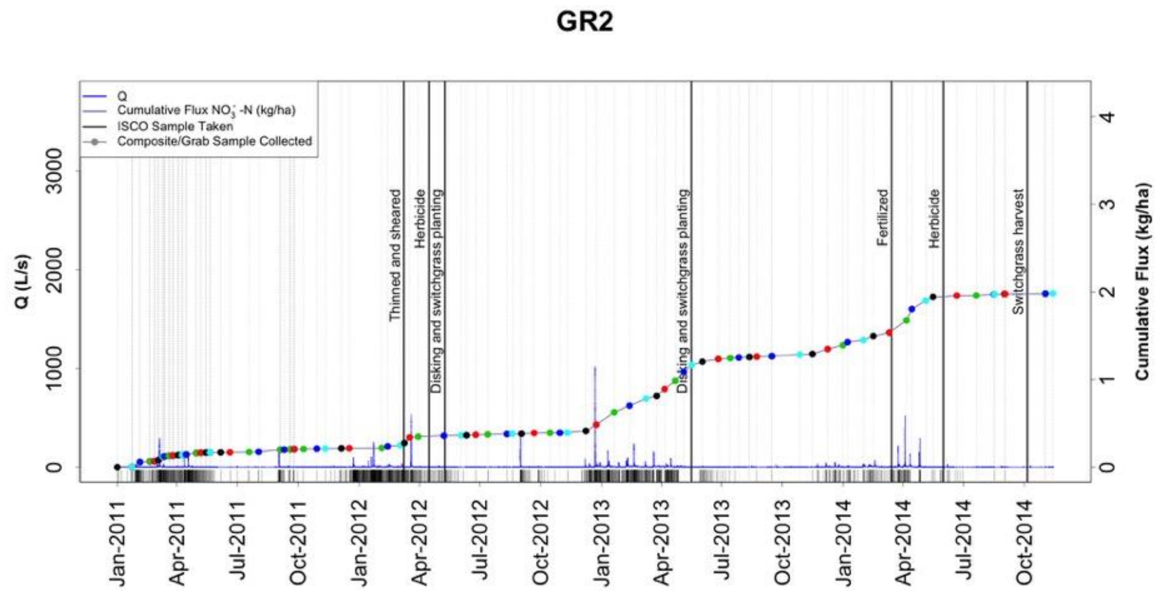

Figure G.42. Cumulative NO_3^--N flux over time (Jan 2011 to Nov 2014) in watershed GR2, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

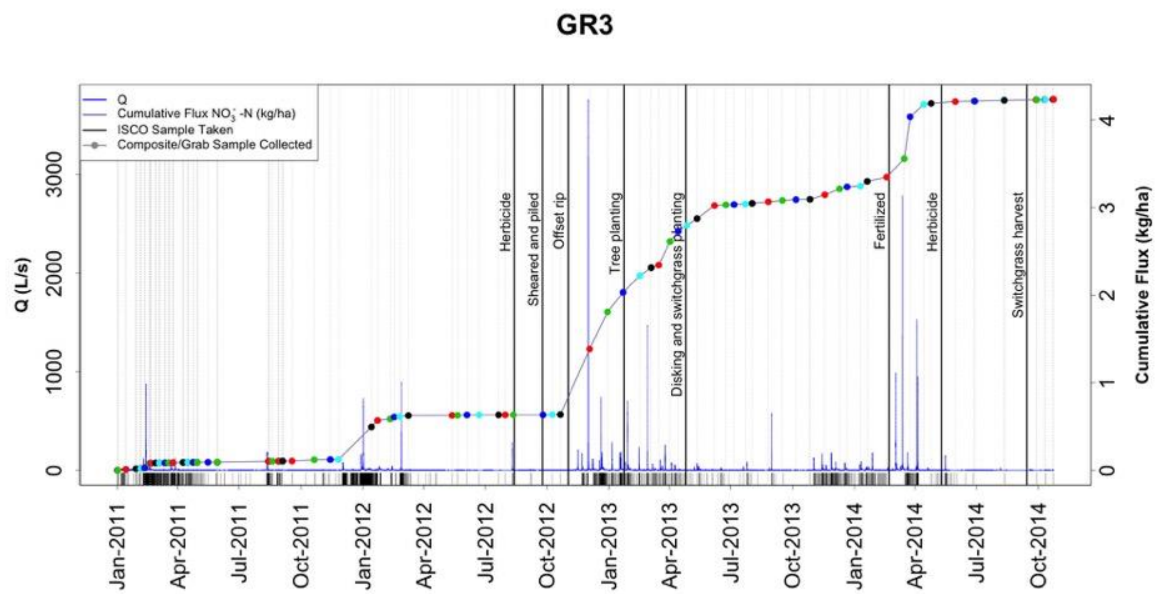

Figure G.43. Cumulative NO_3^--N flux over time (Jan 2011 to Nov 2014) in watershed GR3, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

GR4

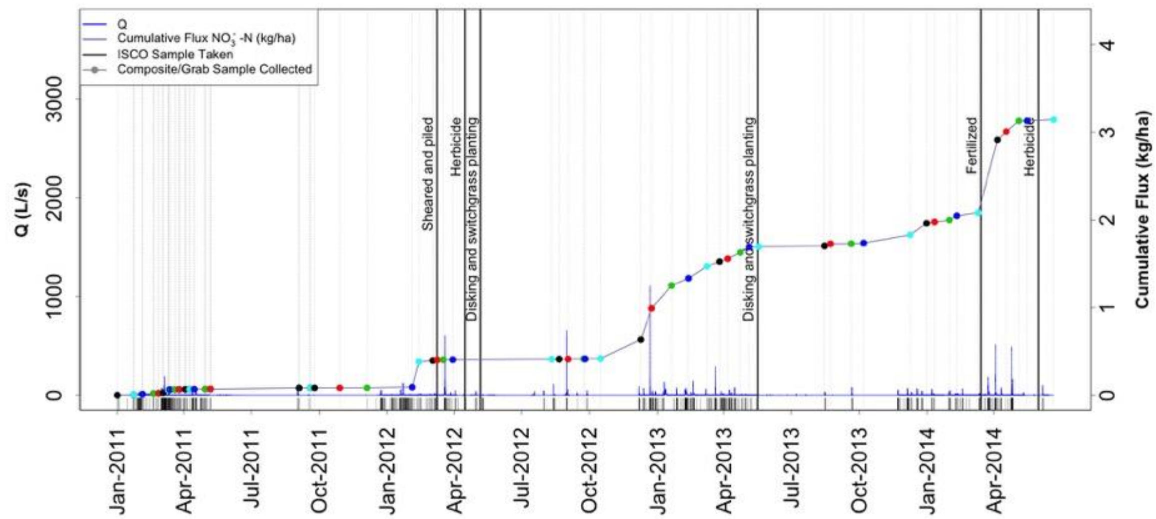

Figure G.44. Cumulative NO_3^--N flux over time (Jan 2011 to Nov 2014) in watershed GR4, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

GRREF

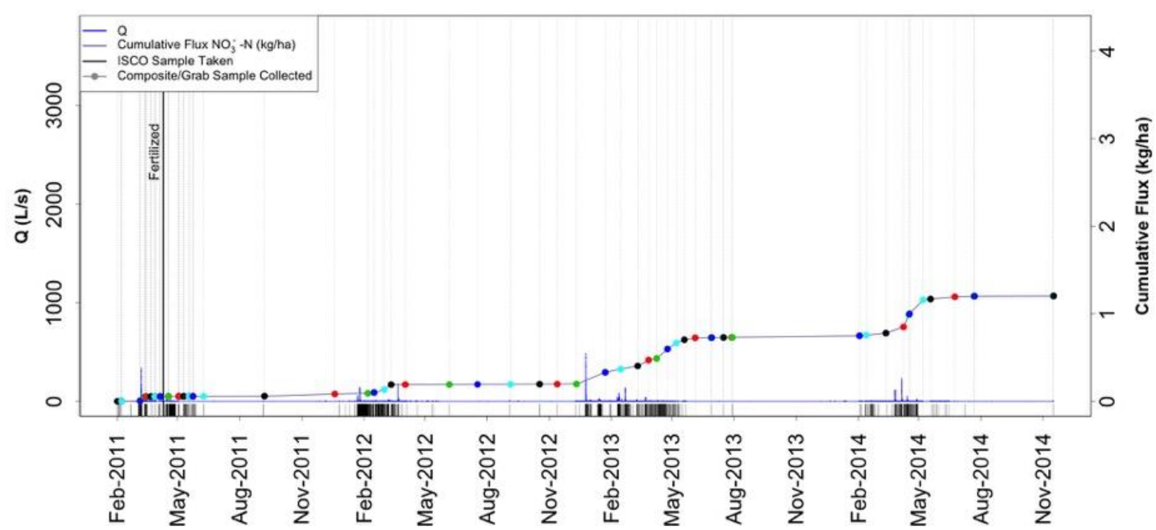

Figure G.45. Cumulative NO_3^--N flux over time (Jan 2011 to Nov 2014) in watershed GRREF, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

Cumulative load versus cumulative volume (2011-2014)

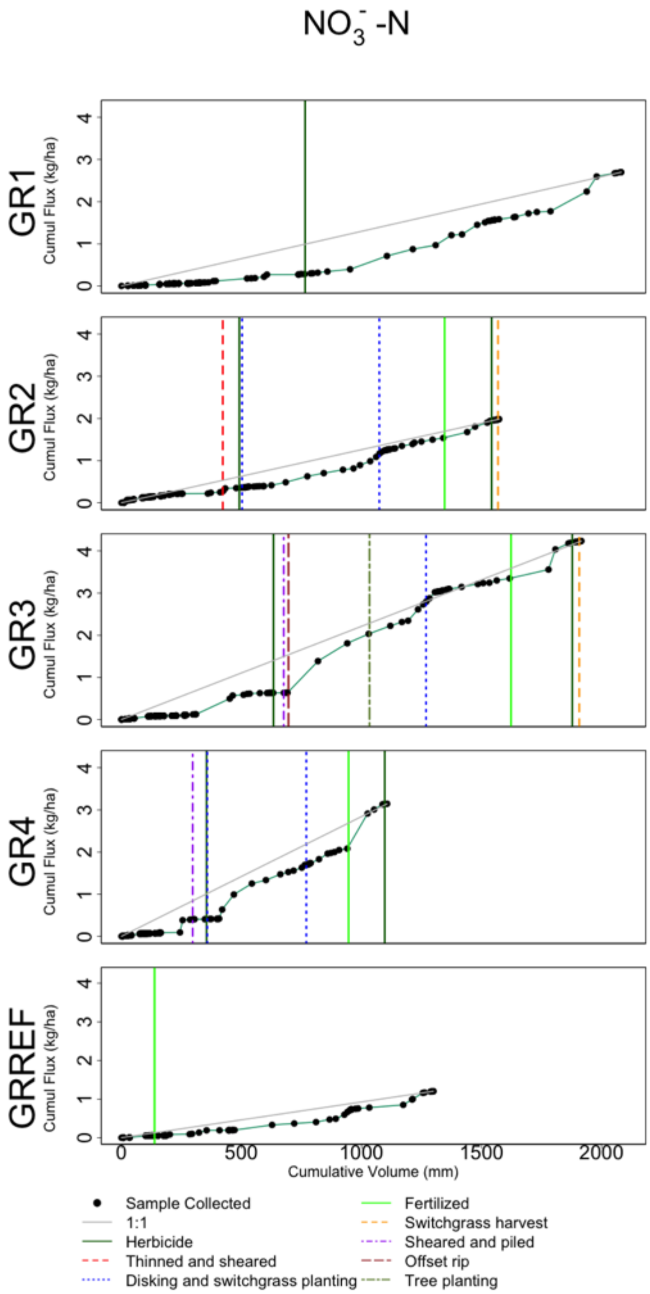

Figure G.46. Cumulative NO_3^--N load (kg ha^{-1}) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

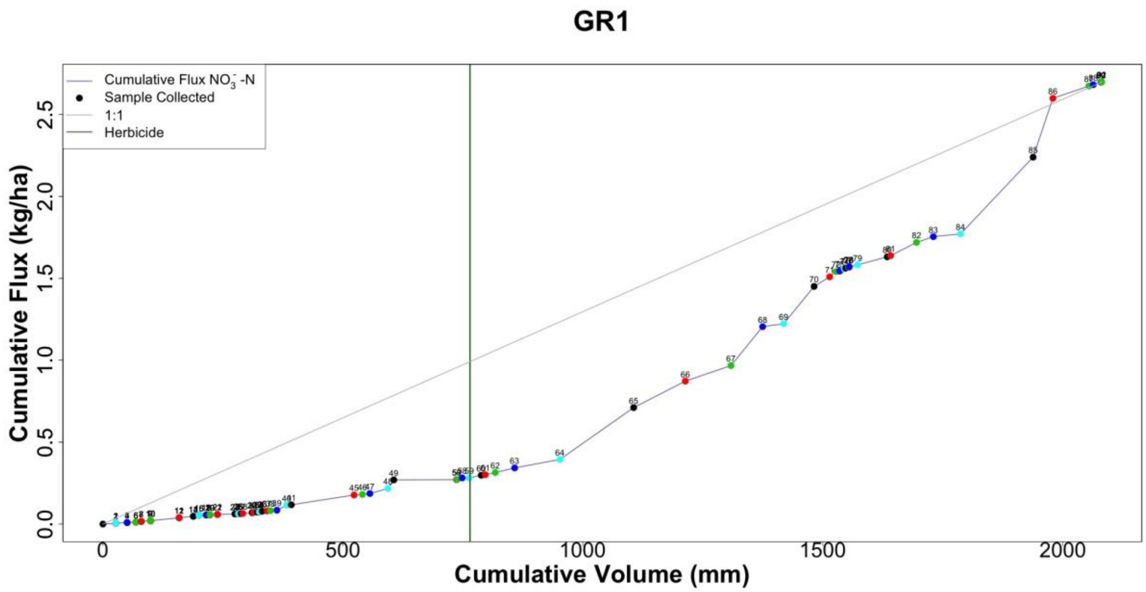

Figure G.47. Cumulative NO_3^--N load (kg ha^{-1}) of control watershed (GR1) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

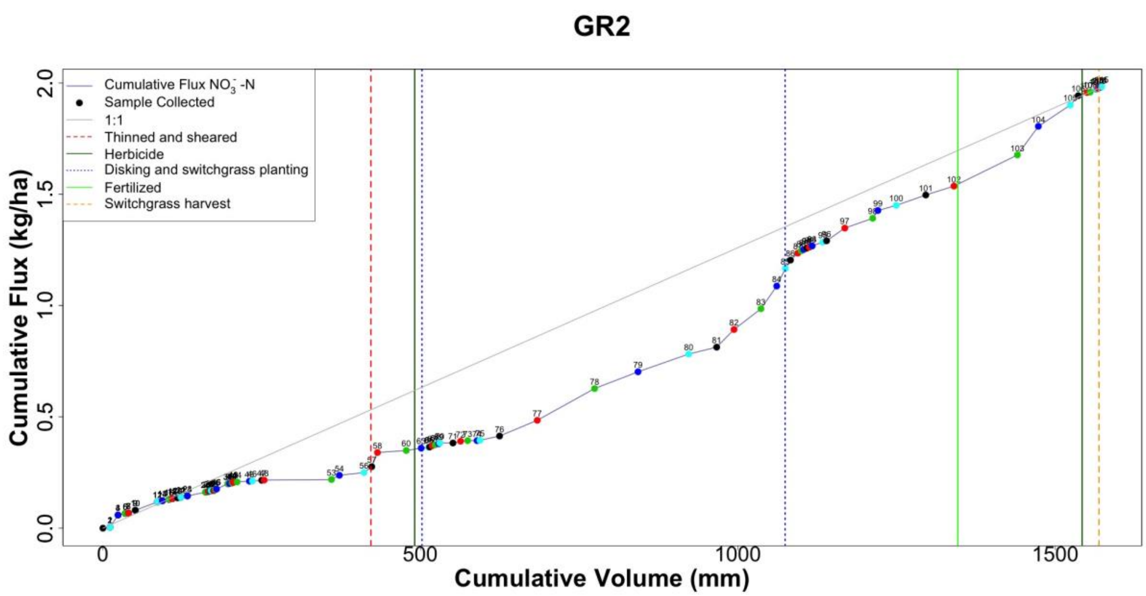

Figure G.48. Cumulative NO_3^--N load (kg ha^{-1}) of intercropped/thinned watershed (GR2) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

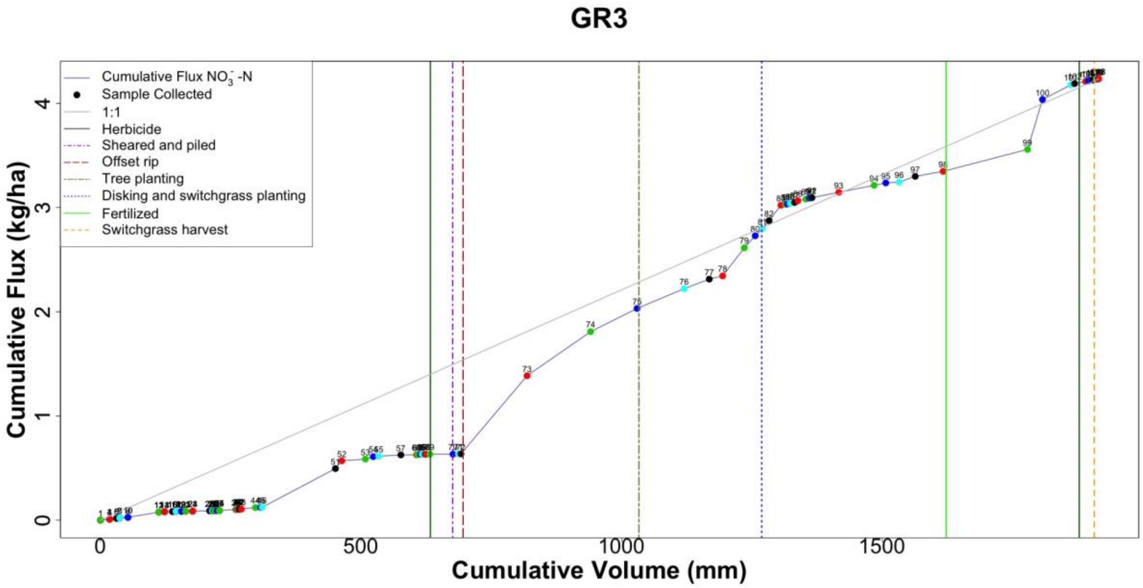

Figure G.49. Cumulative NO_3^--N load (kg ha^{-1}) of intercropped/replanted watershed (GR3) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

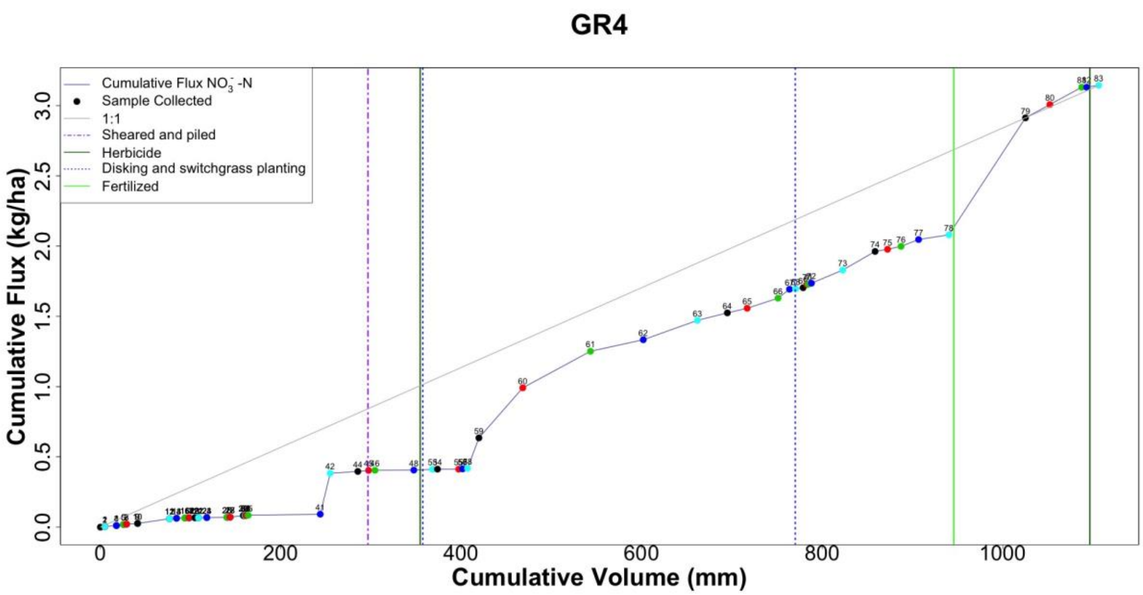

Figure G.50. Cumulative NO_3^--N load (kg ha^{-1}) of switchgrass watershed (GR4) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

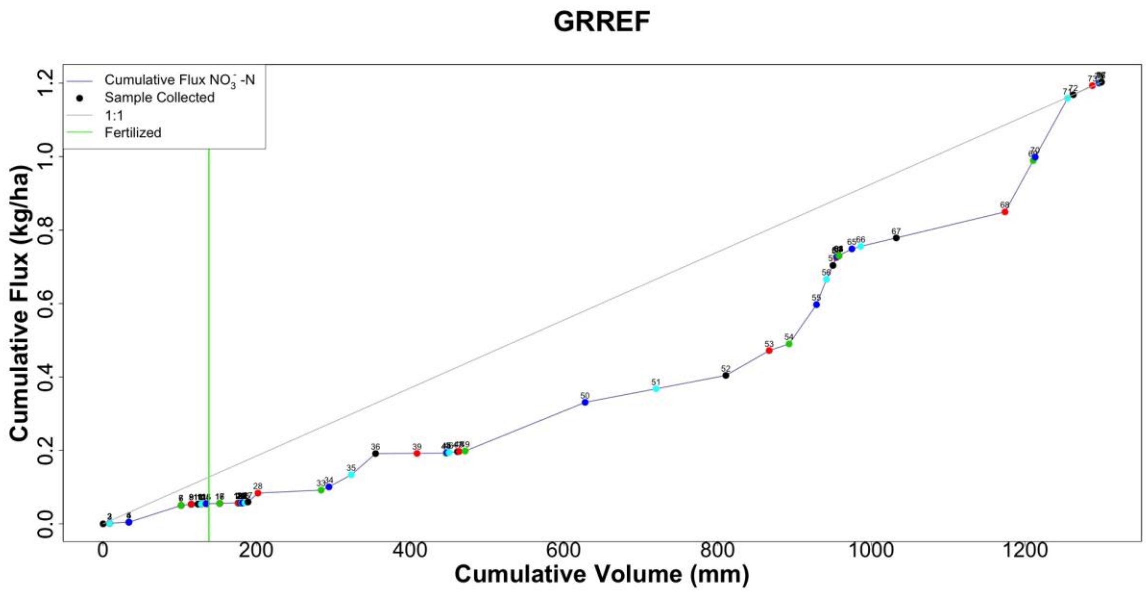

Figure G.51. Cumulative NO_3^--N load (kg ha^{-1}) of mature pine reference watershed (GRREF) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

Cumulative load: treatment versus control watershed (GR1) (2011 to 2014)

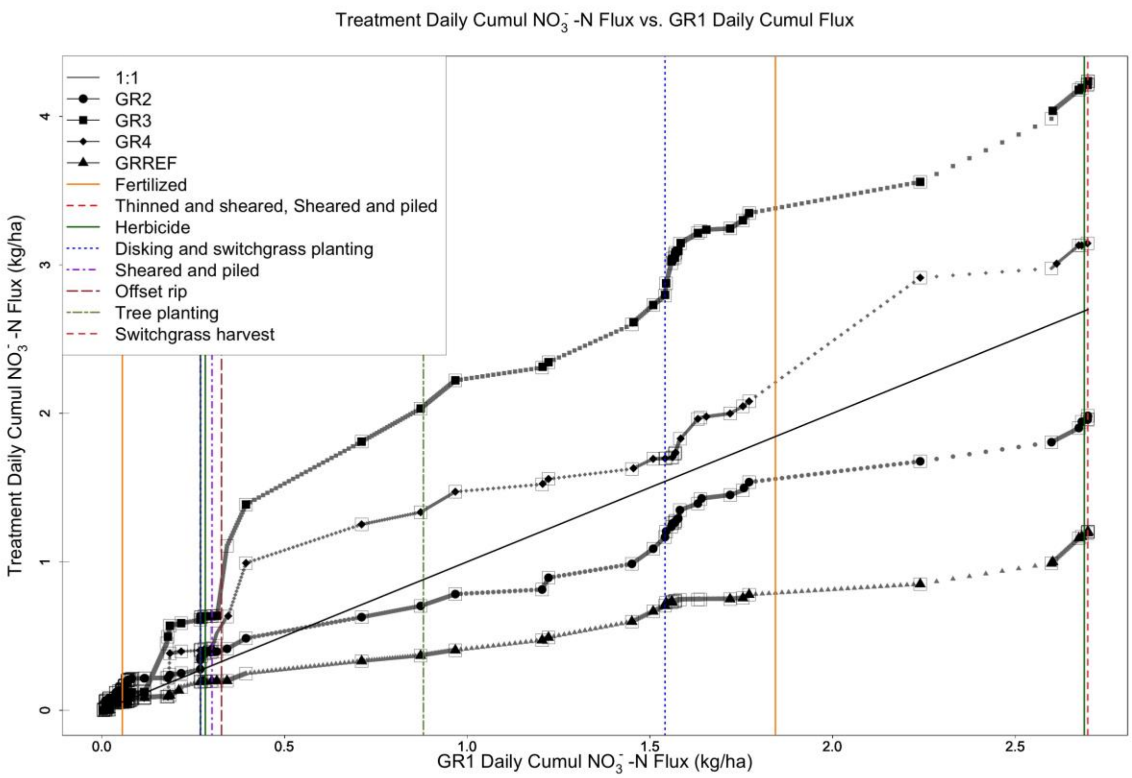

Figure G.52. Daily cumulative NO_3^--N load (kg ha^{-1}) of all watersheds (GR2, GR3, GR4, GRREF) as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

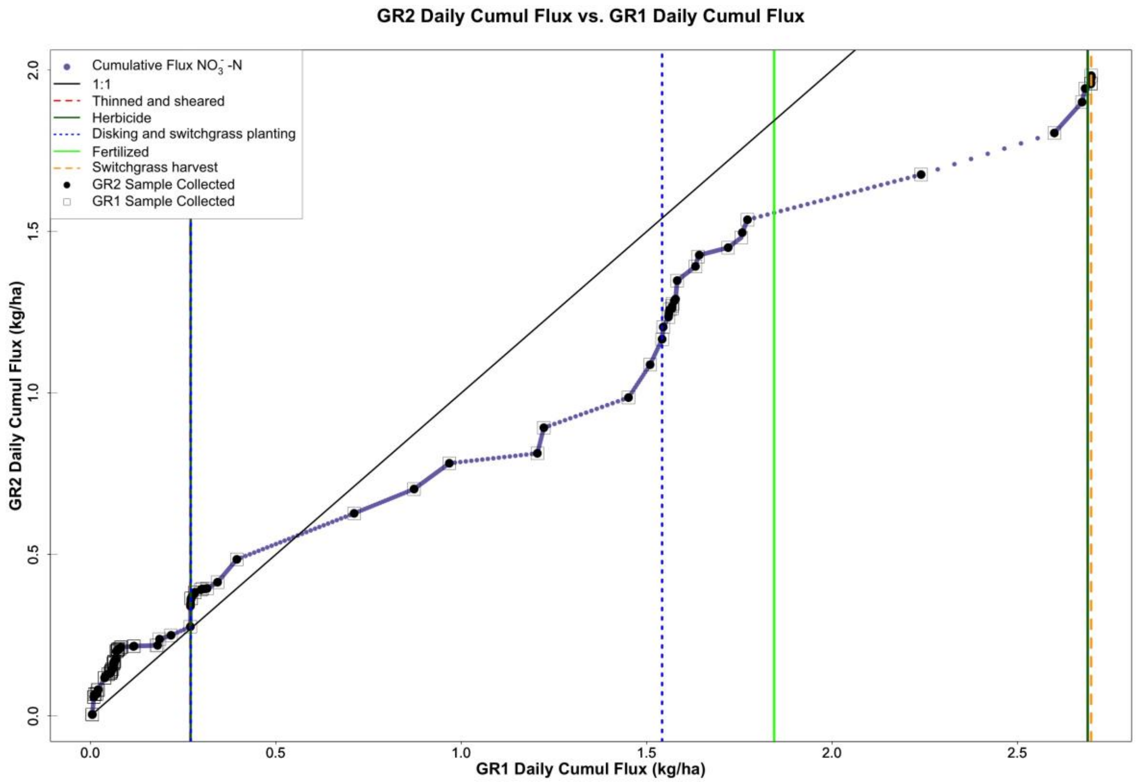

Figure G.53. Daily cumulative NO_3^--N load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

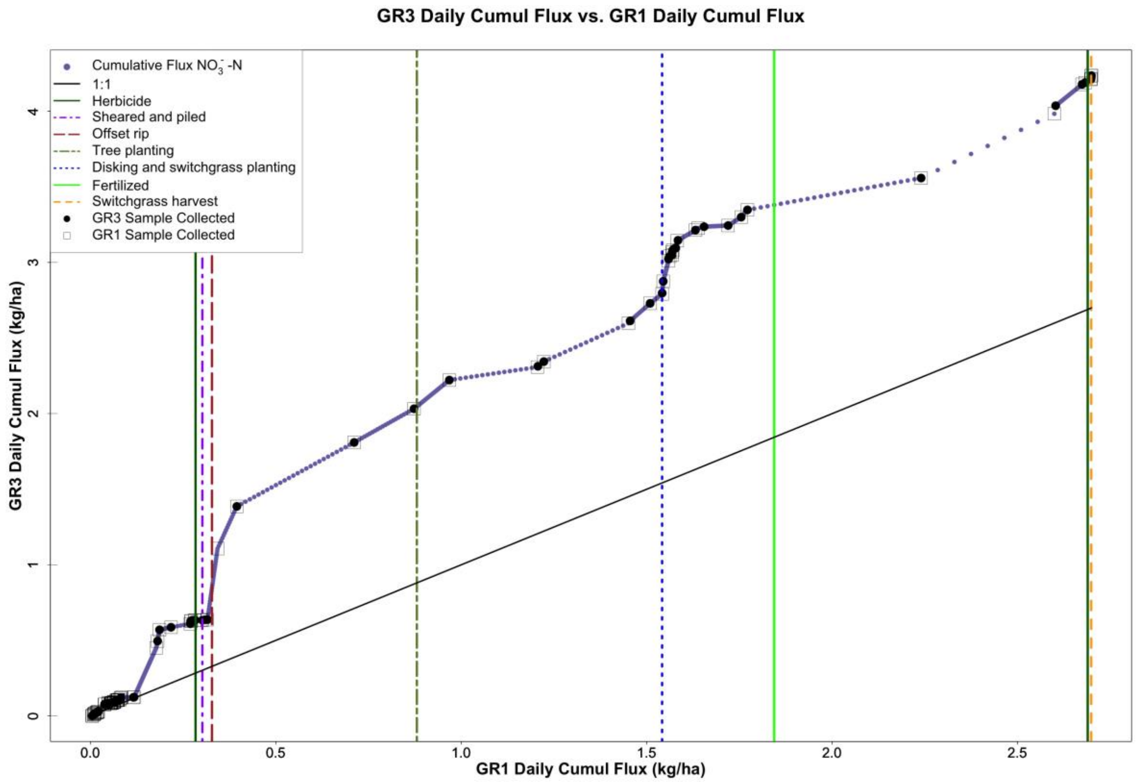

Figure G.54. Daily cumulative NO_3^--N load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

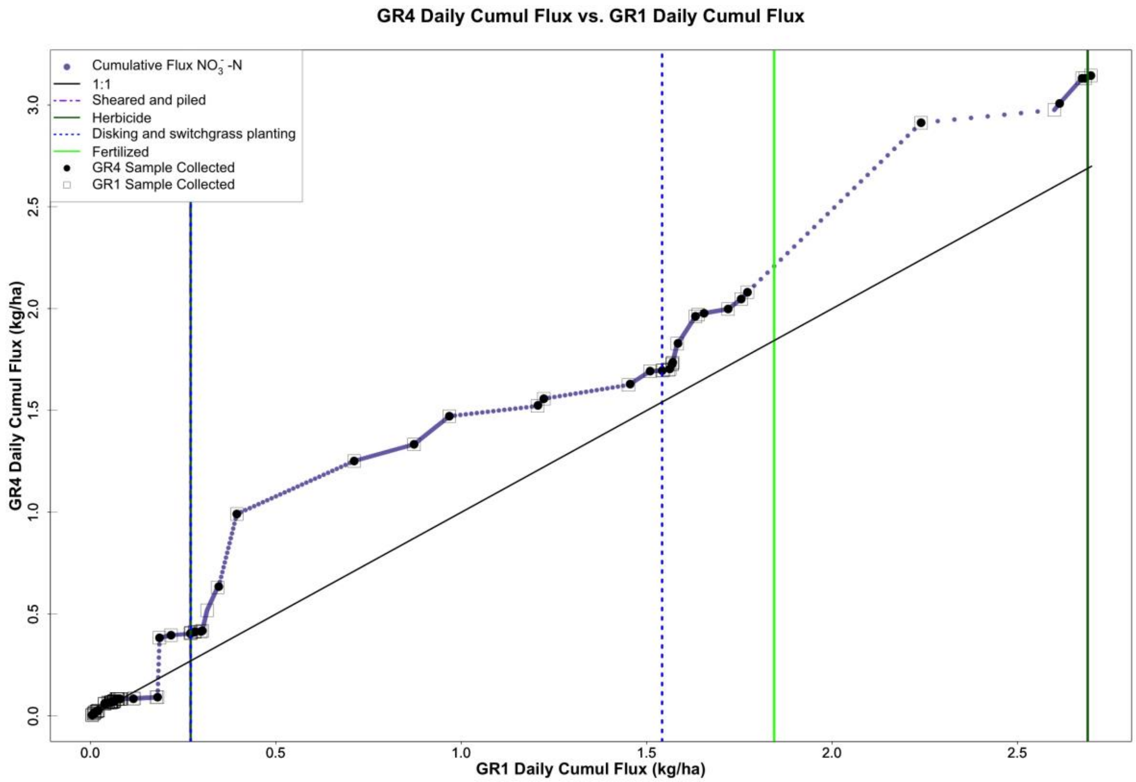

Figure G.55. Daily cumulative NO_3^--N load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

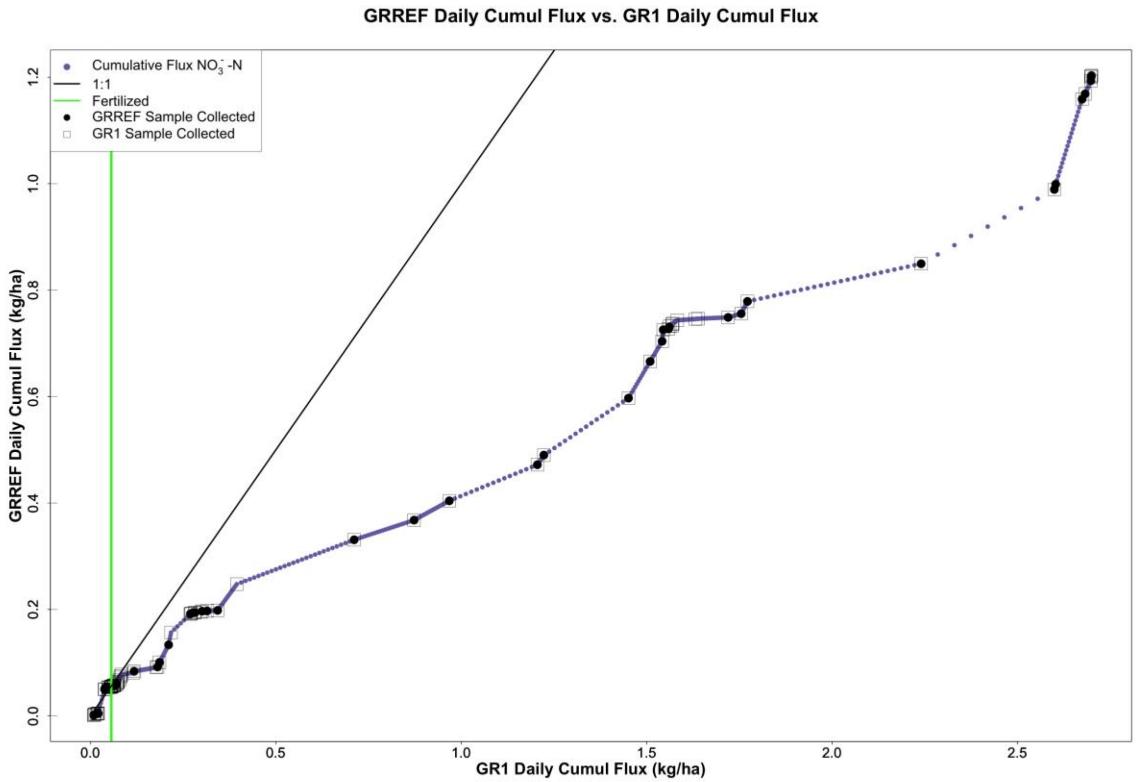

Figure G.56. Daily cumulative NO_3^--N load (kg ha^{-1}) of watershed GRREF as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

__Cumulative load: treatment versus mature reference watershed (GRREF) (2011 to 2014)__

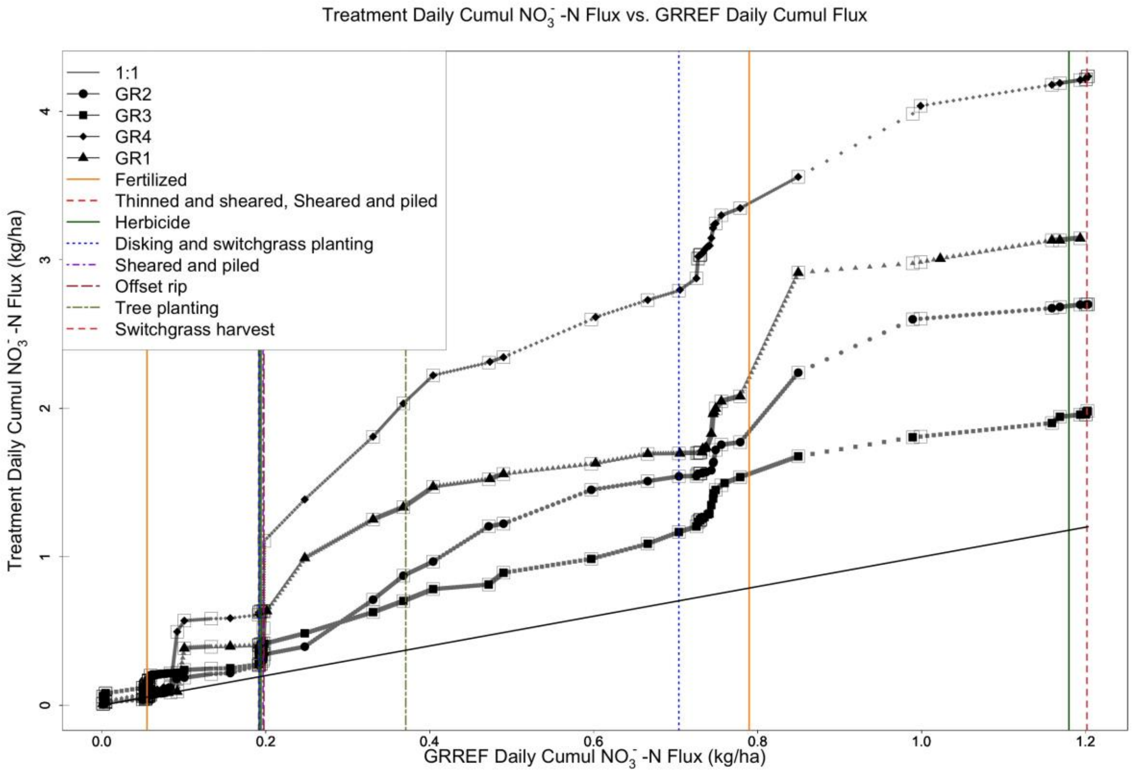

Figure G.57. Daily cumulative NO_3^--N load (kg ha^{-1}) of all watersheds (GR1, GR2, GR3, GR4) as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

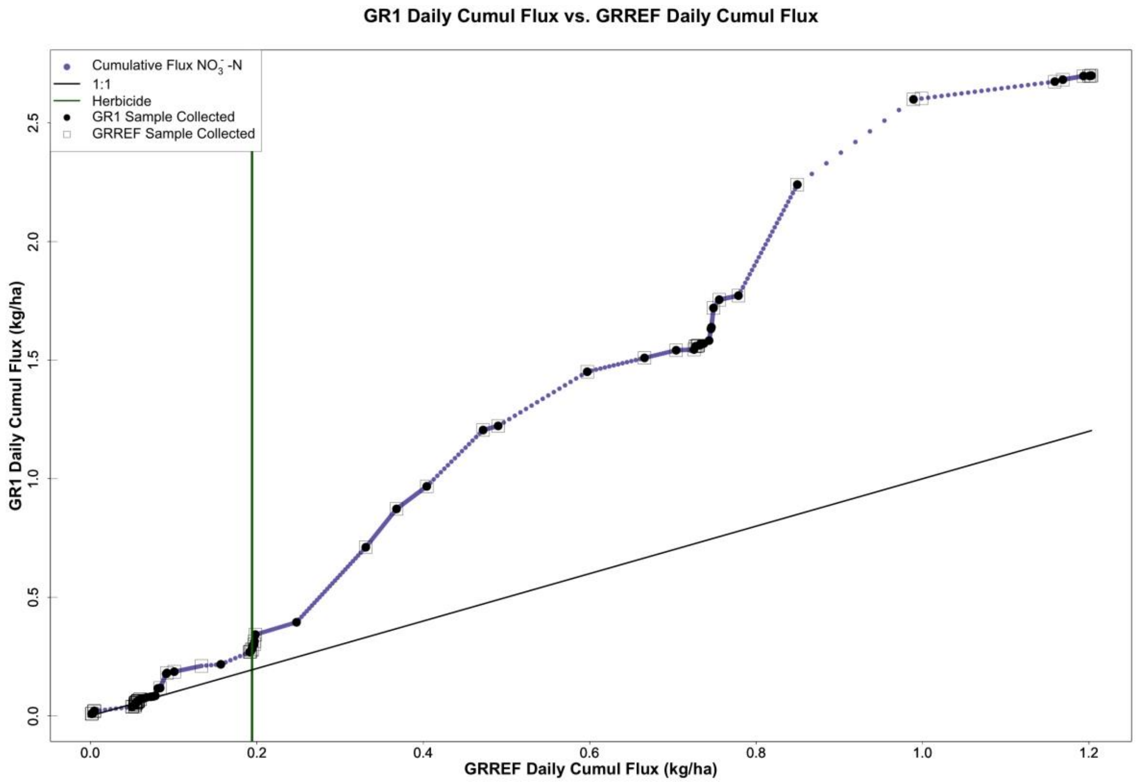

Figure G.58. Daily cumulative NO_3^--N load (kg ha^{-1}) of watershed GR1 as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

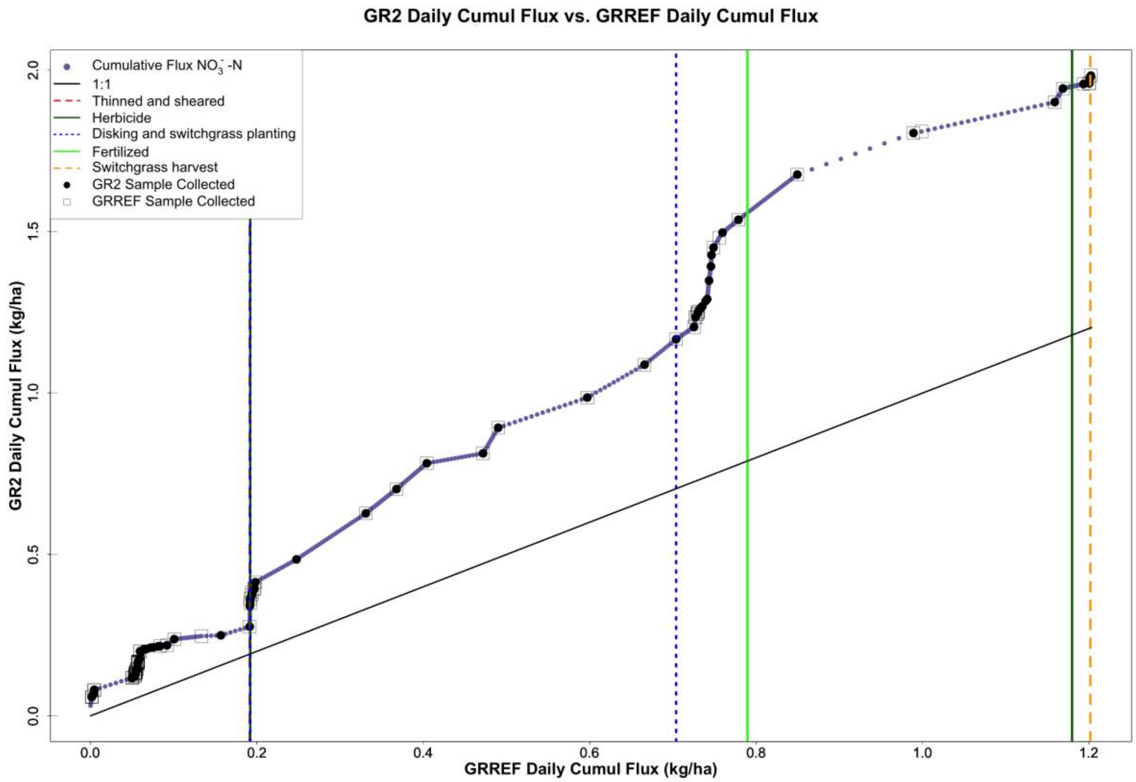

Figure G.59. Daily cumulative NO_3^--N load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

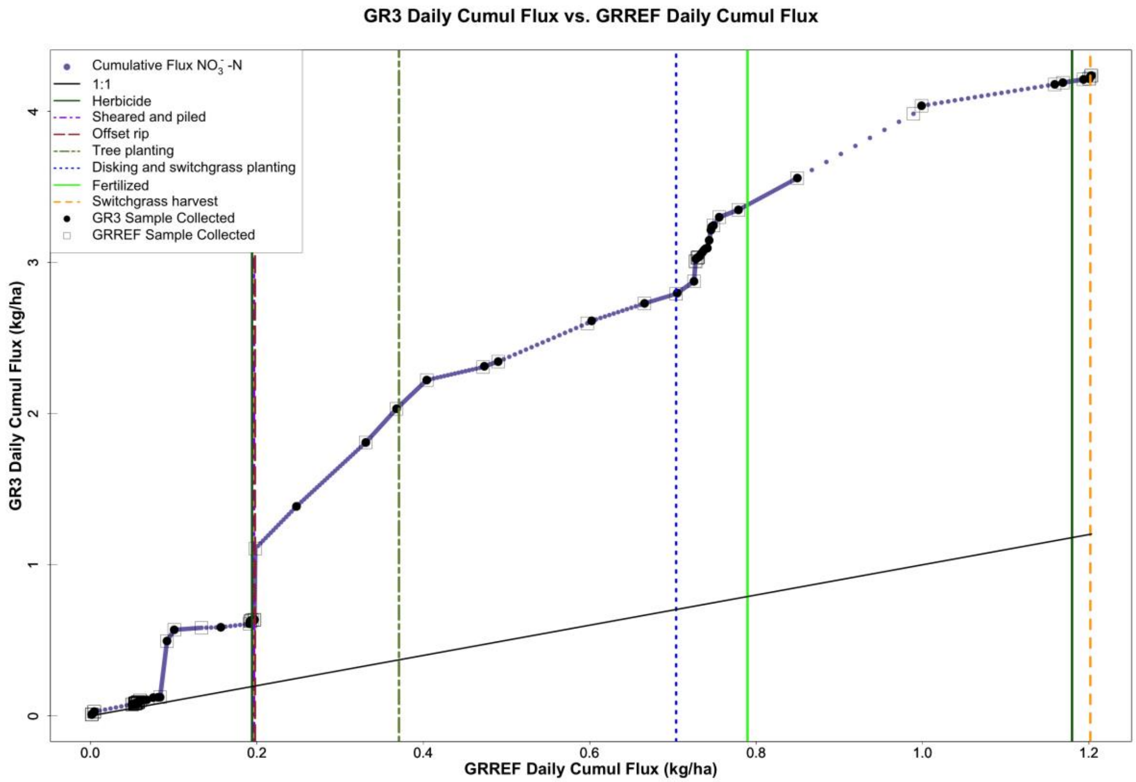

Figure G.60. Daily cumulative NO_3^--N load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

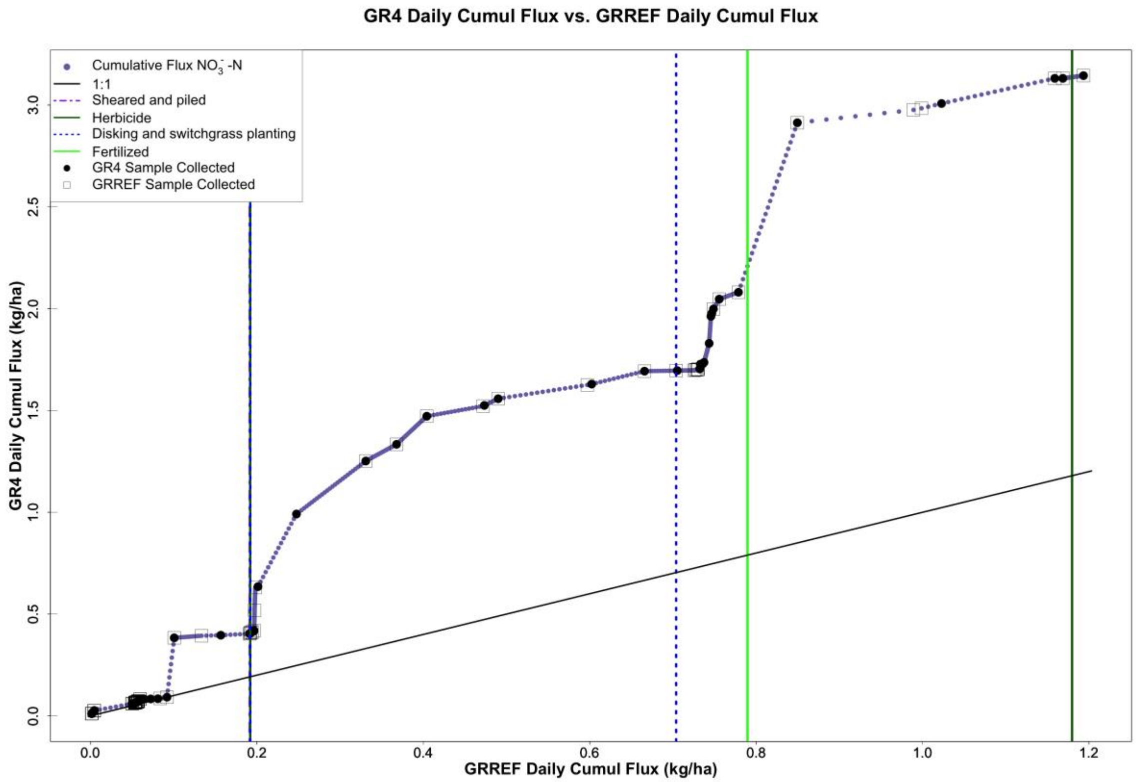

Figure G.61. Daily cumulative NO_3^--N load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative NO_3^--N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

G.4 Ammonium (NH_4^+-N)

Cumulative load over time with hydrograph (2011-2014)

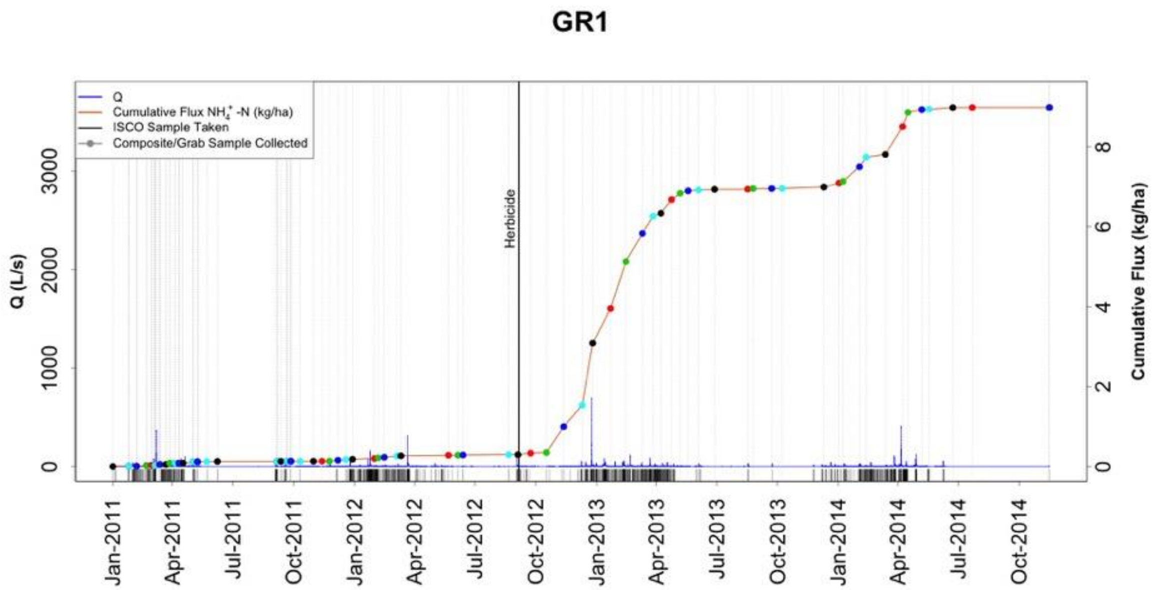

Figure G.62. Cumulative NH_4^+-N flux over time (Jan 2011 to Nov 2014) in watershed GR1, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

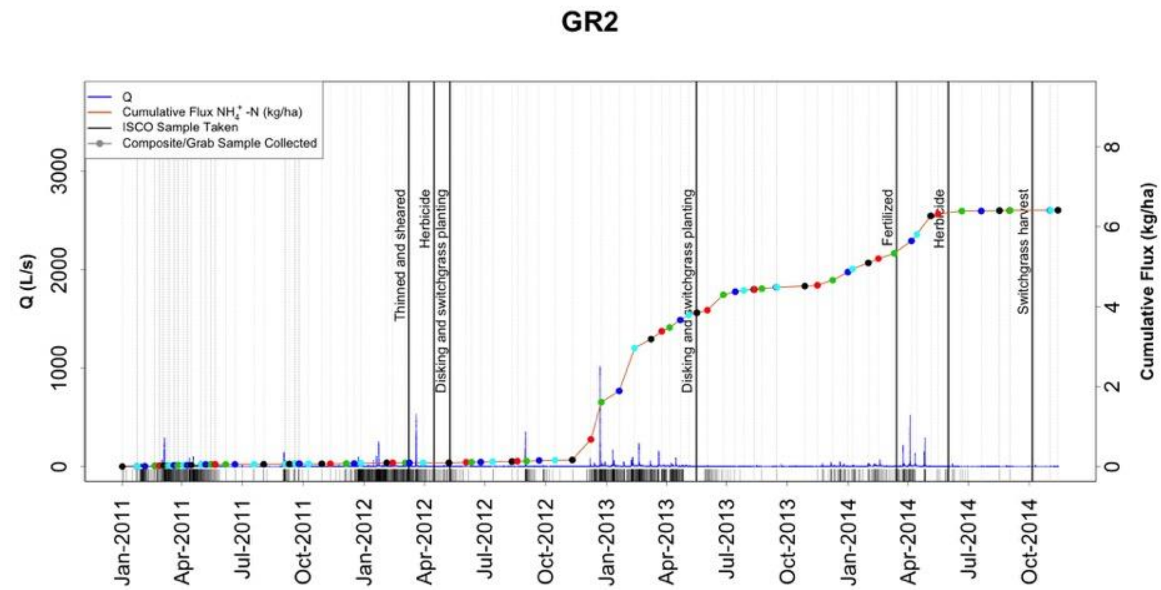

Figure G.63. Cumulative NH_4^+-N flux over time (Jan 2011 to Nov 2014) in watershed GR2, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

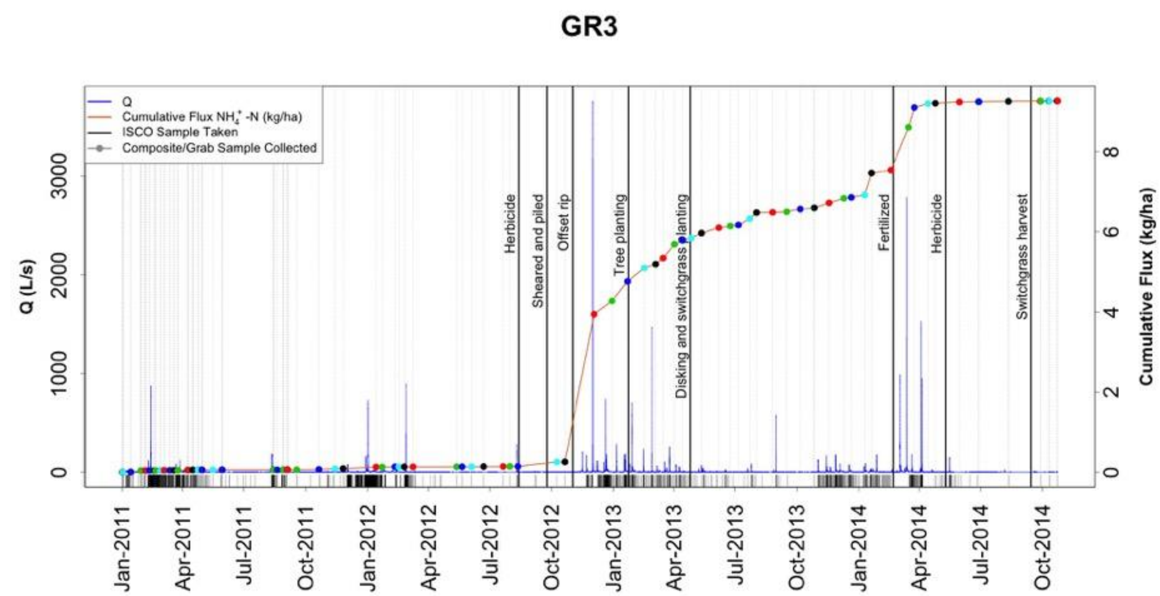

Figure G.64. Cumulative NH_4^+-N flux over time (Jan 2011 to Nov 2014) in watershed GR3, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

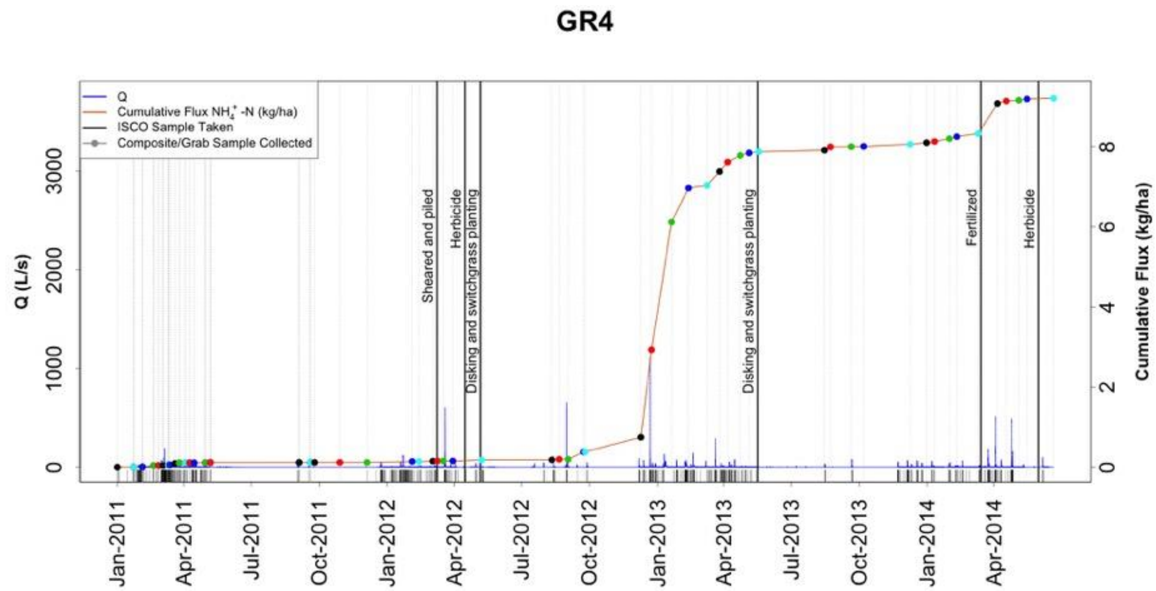

Figure G.65. Cumulative NH_4^+-N flux over time (Jan 2011 to Nov 2014) in watershed GR4, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

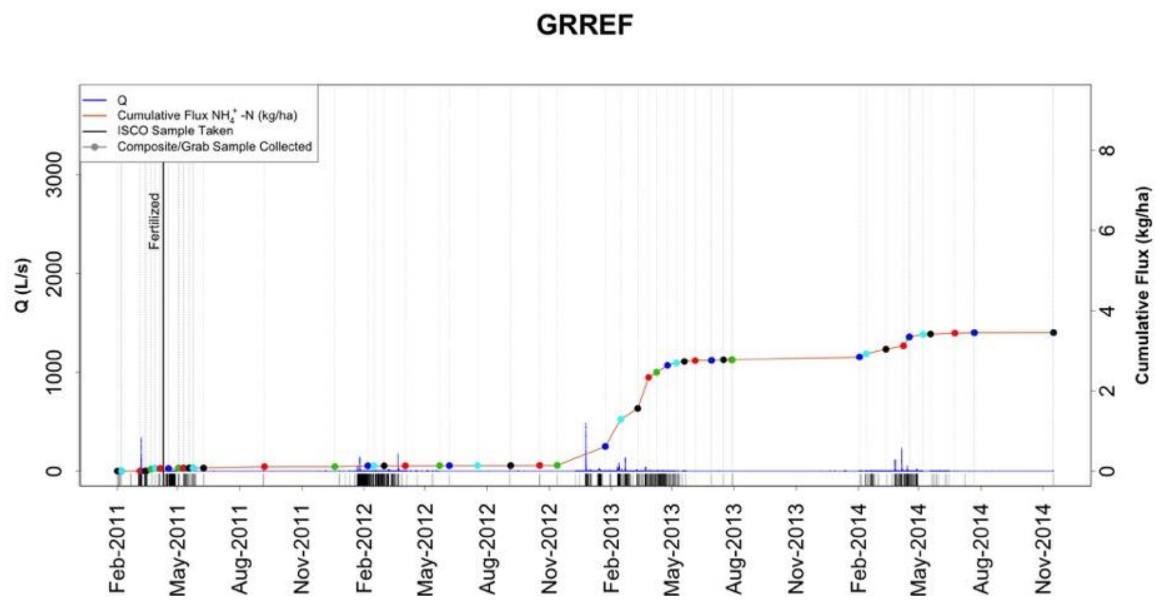

Figure G.66. Cumulative NH_4^+-N flux over time (Jan 2011 to Nov 2014) in watershed GRREF, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

Cumulative load versus cumulative volume (2011-2014)

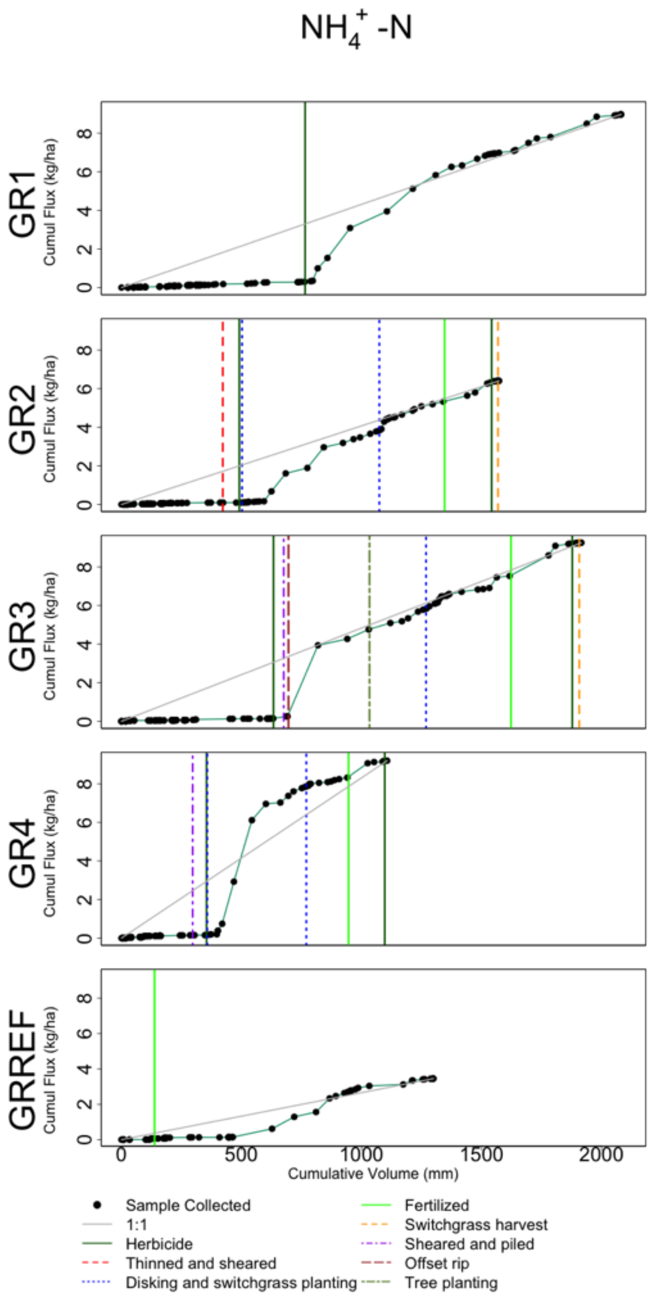

Figure G.67. Cumulative NH_4^+-N flux (kg ha^{-1}) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

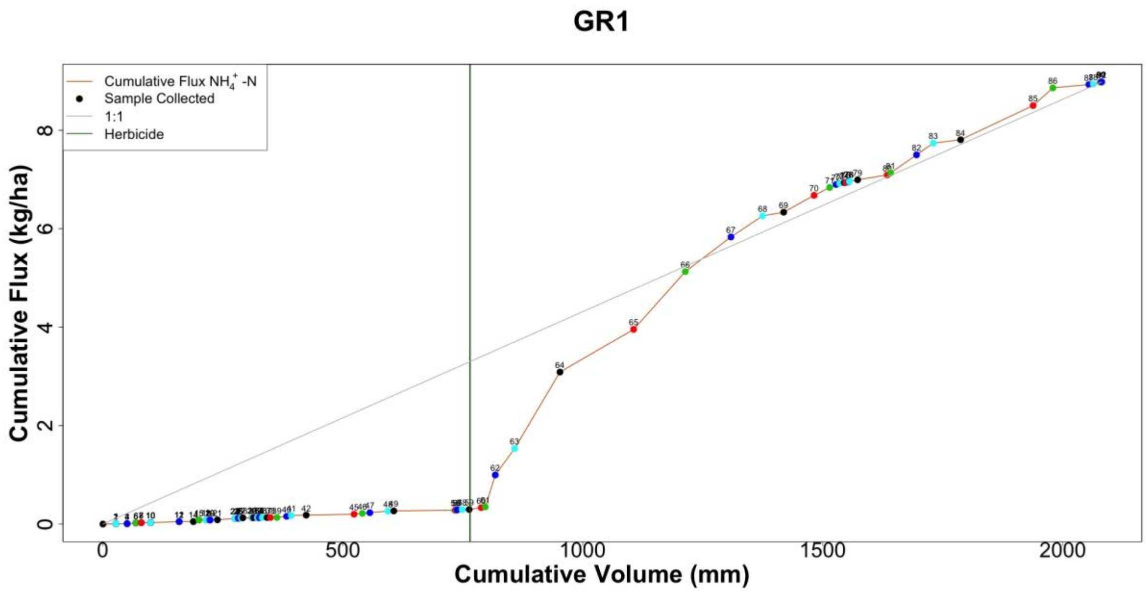

Figure G.68. Cumulative NH_4^+-N load (kg ha^{-1}) of control watershed (GR1) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

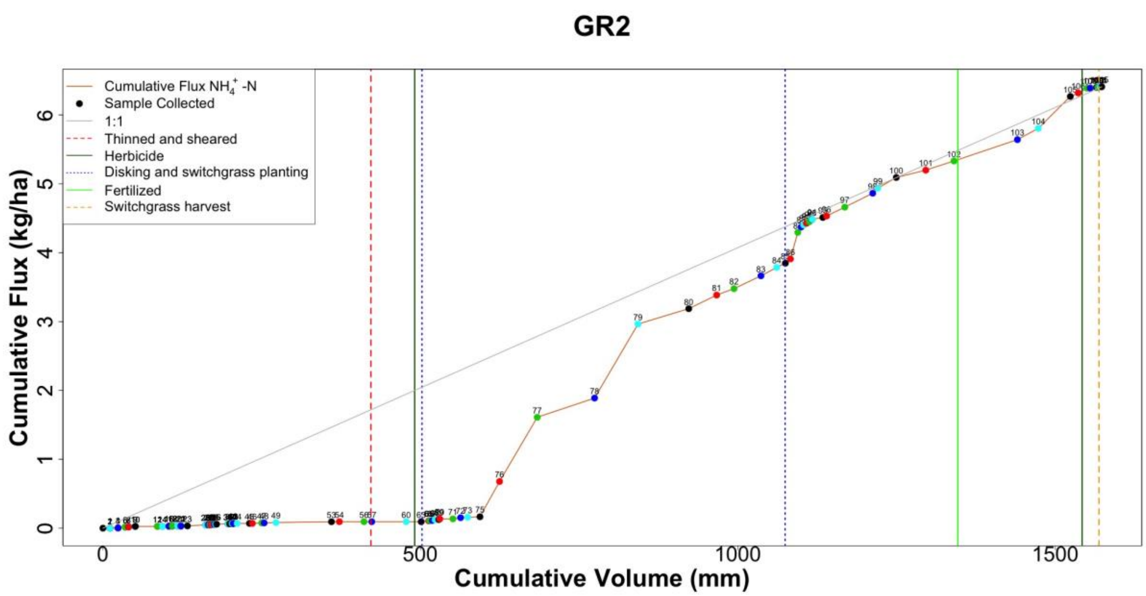

Figure G.69. Cumulative NH_4^+-N load (kg ha^{-1}) of intercropped/thinned watershed (GR2) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

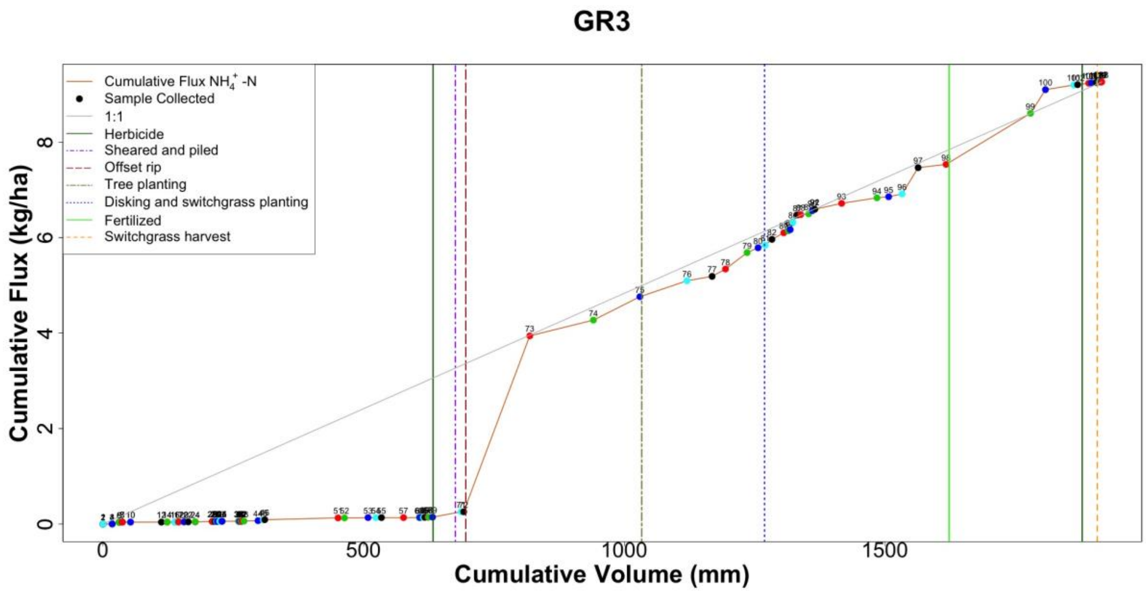

Figure G.70. Cumulative NH_4^+-N load (kg ha^{-1}) of intercropped/replanted watershed (GR3) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

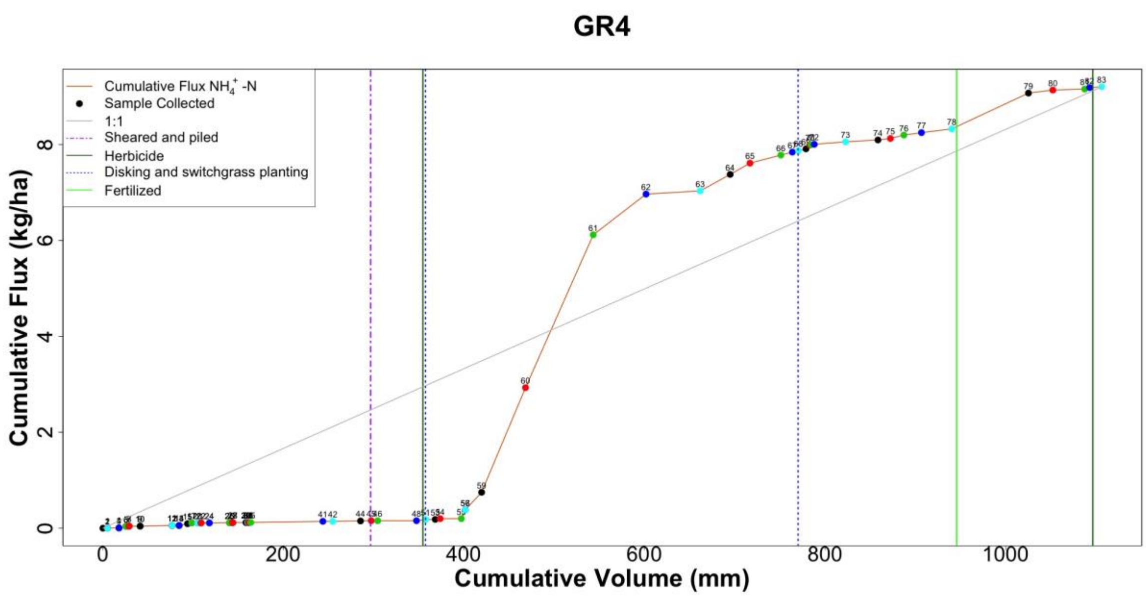

Figure G.71. Cumulative NH_4^+-N load (kg ha^{-1}) of switchgrass watershed (GR4) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

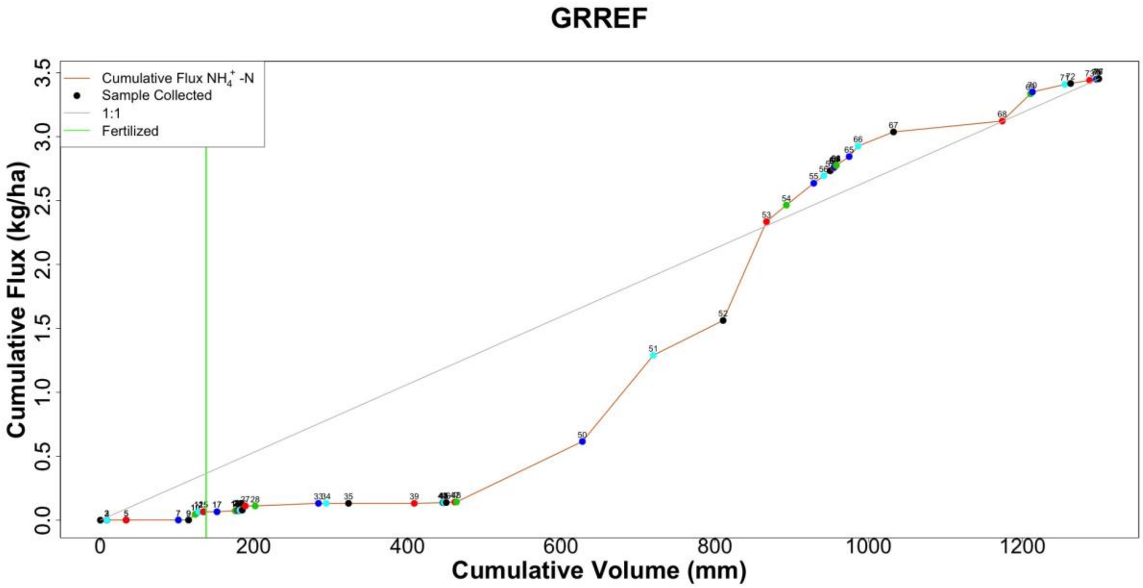

Figure G.72. Cumulative NH_4^+-N load (kg ha^{-1}) of mature pine reference watershed (GRREF) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

Cumulative load: treatment versus control watershed (GR1) (2011 to 2014)

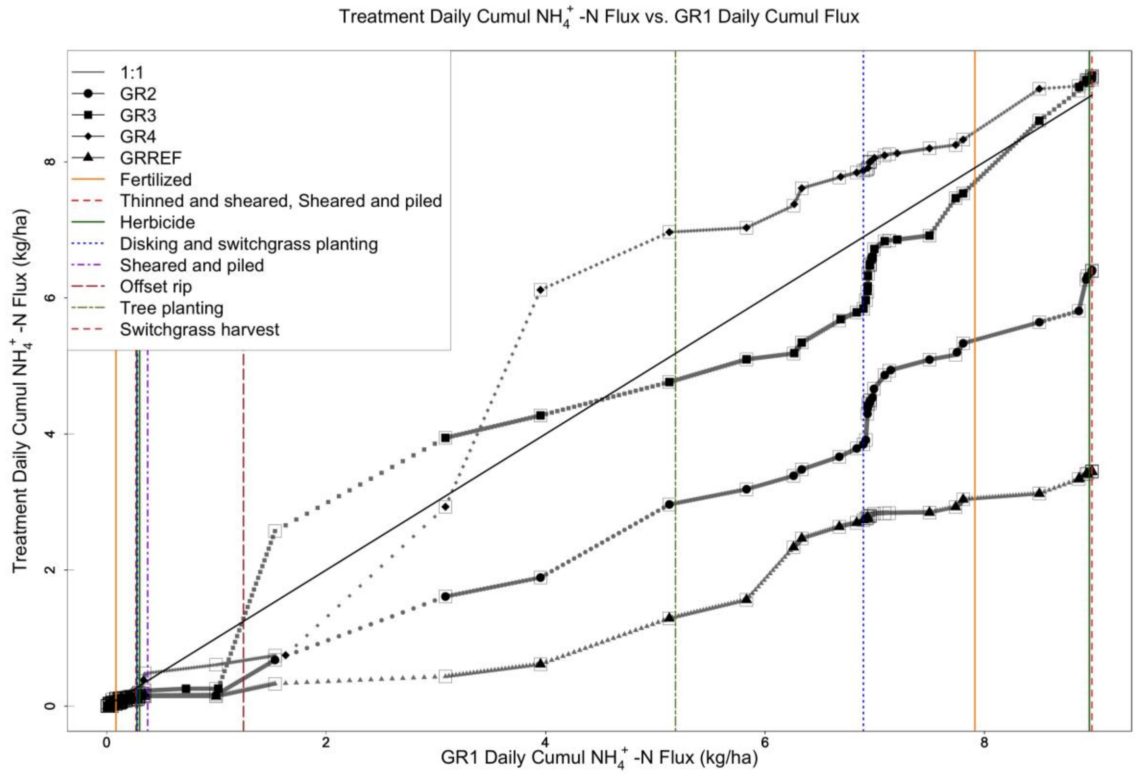

Figure G.73. Daily cumulative NH_4^+-N load (kg ha^{-1}) of all watersheds (GR2, GR3, GR4, GRREF) as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

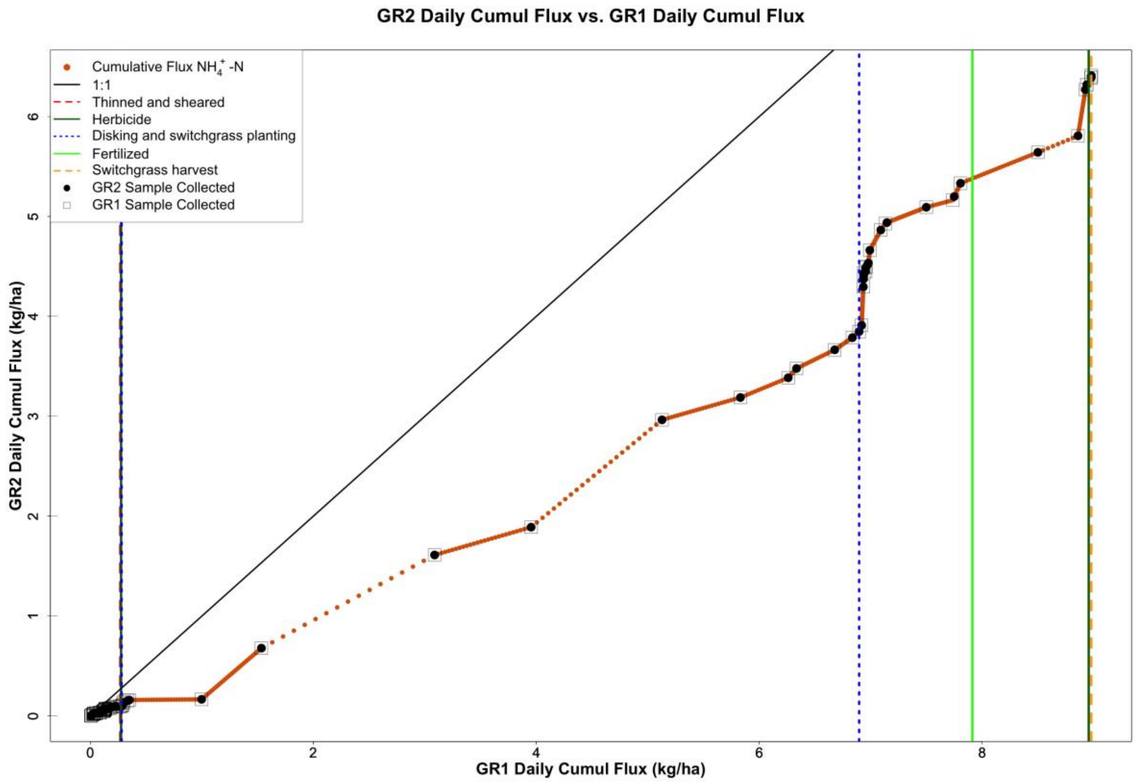

Figure G.74. Daily cumulative NH_4^+-N load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

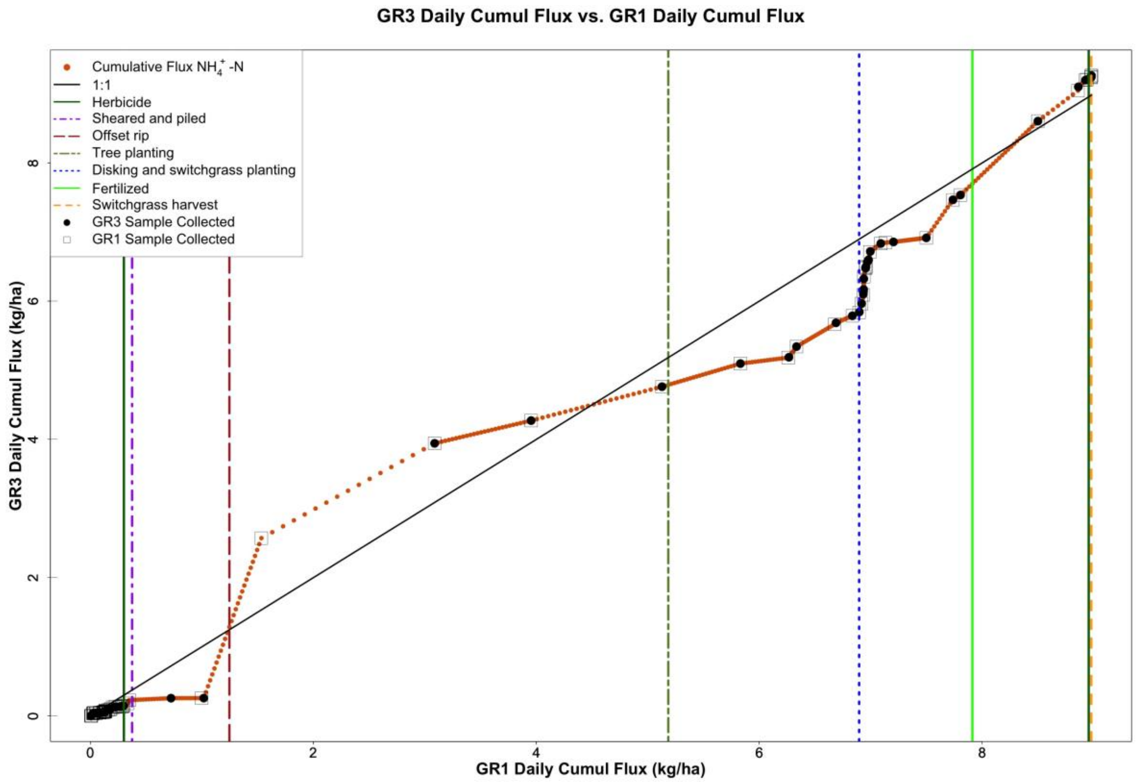

Figure G.75. Daily cumulative NH_4^+-N load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

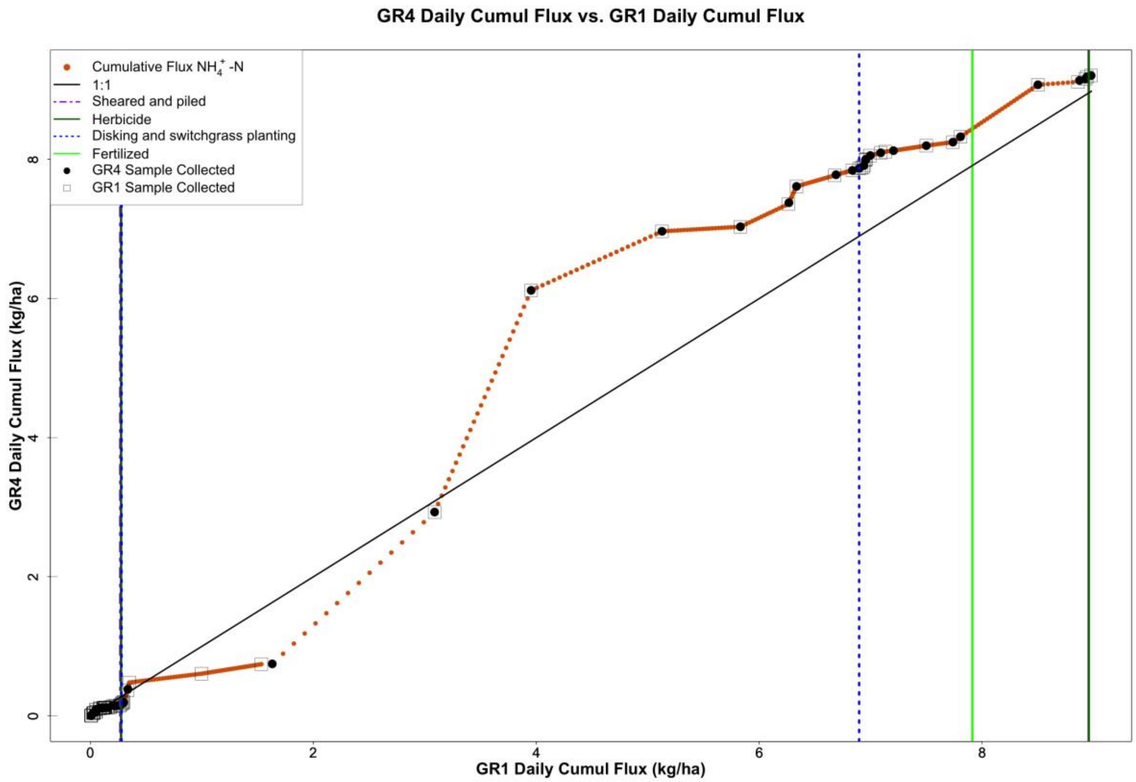

Figure G.76. Daily cumulative NH_4^+-N load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

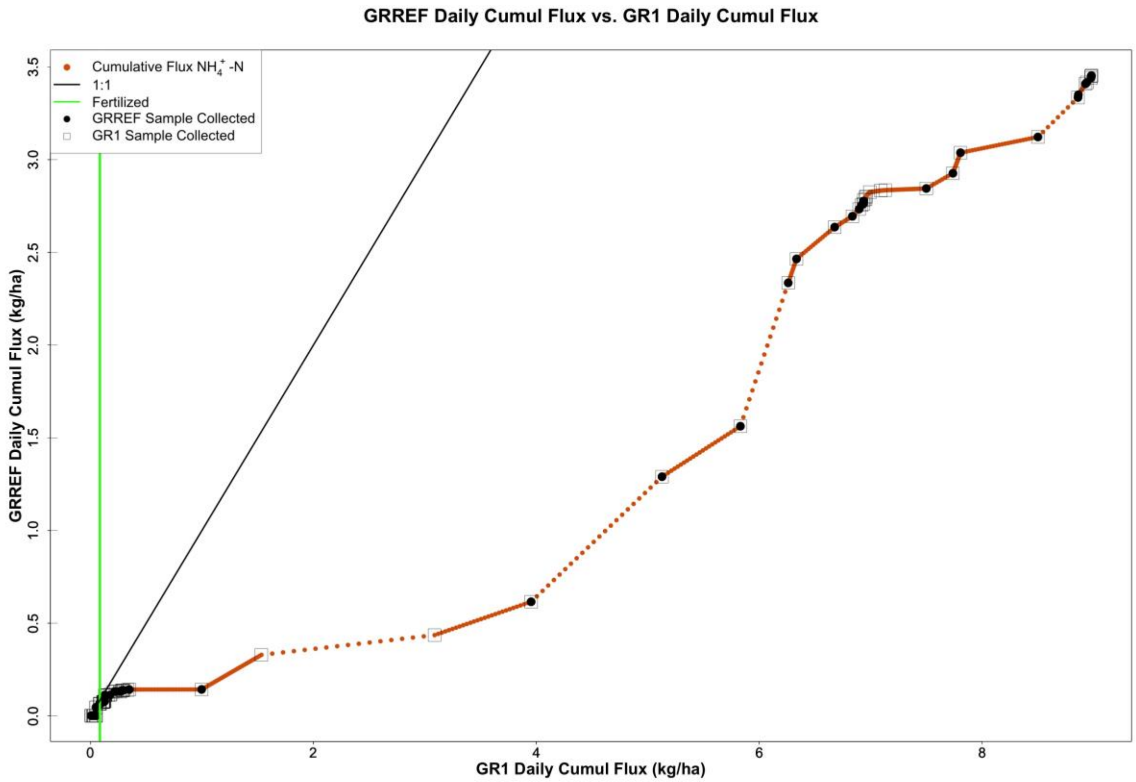

Figure G.77. Daily cumulative NH_4^+-N load (kg ha^{-1}) of watershed GRREF as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

Cumulative load: treatment versus mature reference watershed (GRREF) (2011 to 2014)

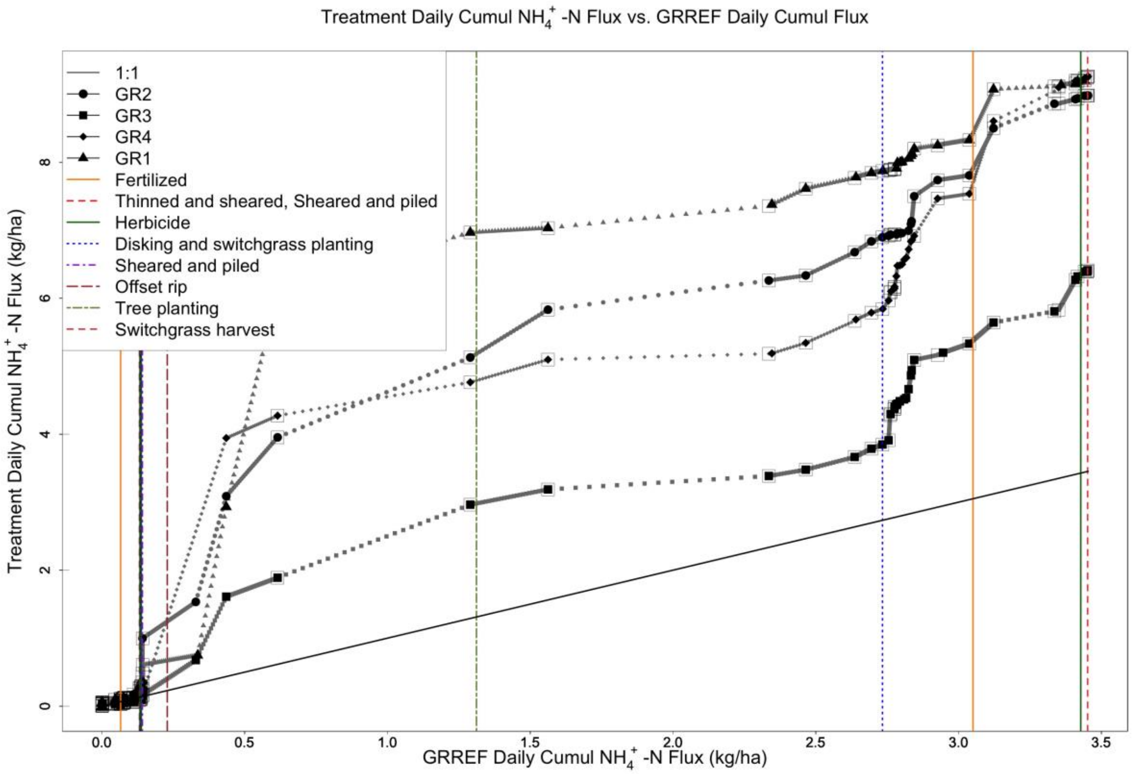

Figure G.78. Daily cumulative NH_4^+-N load (kg ha^{-1}) of all watersheds (GR1, GR2, GR3, GR4) as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

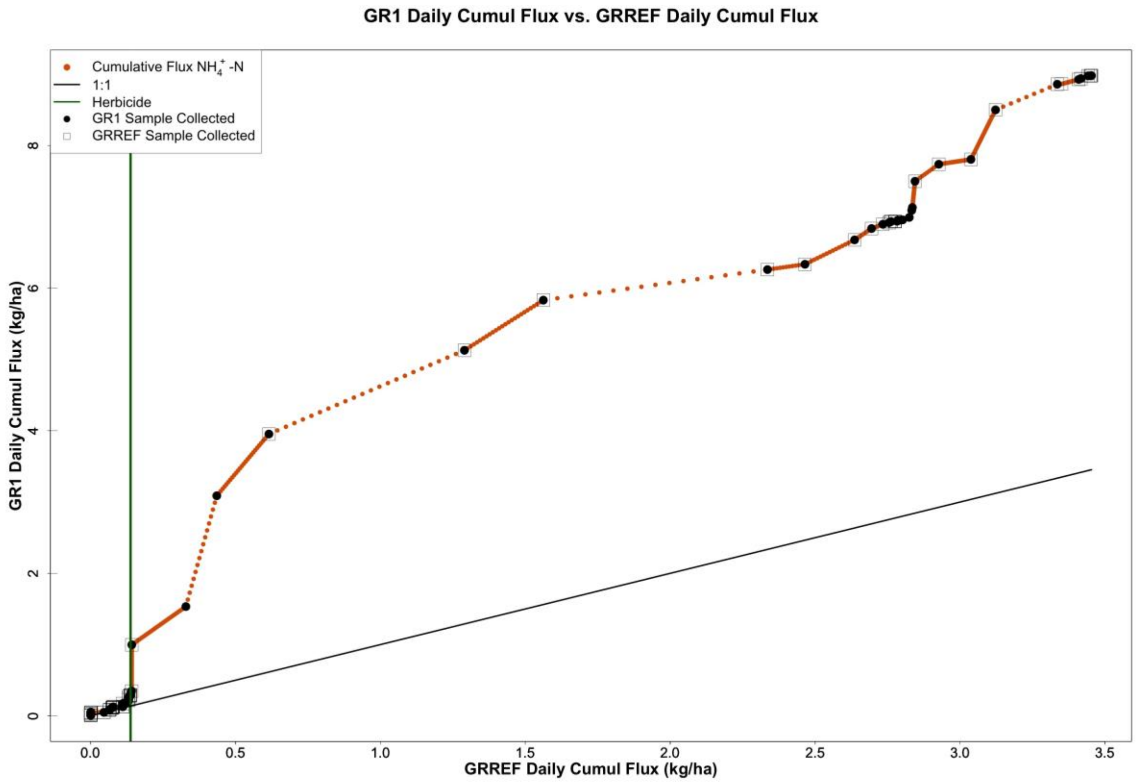

Figure G.79. Daily cumulative NH_4^+-N load (kg ha^{-1}) of watershed GR1 as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

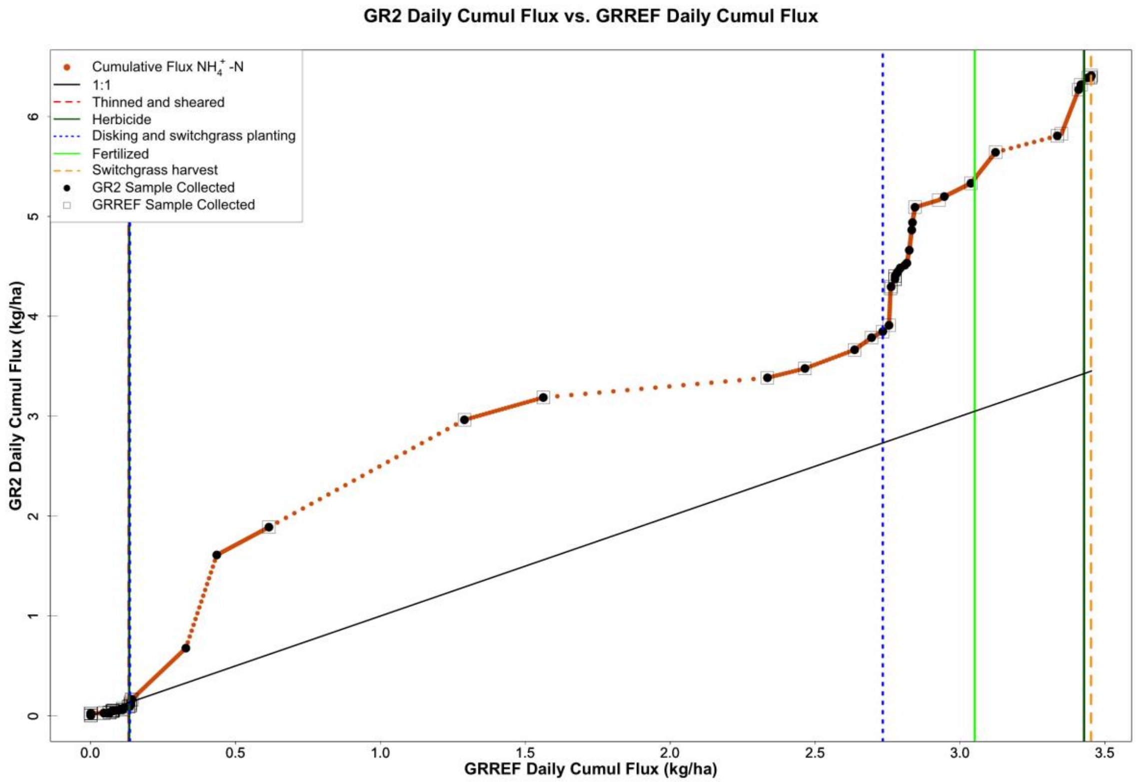

Figure G.80. Daily cumulative NH_4^+-N load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

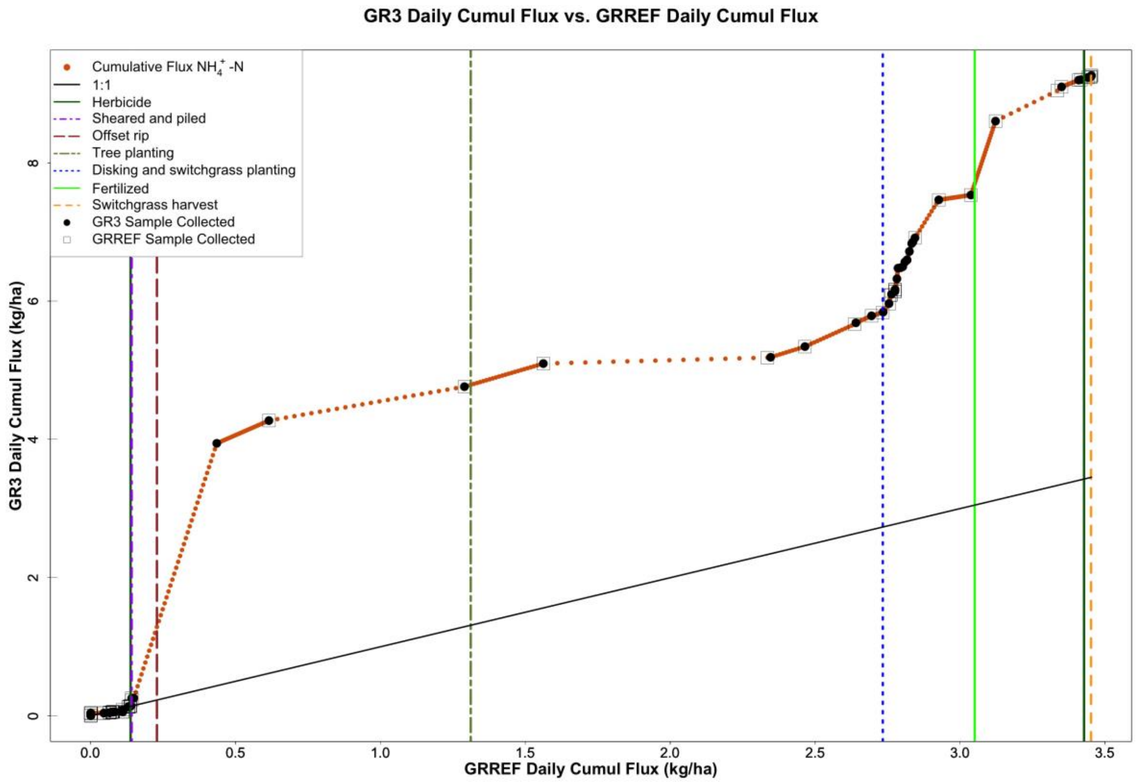

Figure G.81. Daily cumulative NH_4^+-N load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

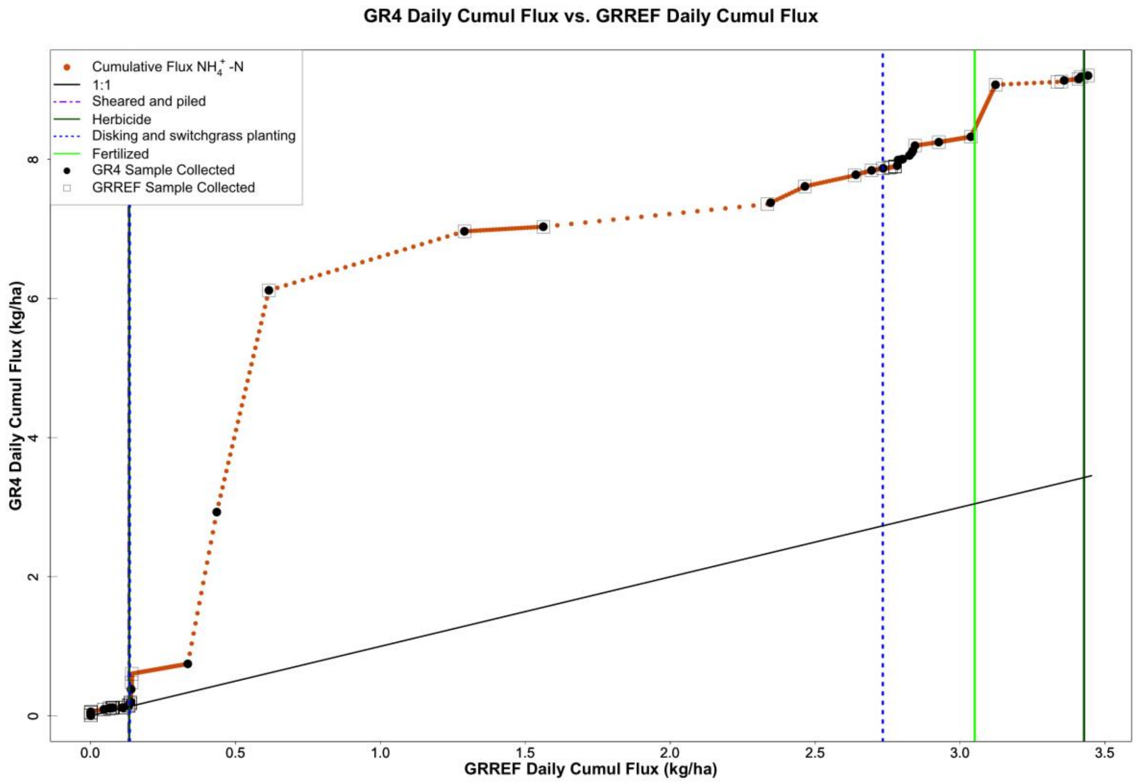

Figure G.82. Daily cumulative NH_4^+-N load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative NH_4^+-N load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

G.5 Total Kjeldahl Nitrogen (TKN)

Cumulative load over time with hydrograph (2011-2014)

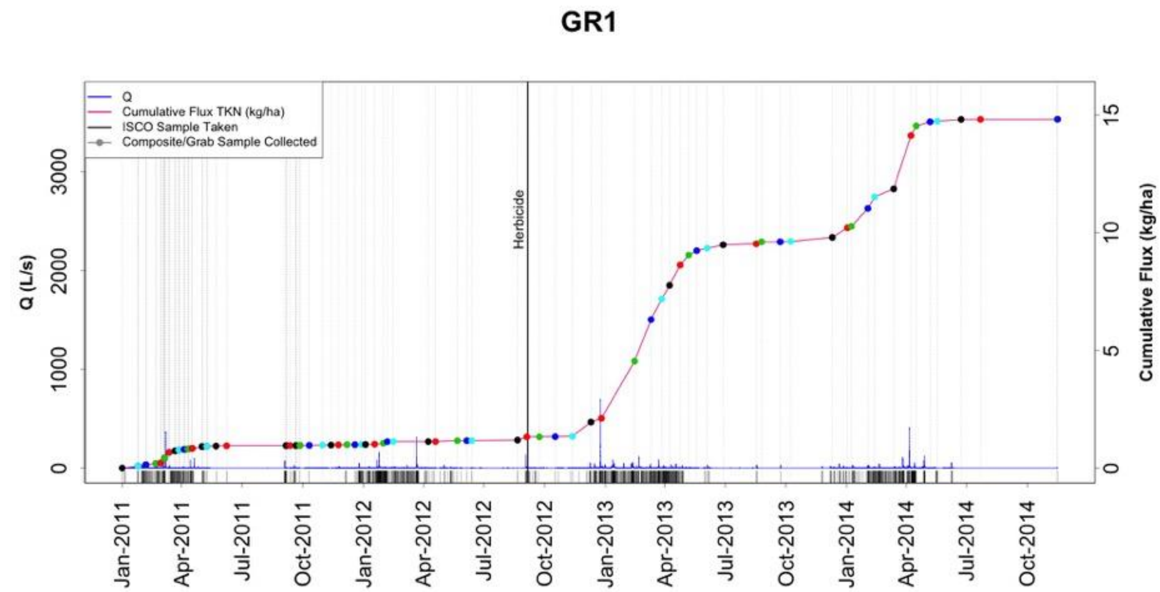

Figure G.83. Cumulative TKN flux over time (Jan 2011 to Nov 2014) in watershed GR1, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

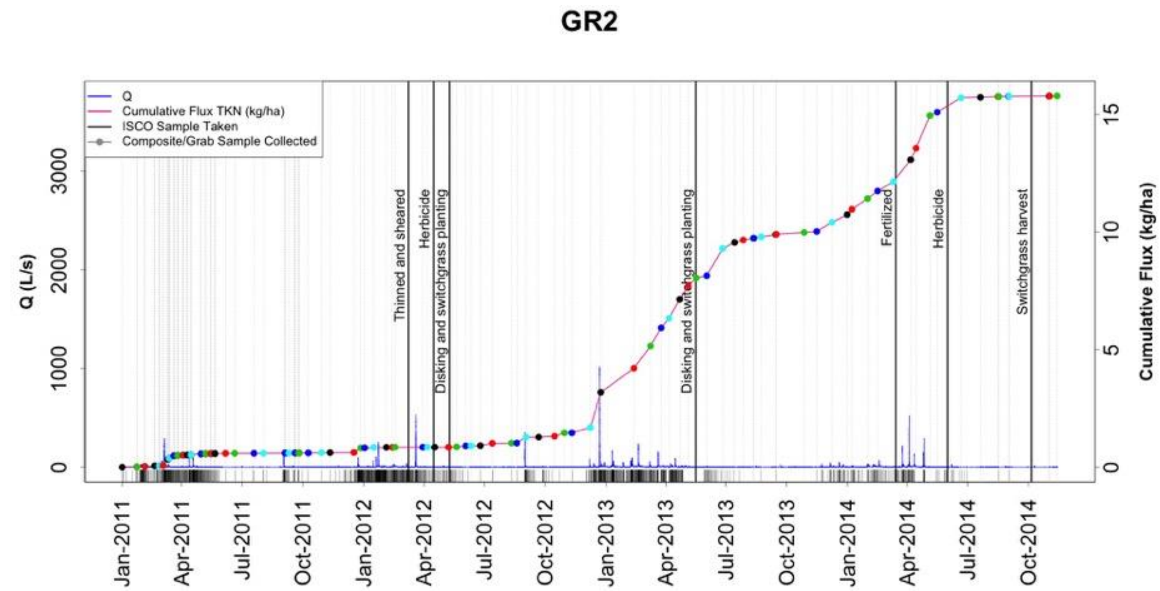

Figure G.84. Cumulative TKN flux over time (Jan 2011 to Nov 2014) in watershed GR2, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

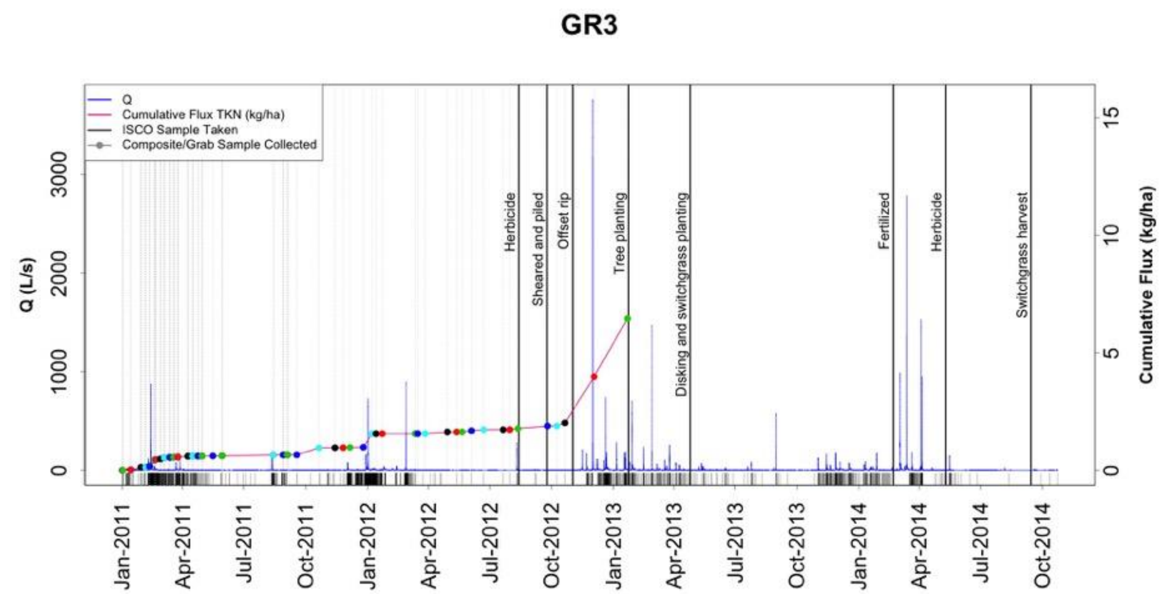

Figure G.85. Cumulative TKN flux over time (Jan 2011 to Nov 2014) in watershed GR3, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

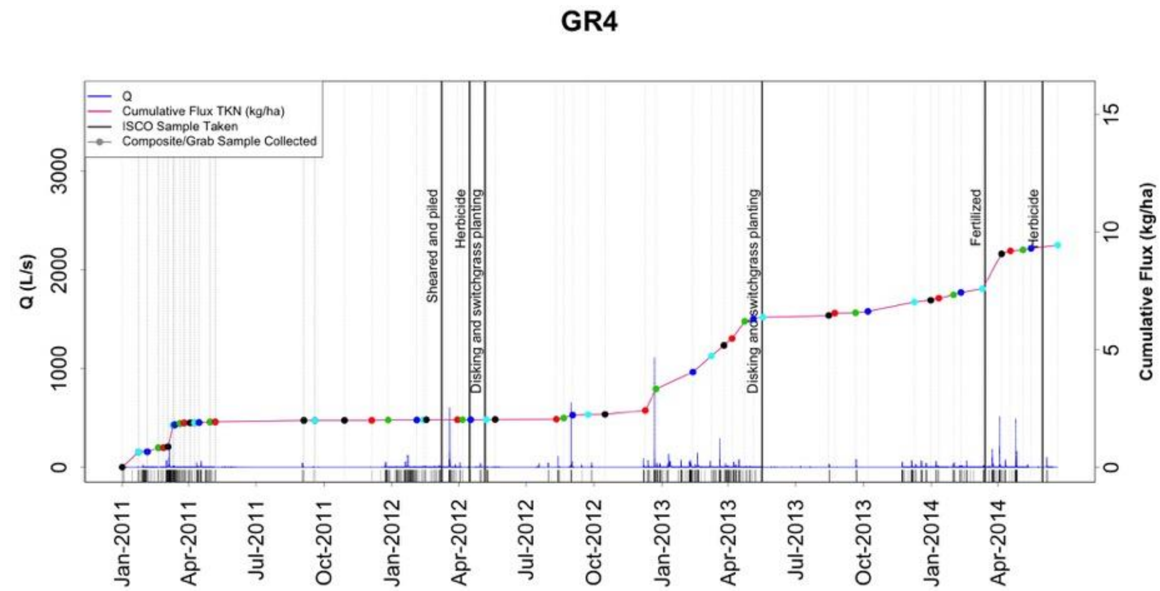

Figure G.86. Cumulative TKN flux over time (Jan 2011 to Nov 2014) in watershed GR4, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

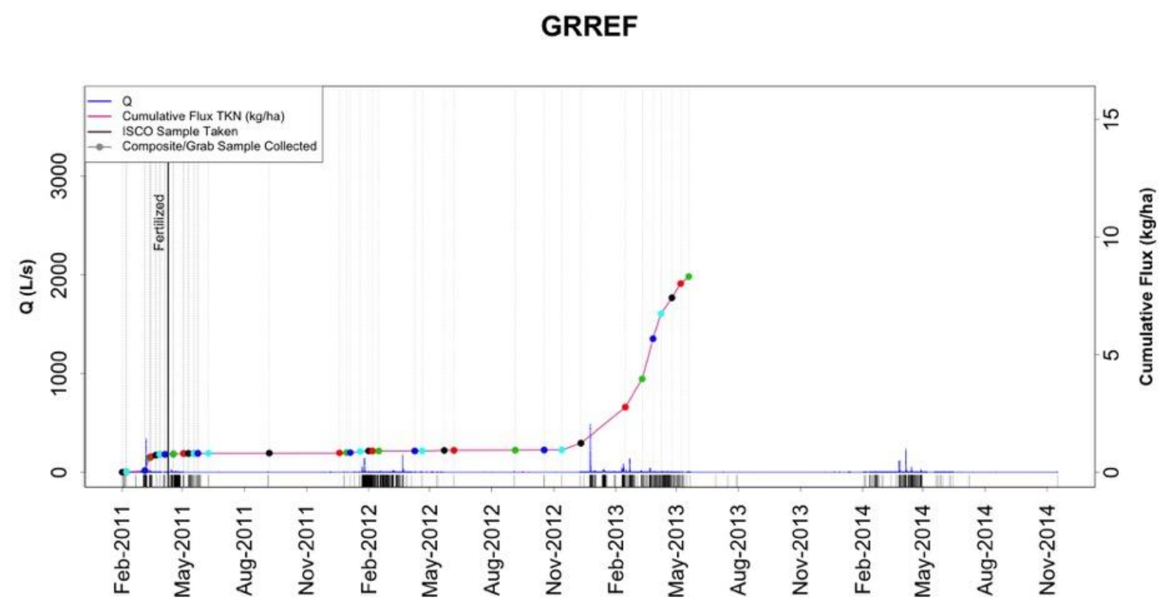

Figure G.87. Cumulative TKN flux over time (Jan 2011 to Nov 2014, missing data) in watershed GRREF, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

Cumulative load versus cumulative volume (2011-2014)

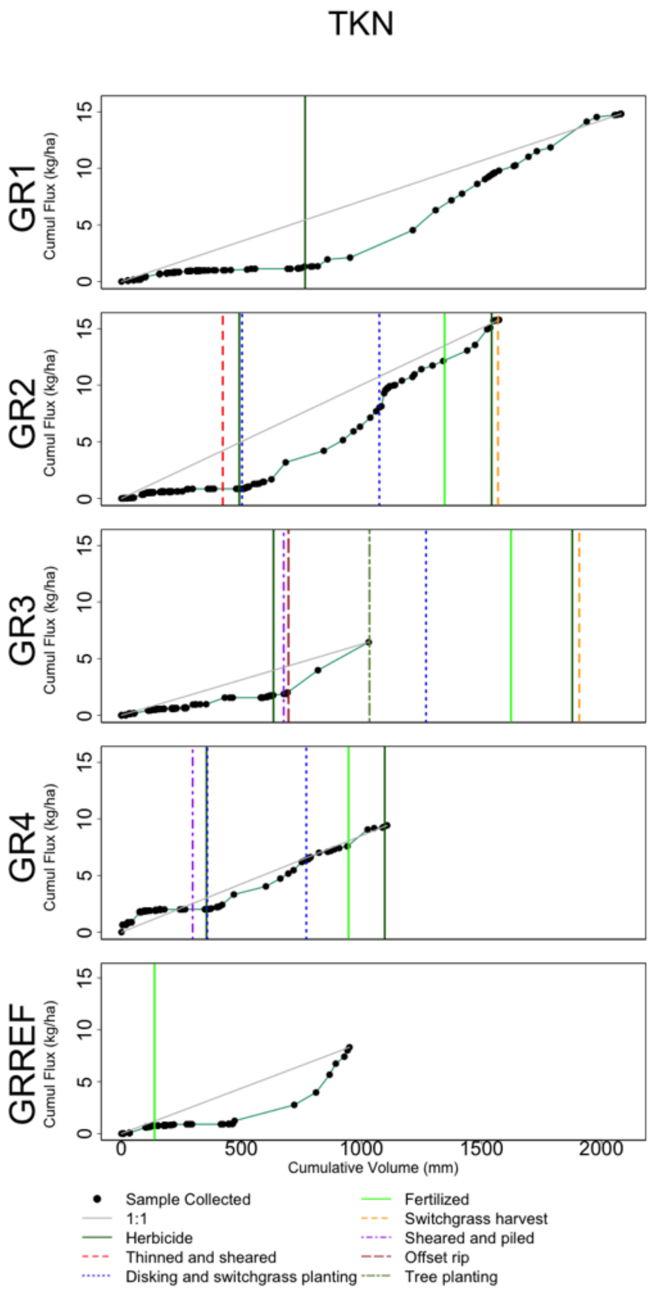

Figure G.88. Cumulative TKN flux (kg ha^{-1}) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

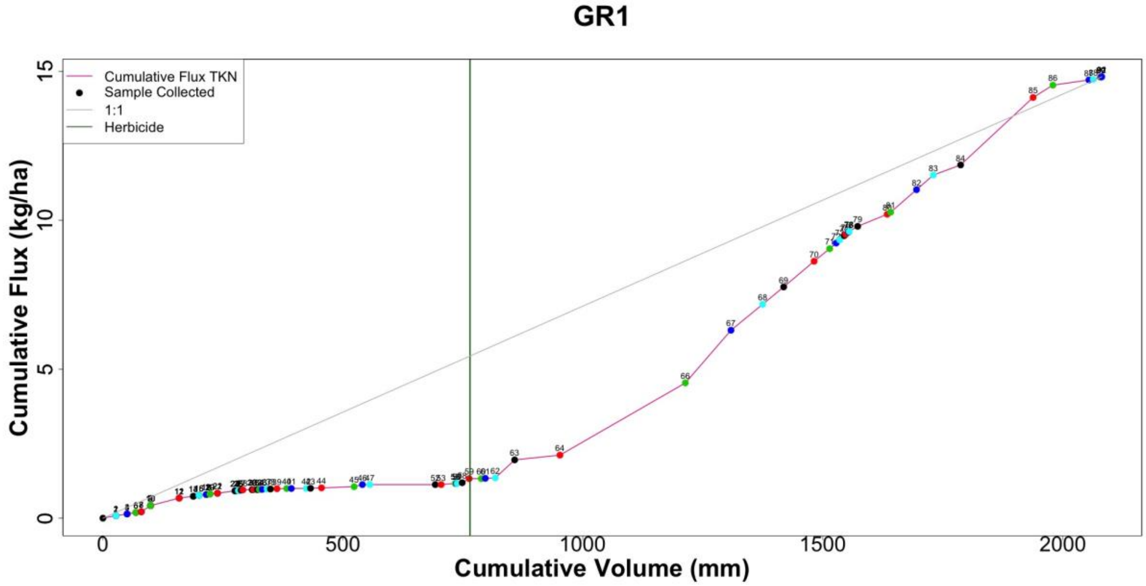

Figure G.89. Cumulative TKN load (kg ha^{-1}) of control watershed (GR1) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

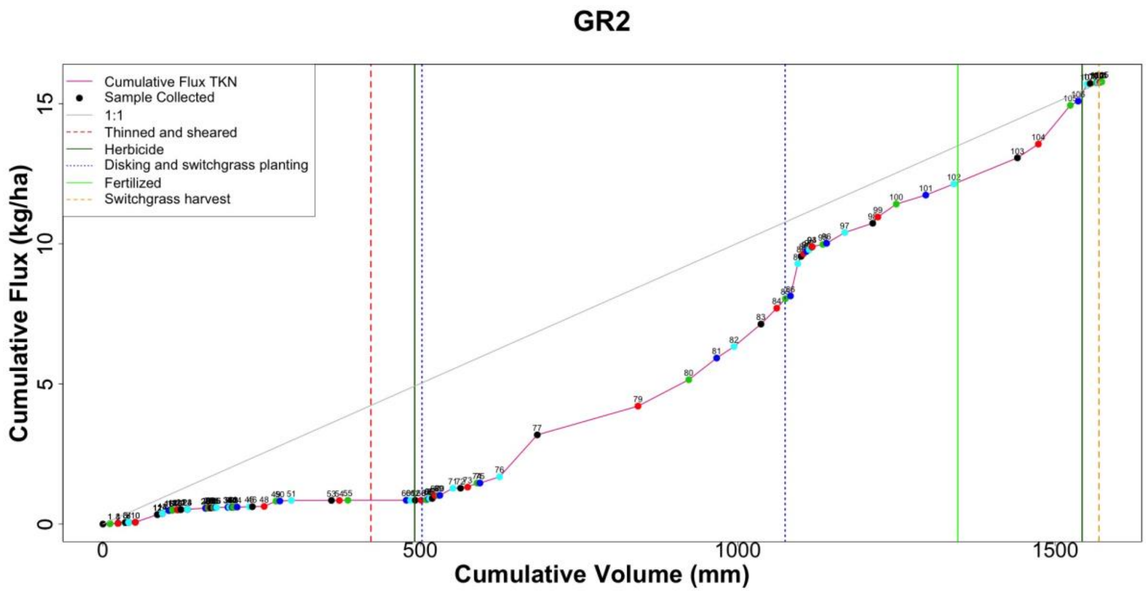

Figure G.90. Cumulative TKN load (kg ha^{-1}) of intercropped/thinned watershed (GR2) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

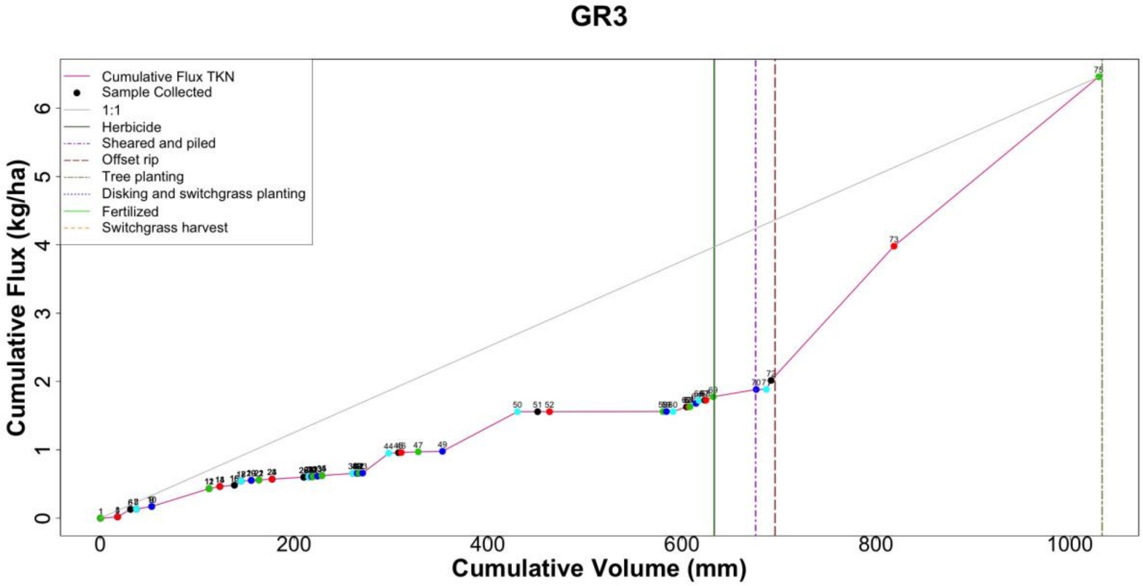

Figure G.91. Cumulative TKN load (kg ha-1) of intercropped/replanted watershed (GR3) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

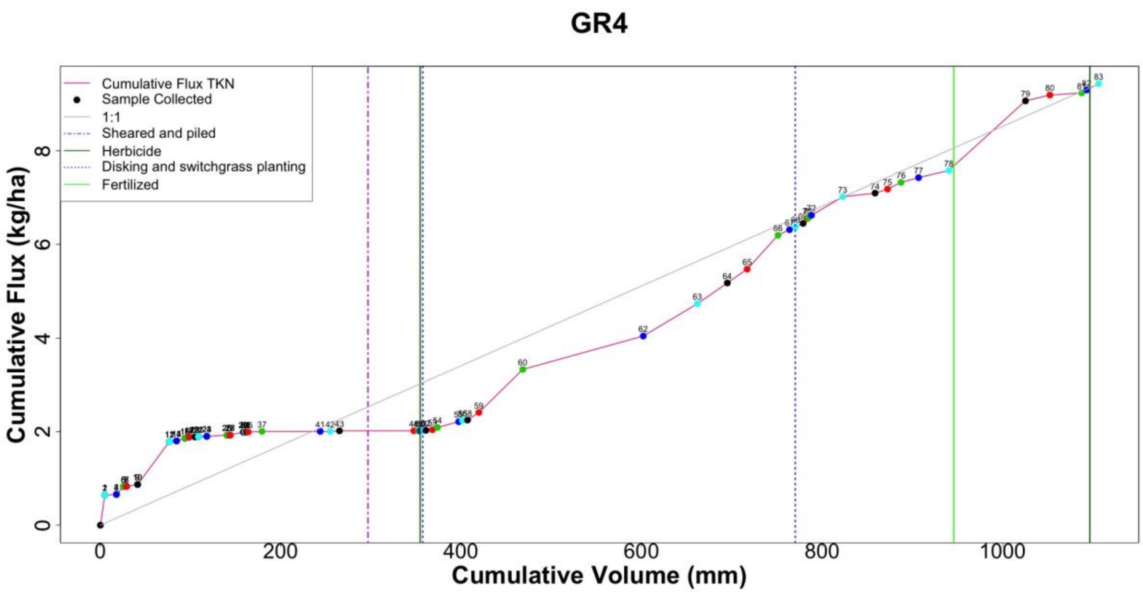

Figure G.92. Cumulative TKN load (kg ha-1) of intercropped/thinned watershed (GR2) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

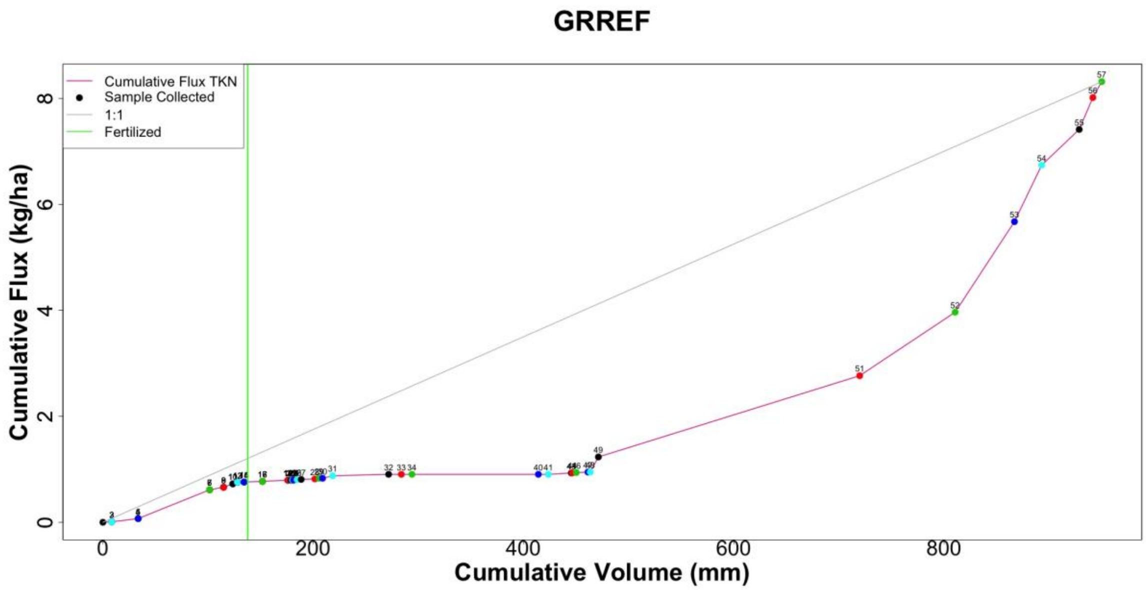

Figure G.93. Cumulative TKN load (kg ha^{-1}) of mature pine reference watershed (GRREF) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

Cumulative load: treatment versus control watershed (GR1) (2011 to 2014)

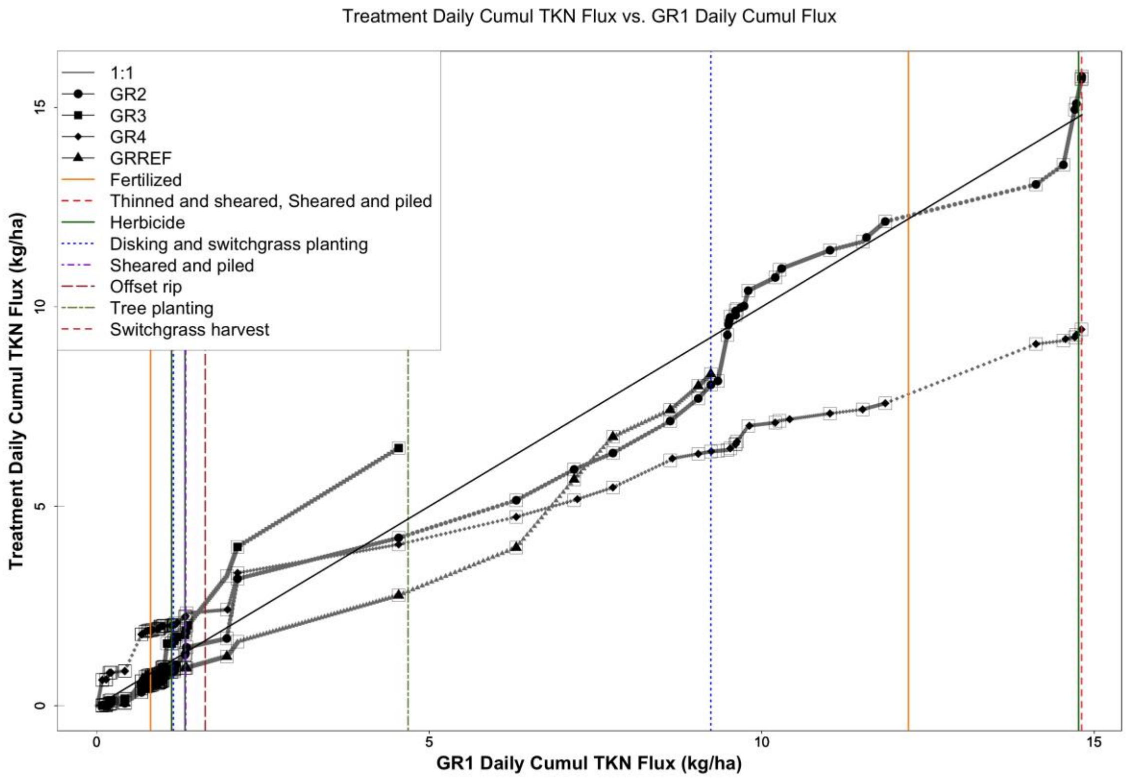

Figure G.94. Daily cumulative TKN load (kg ha^{-1}) of all watersheds (GR2, GR3, GR4, GRREF) as a function of daily cumulative TKN load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

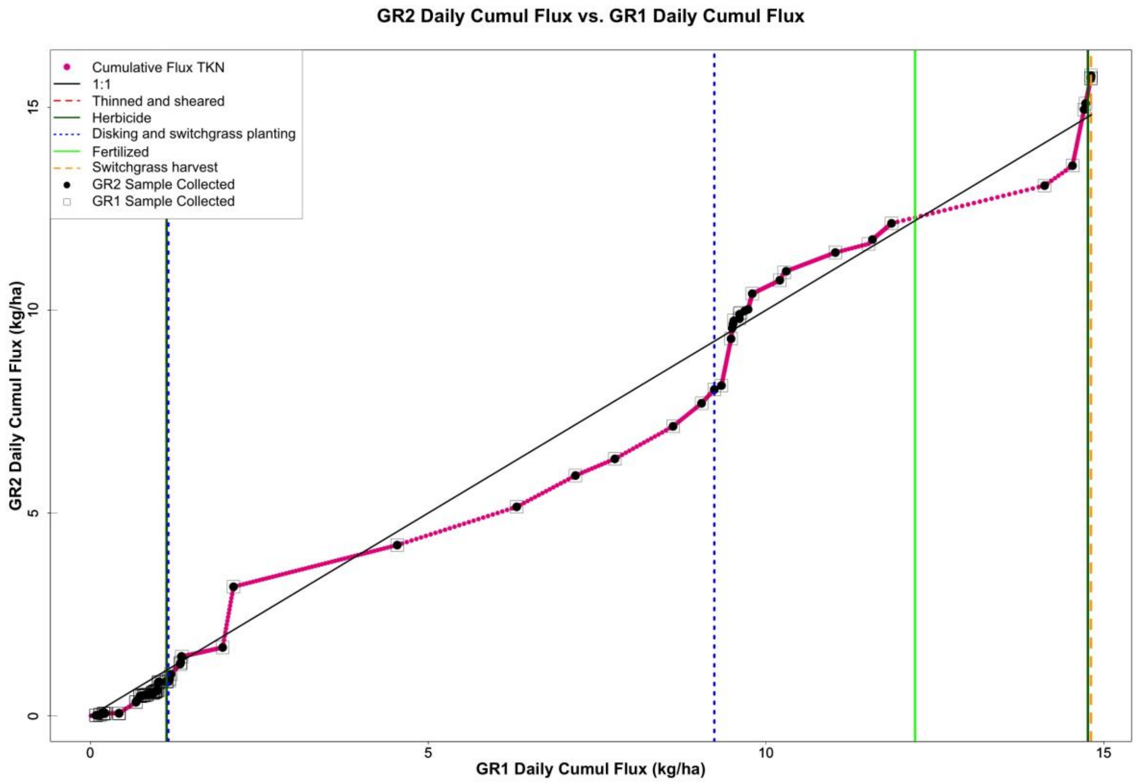

Figure G.95. Daily cumulative TKN load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative TKN load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

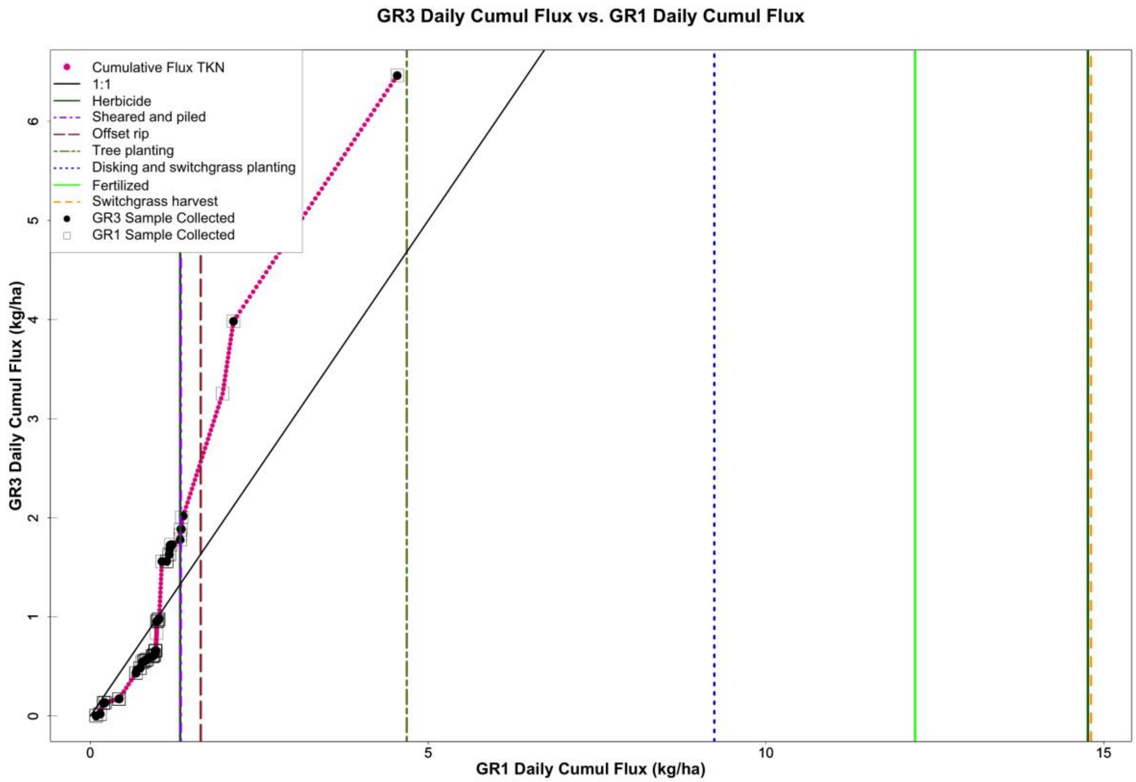

Figure G.96. Daily cumulative TKN load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative TKN load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

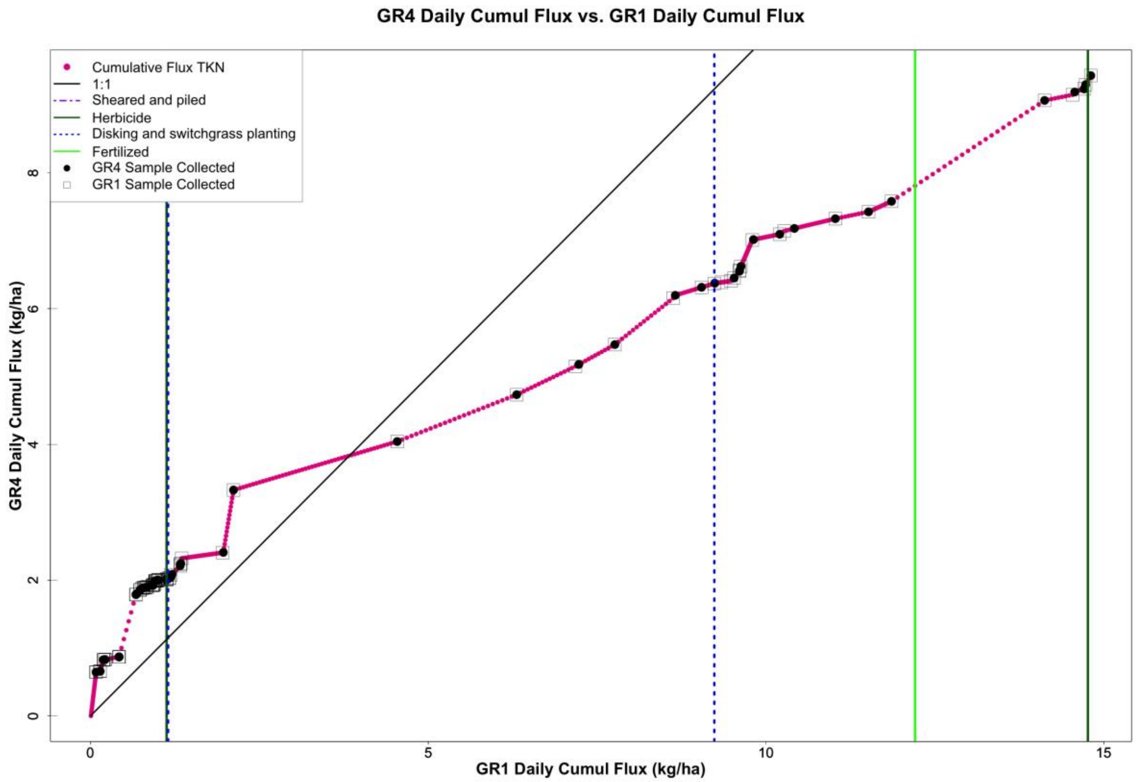

Figure G.97. Daily cumulative TKN load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative TKN load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

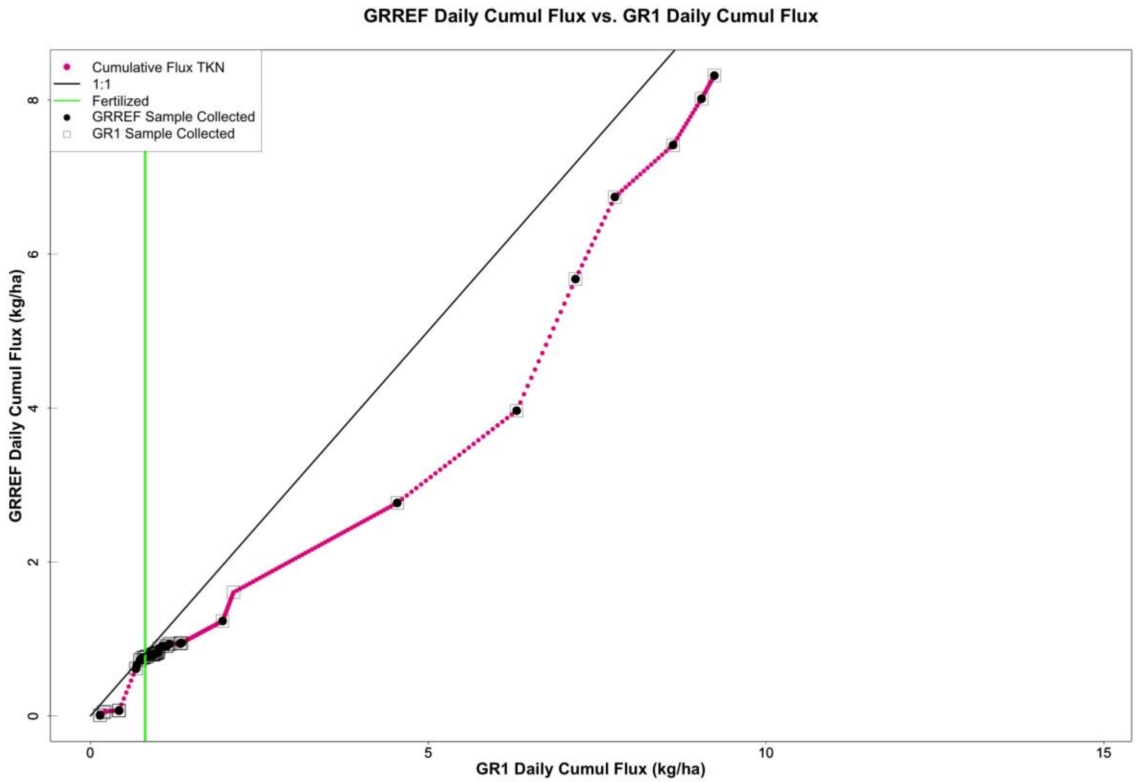

Figure G.98. Daily cumulative TKN load (kg ha^{-1}) of watershed GRREF as a function of daily cumulative TKN load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

Cumulative load: treatment versus mature reference watershed (GRREF) (2011 to 2014)

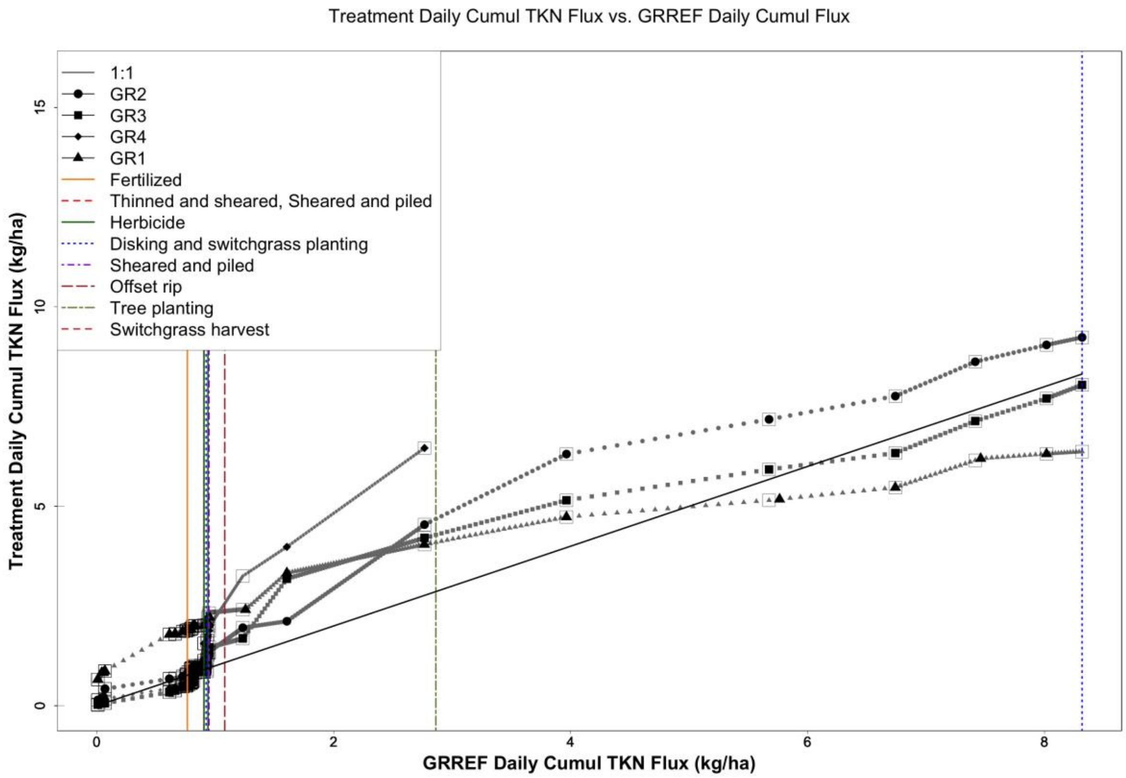

Figure G.99. Daily cumulative TKN load (kg ha^{-1}) of all watersheds (GR1, GR2, GR3, GR4) as a function of daily cumulative TKN load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

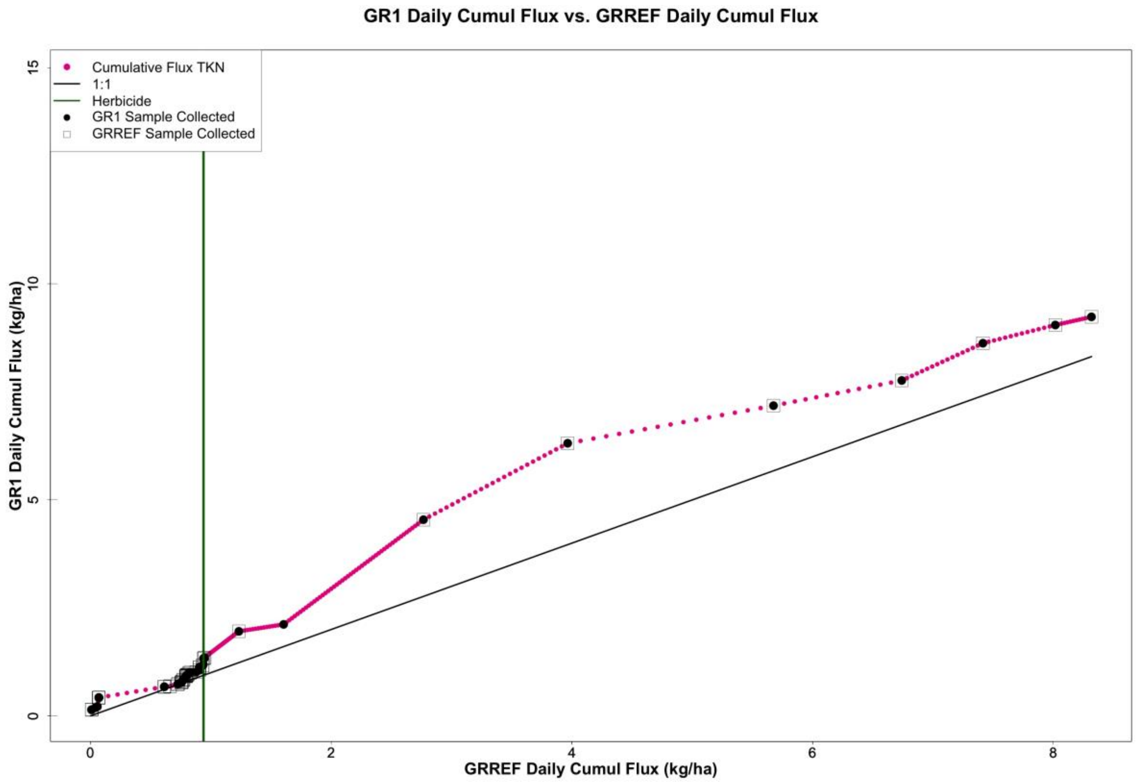

Figure G.100. Daily cumulative TKN load (kg ha^{-1}) of watersheds GR1 as a function of daily cumulative TKN load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

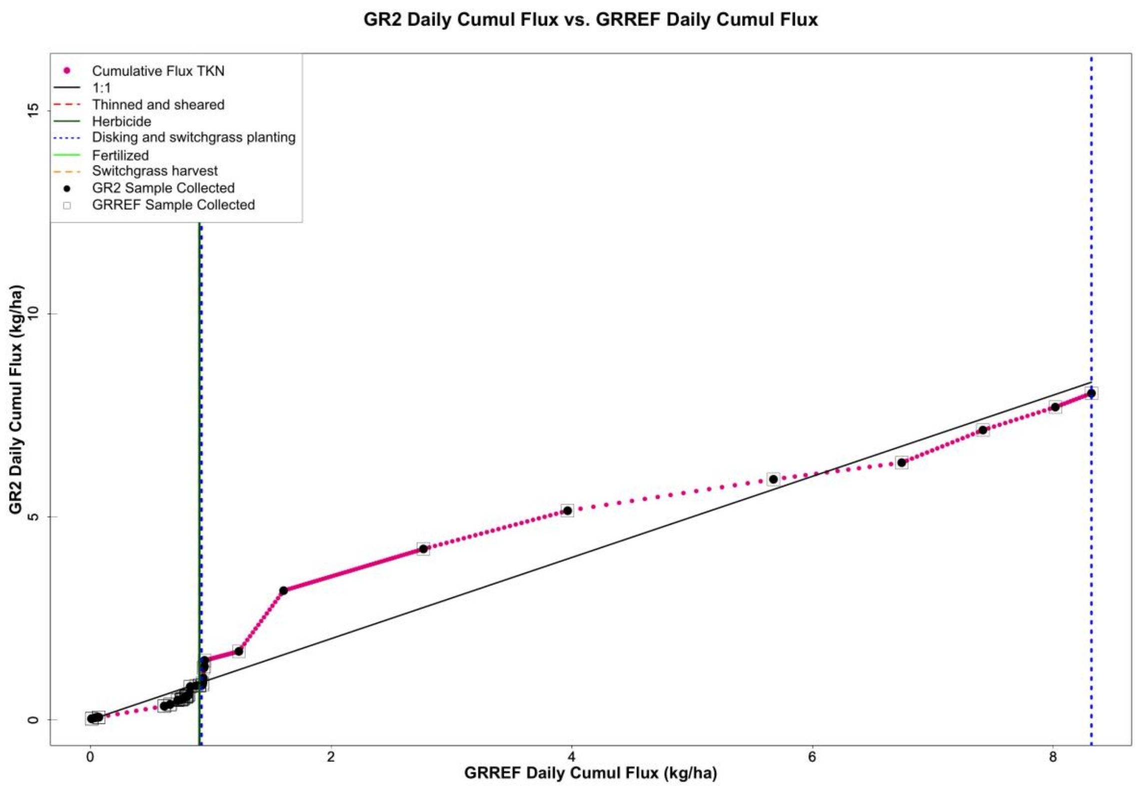

Figure G.101. Daily cumulative TKN load (kg ha^{-1}) of watersheds GR2 as a function of daily cumulative TKN load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

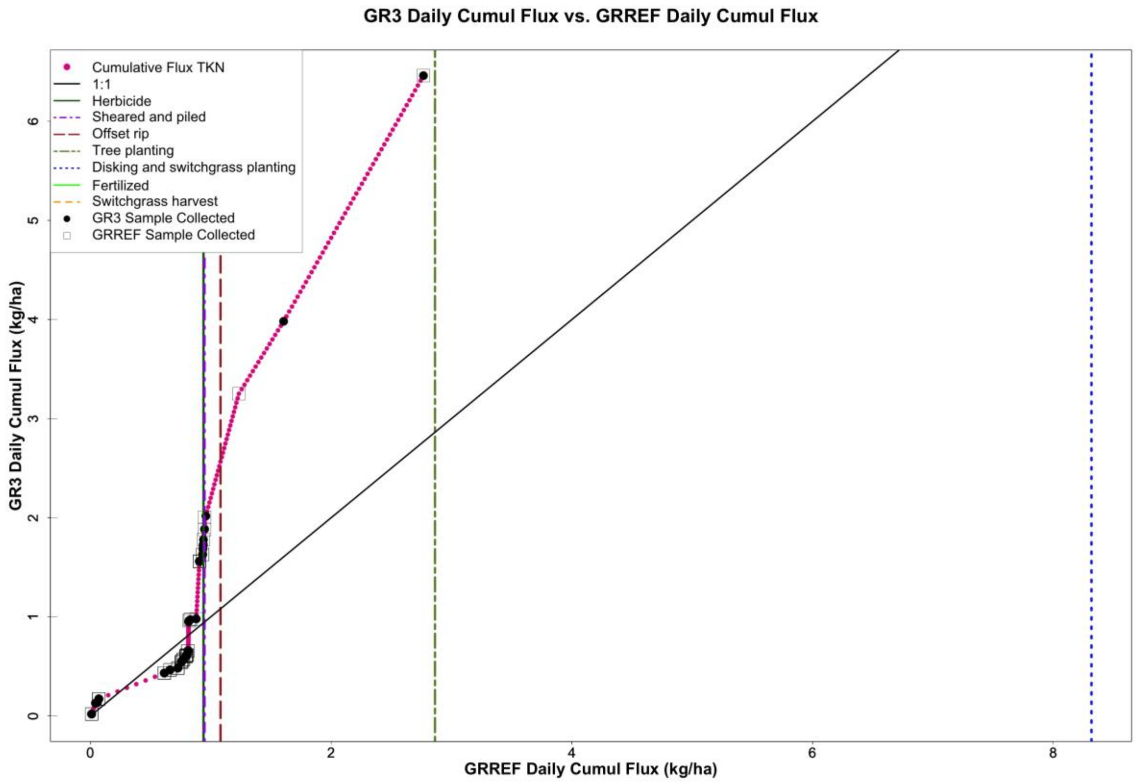

Figure G.102. Daily cumulative TKN load (kg ha^{-1}) of watersheds GR3 as a function of daily cumulative TKN load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

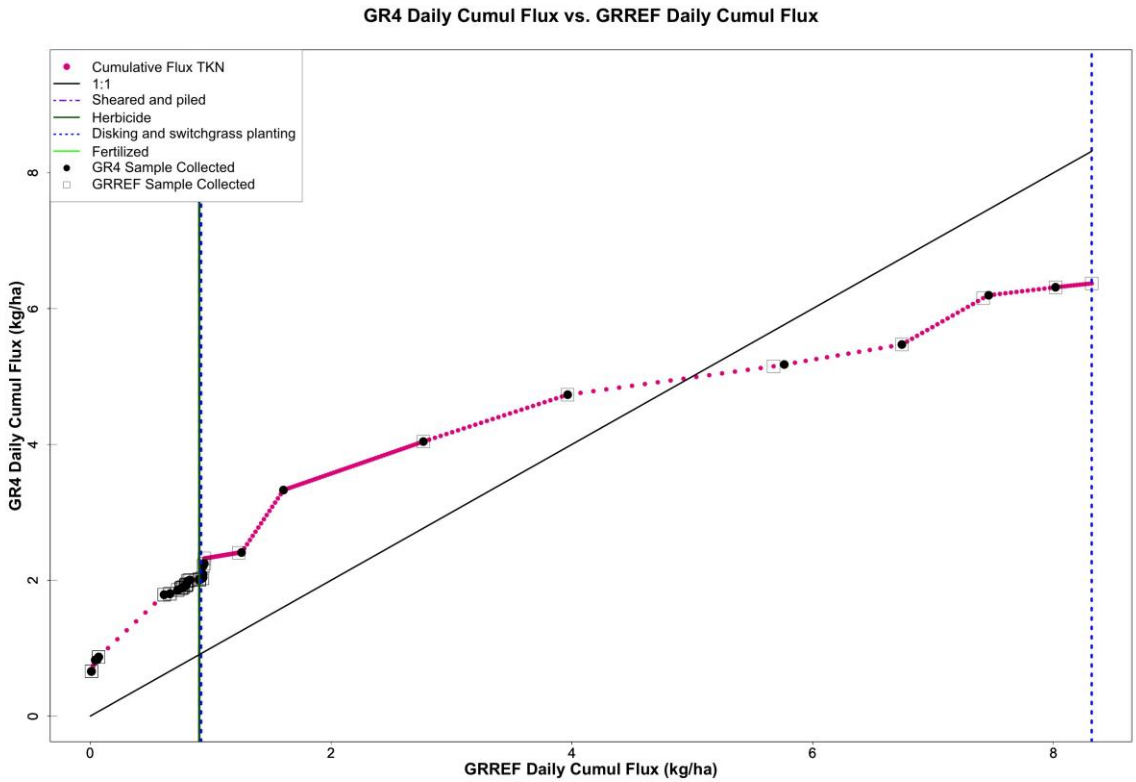

Figure G.103. Daily cumulative TKN load (kg ha^{-1}) of watersheds GR4 as a function of daily cumulative TKN load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

G.6 Total Phosphorous (TP)

Cumulative load over time with hydrograph (2011-2014)

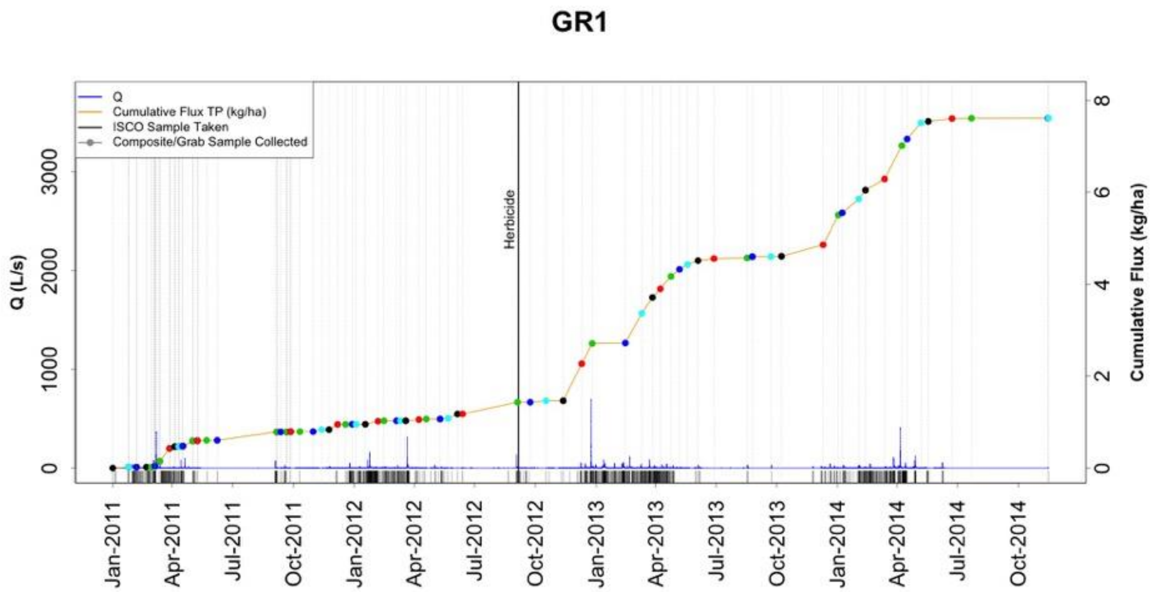

Figure G.104. Cumulative TP flux over time (Jan 2011 to Nov 2014) in watershed GR1, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

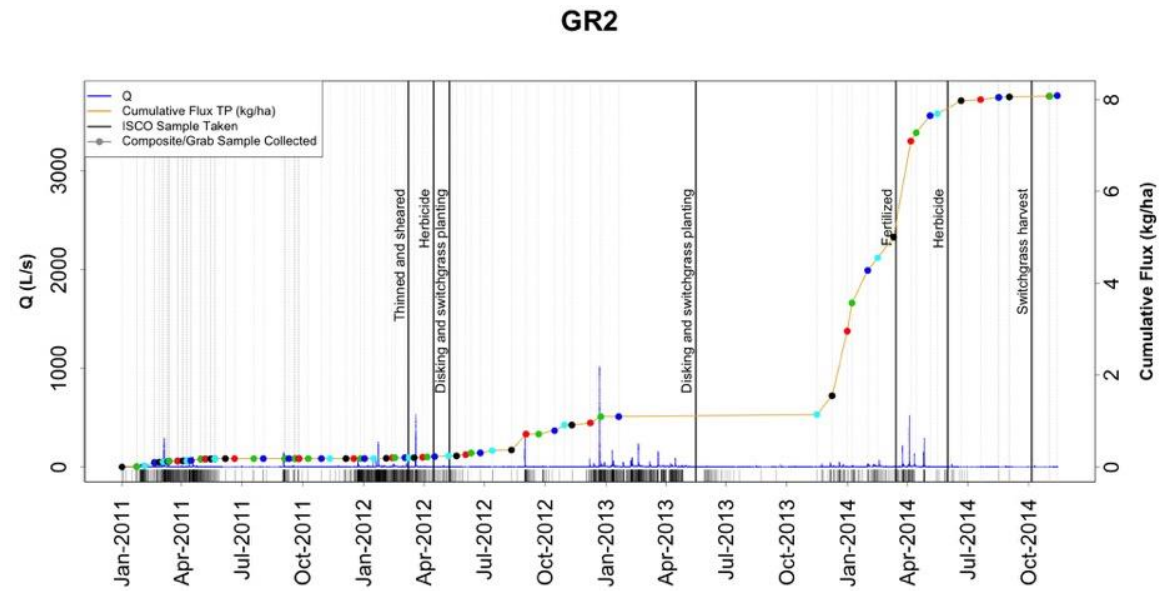

Figure G.105. Cumulative TP flux over time (Jan 2011 to Nov 2014) in watershed GR2, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

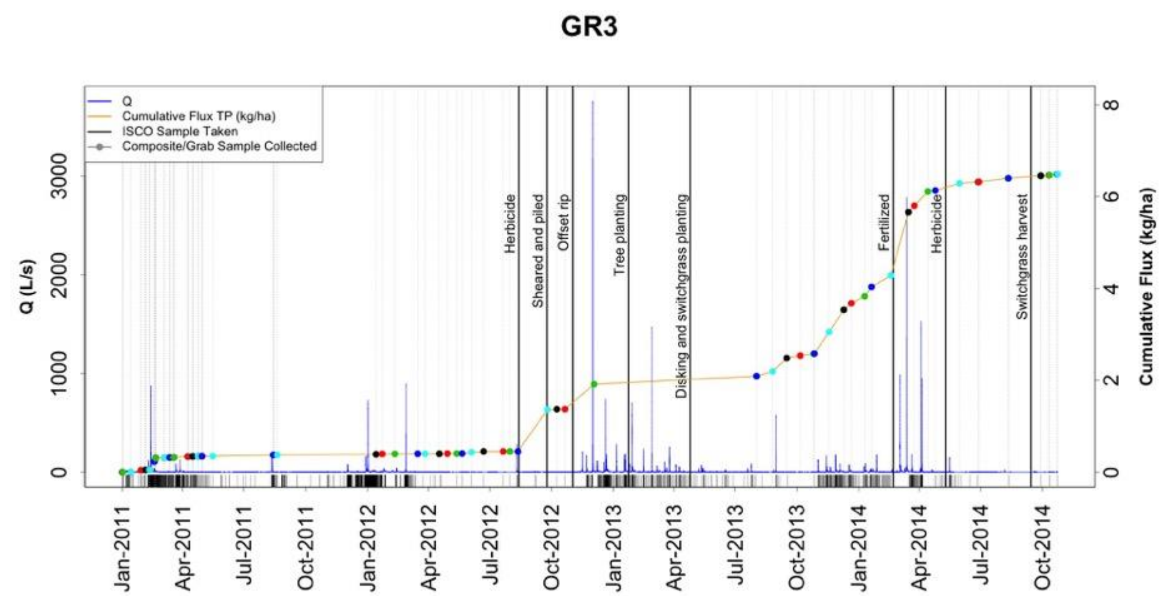

Figure G.106. Cumulative TP flux over time (Jan 2011 to Nov 2014) in watershed GR3, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

GR4

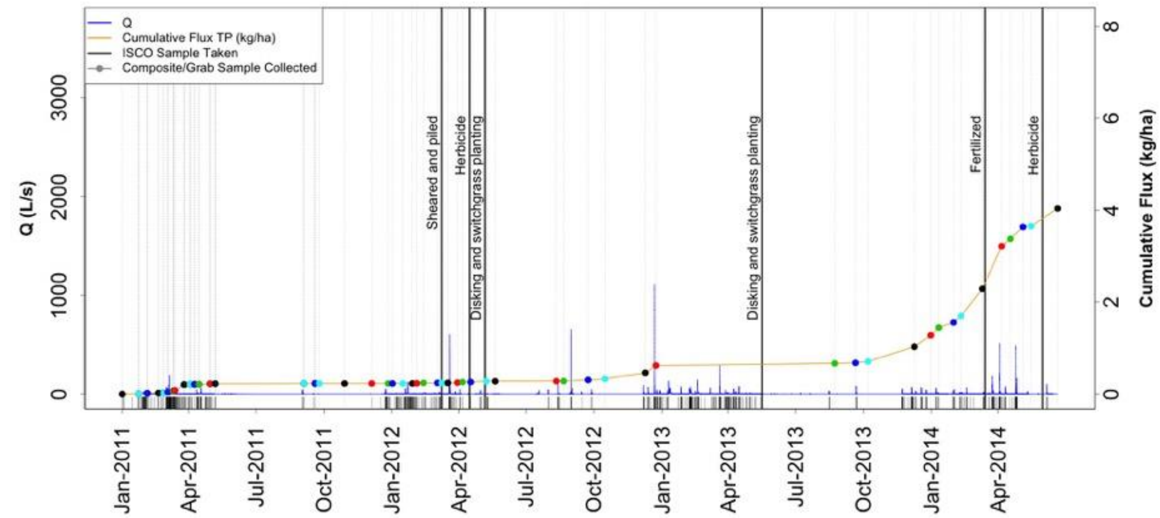

Figure G.107. Cumulative TP flux over time (Jan 2011 to Nov 2014) in watershed GR4, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

GRREF

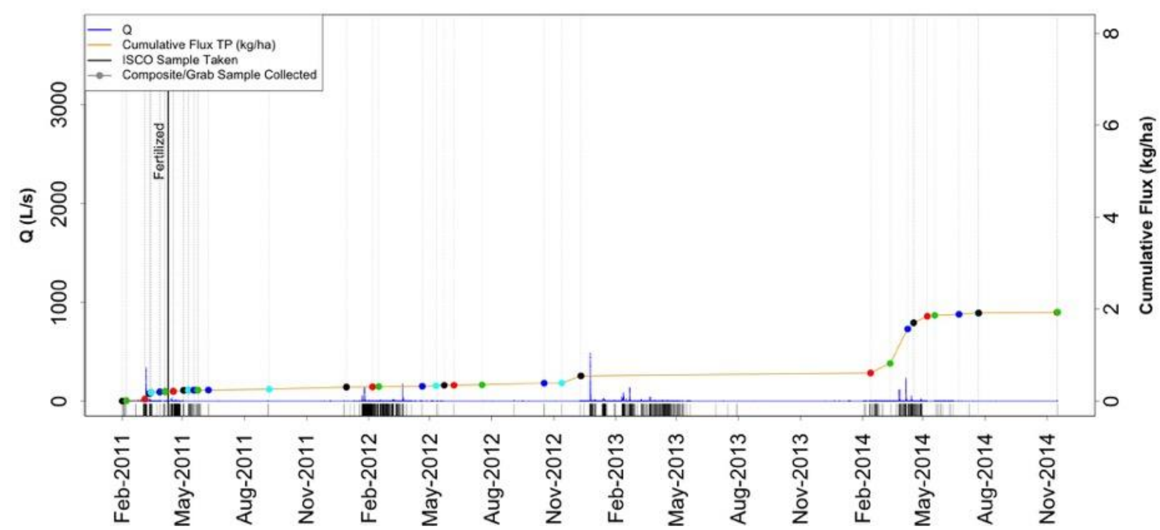

Figure G.108. Cumulative TP flux over time (Jan 2011 to Nov 2014) in watershed GRREF, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

Cumulative load versus cumulative volume (2011-2014)

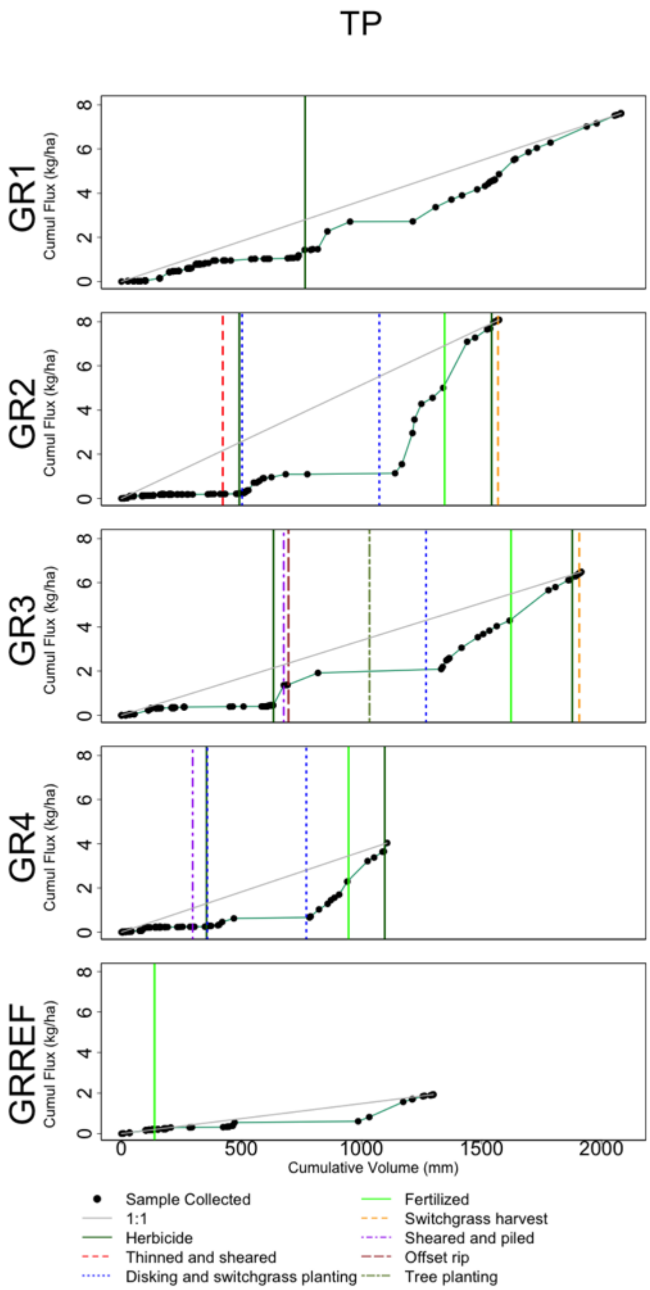

Figure G.109. Cumulative TP flux (kg ha^{-1}) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

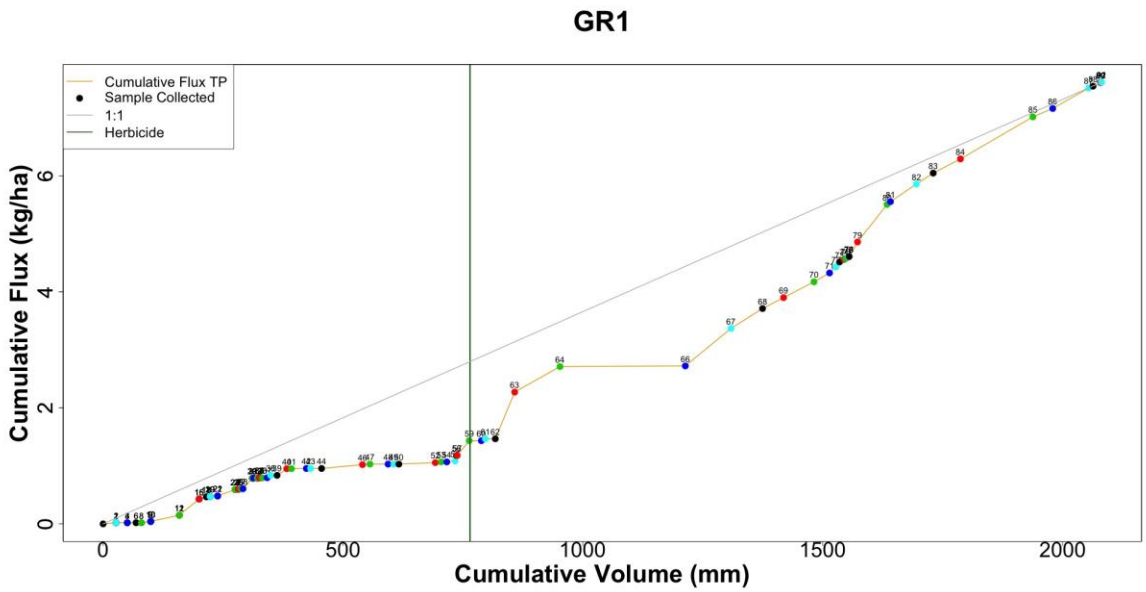

Figure G.110. Cumulative total phosphorous (TP) load (kg ha^{-1}) of control watershed (GR1) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

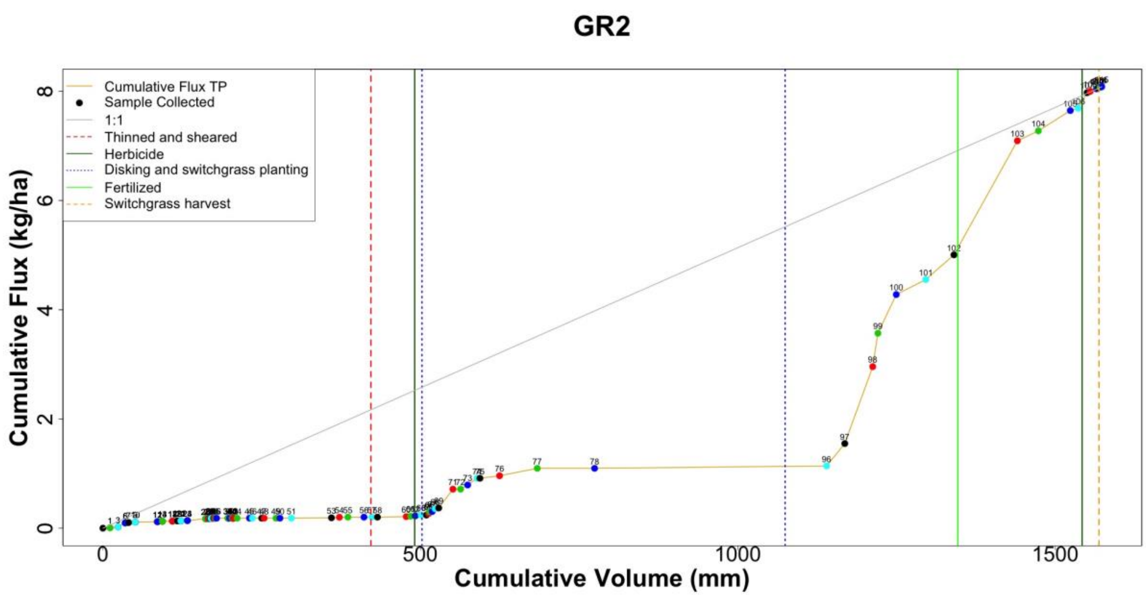

Figure G.111. Cumulative total phosphorous (TP) load (kg ha^{-1}) of intercropped/thinned watershed (GR2) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

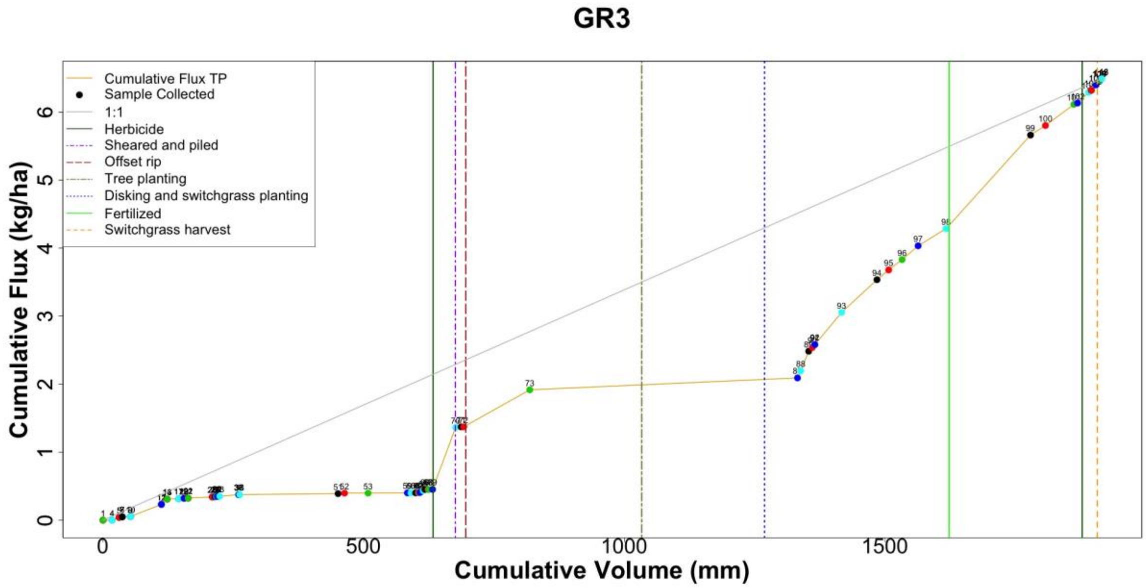

Figure G.112. Cumulative total phosphorous (TP) load (kg ha^{-1}) of intercropped/replanted watershed (GR3) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

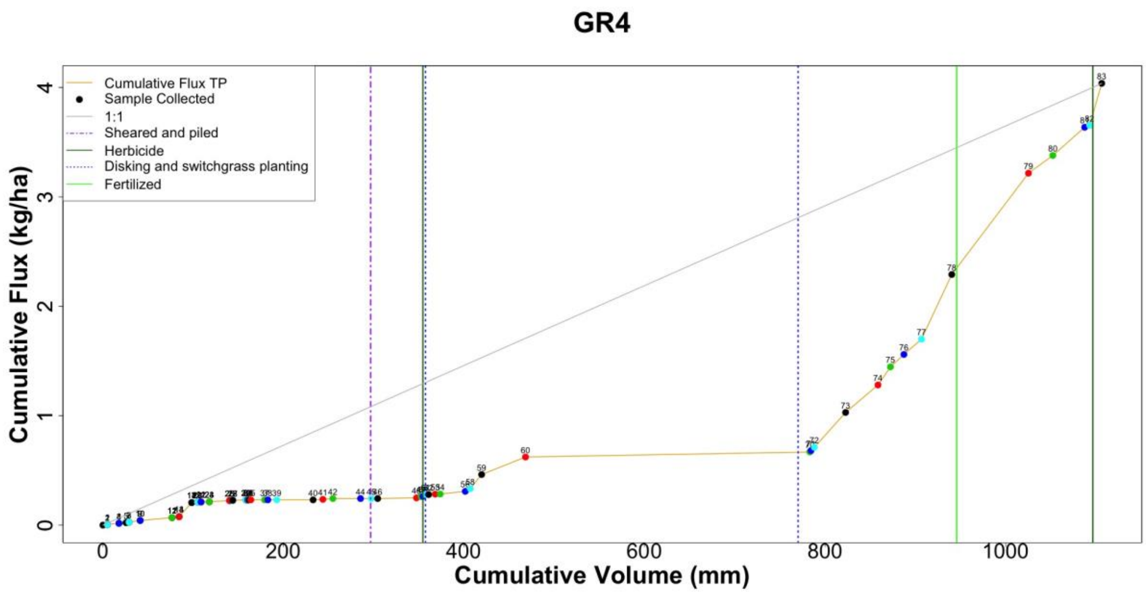

Figure G.113. Cumulative total phosphorous (TP) load (kg ha^{-1}) of switchgrass watershed (GR4) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

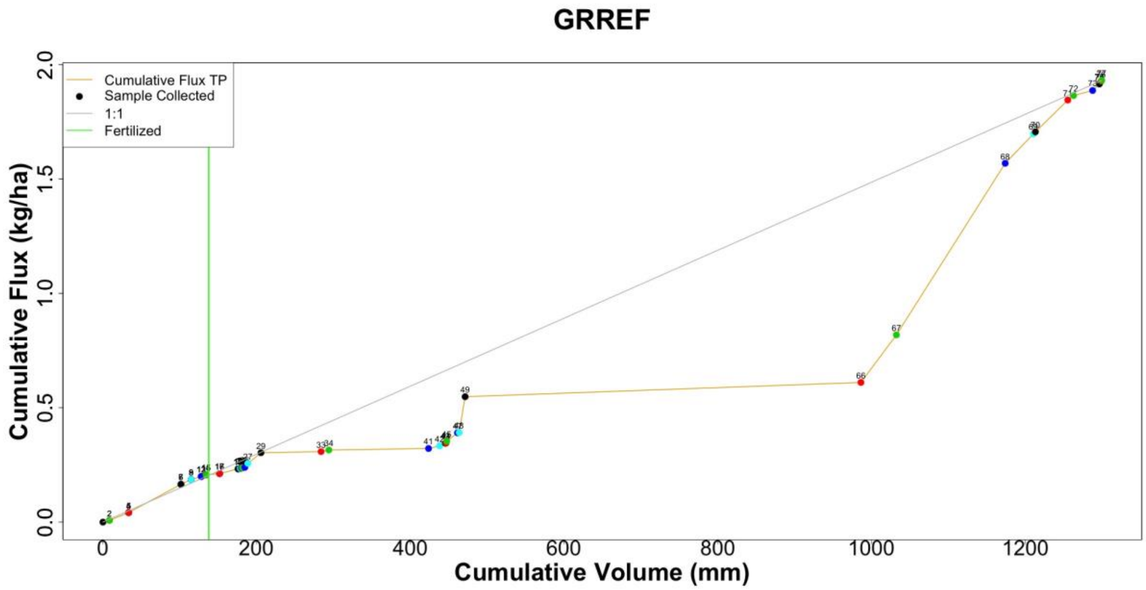

Figure G.114. Cumulative total phosphorous (TP) load (kg ha^{-1}) of mature pine reference watershed (GRREF) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

Cumulative load: treatment versus control watershed (GR1) (2011 to 2014)

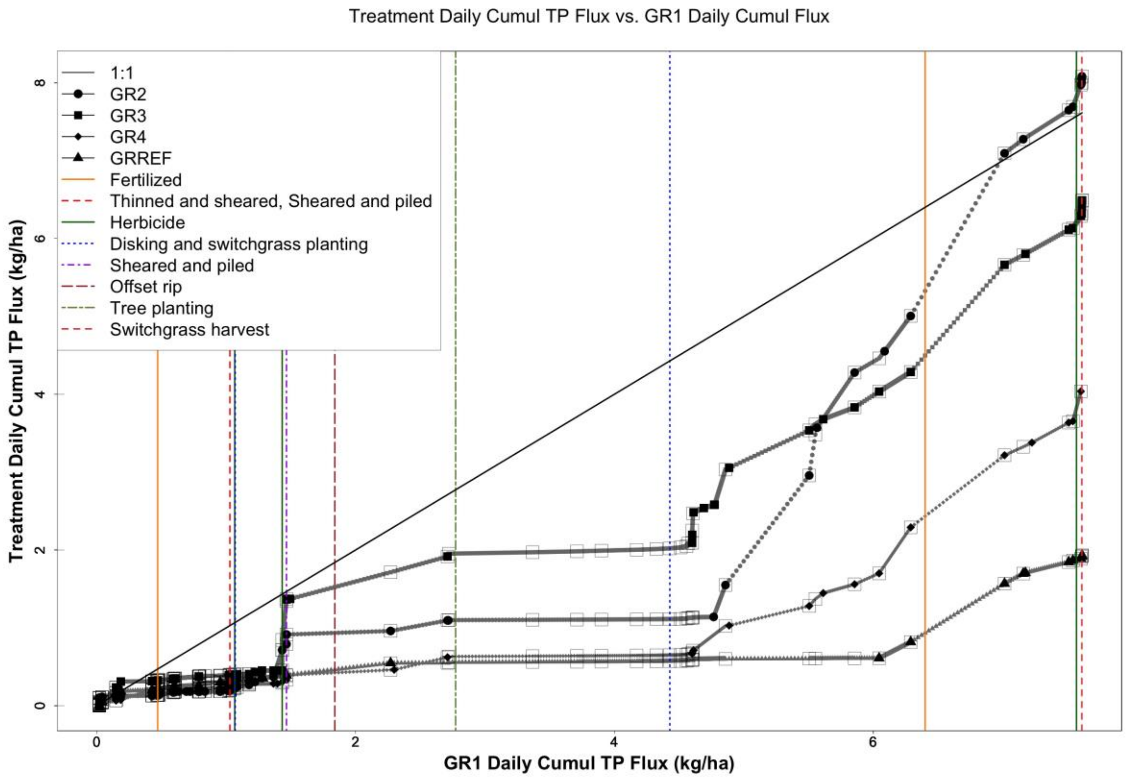

Figure G.115. Daily cumulative TP load (kg ha^{-1}) of all watersheds (GR2, GR3, GR4, and GRREF) as a function of daily cumulative TP load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

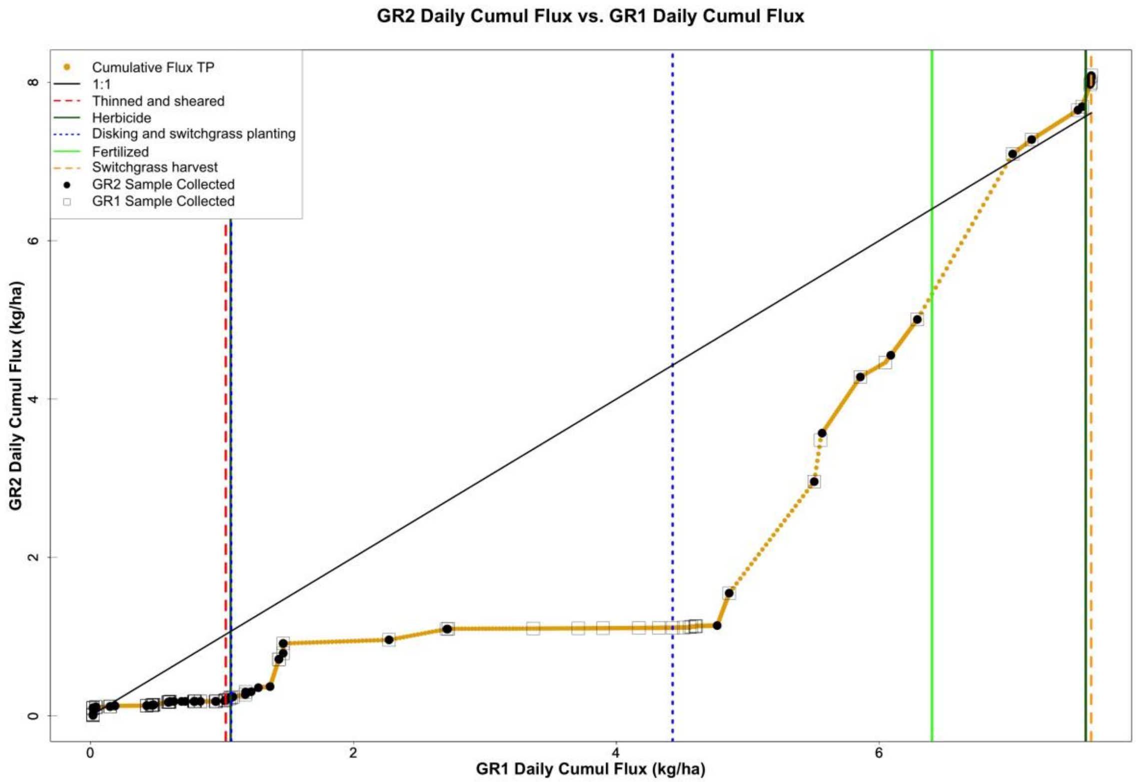

Figure G.116. Daily cumulative TP load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative TP load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

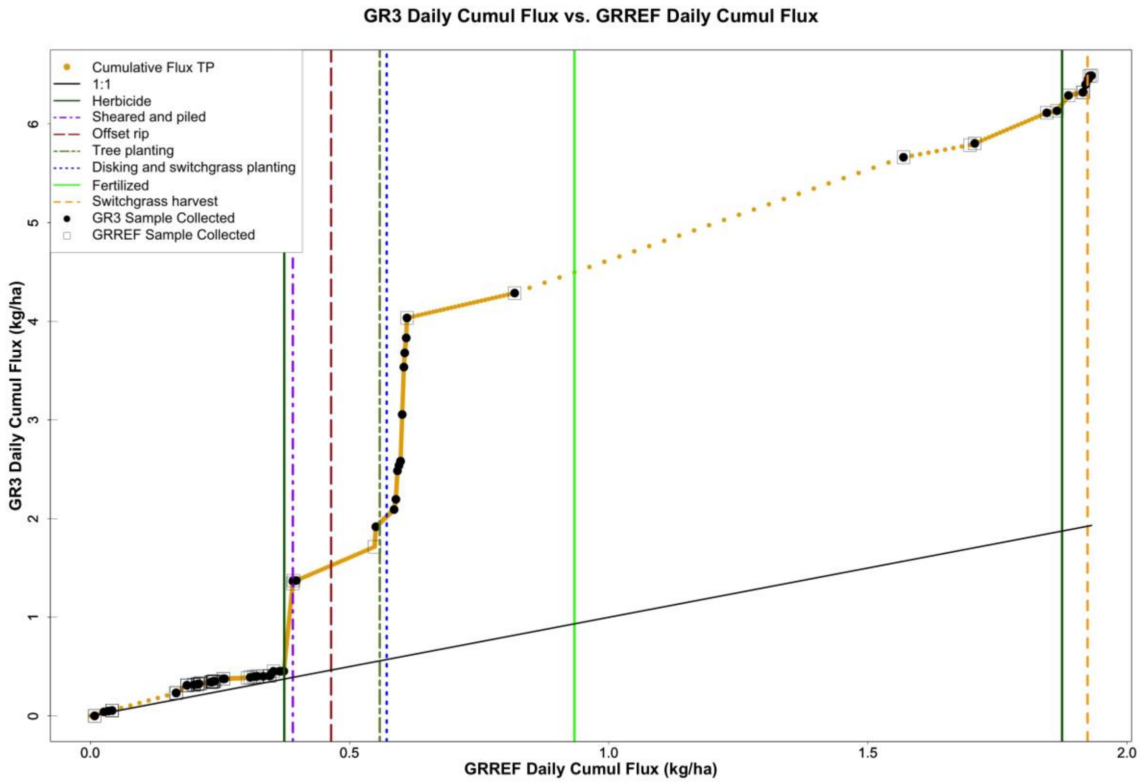

Figure G.117. Daily cumulative TP load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative TP load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

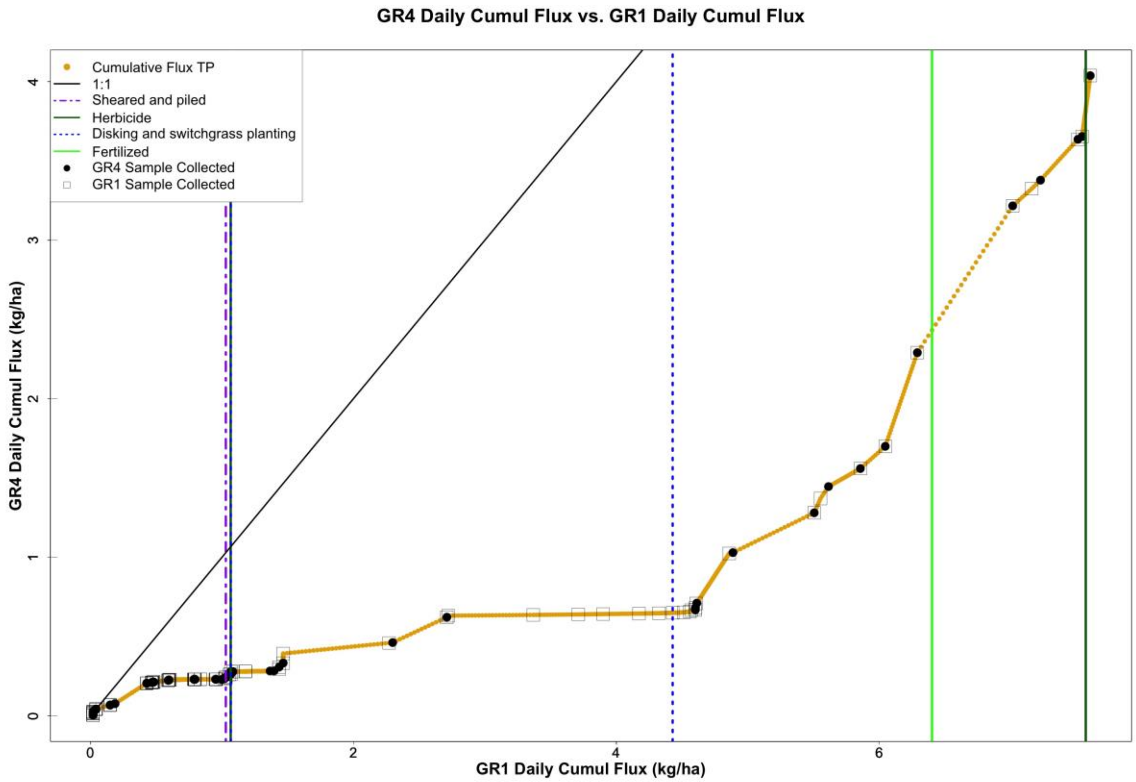

Figure G.118. Daily cumulative TP load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative TP load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

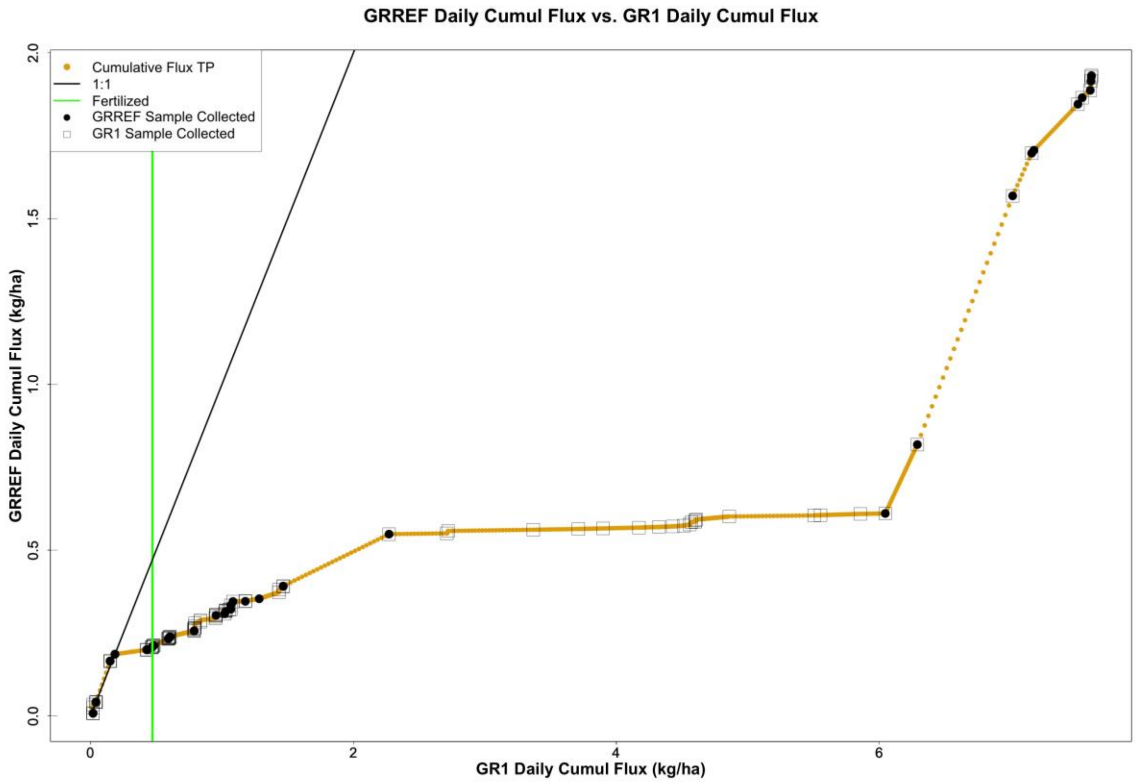

Figure G.119. Daily cumulative TP load (kg ha^{-1}) of watershed GRREF as a function of daily cumulative TP load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

Cumulative load: treatment versus mature reference watershed (GRREF) (2011 to 2014)

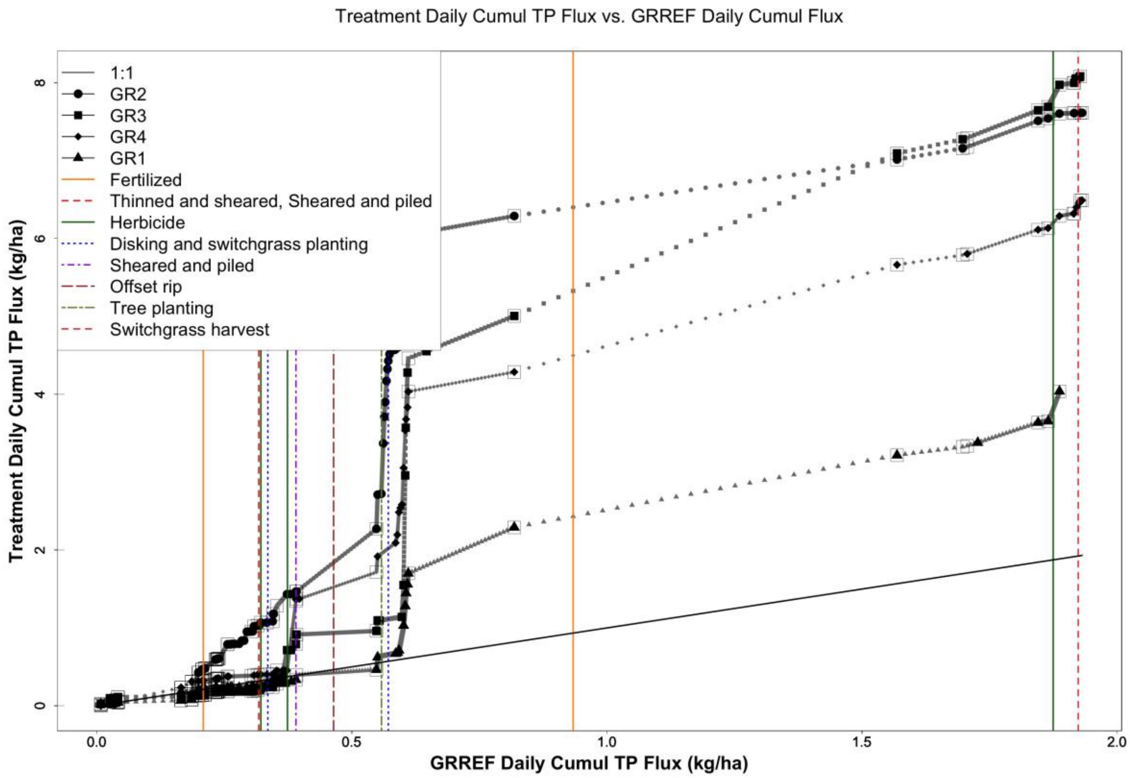

Figure G.120. Daily cumulative TP load (kg ha^{-1}) of all watersheds (GR1, GR2, GR3, GR4) as a function of daily cumulative TP load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

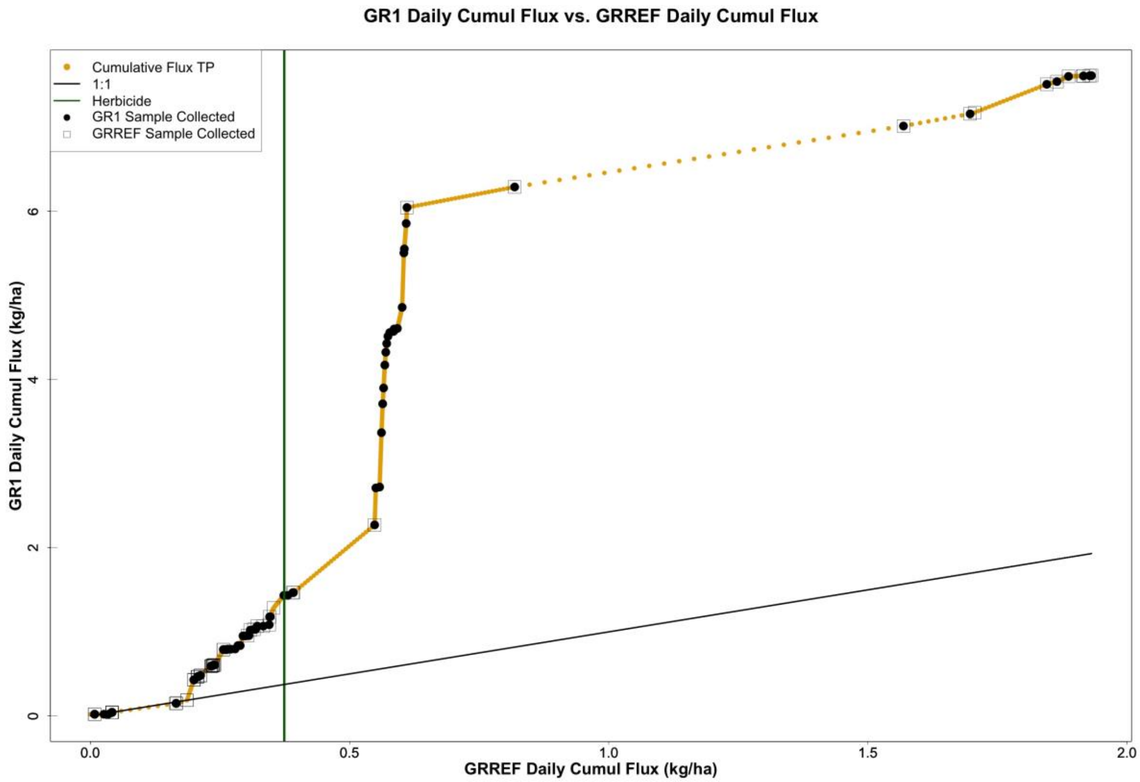

Figure G.121. Daily cumulative TP load (kg ha^{-1}) of watershed GR1 as a function of daily cumulative TP load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

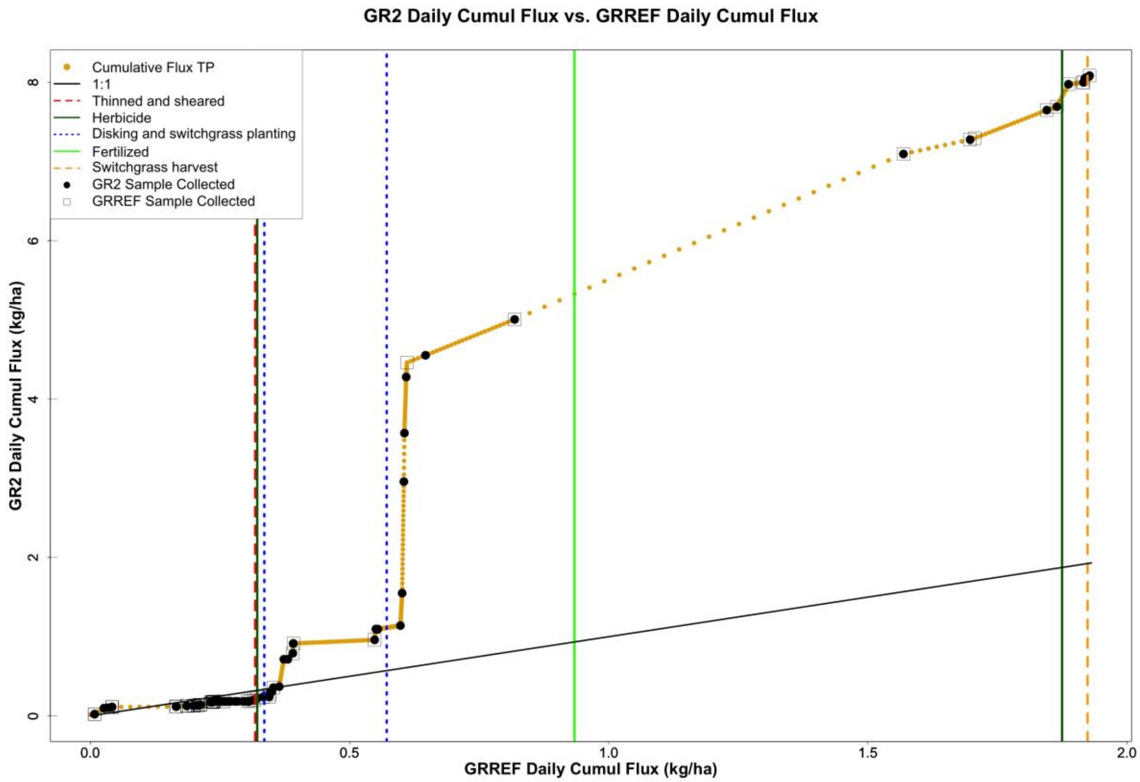

Figure G.122. Daily cumulative TP load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative TP load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

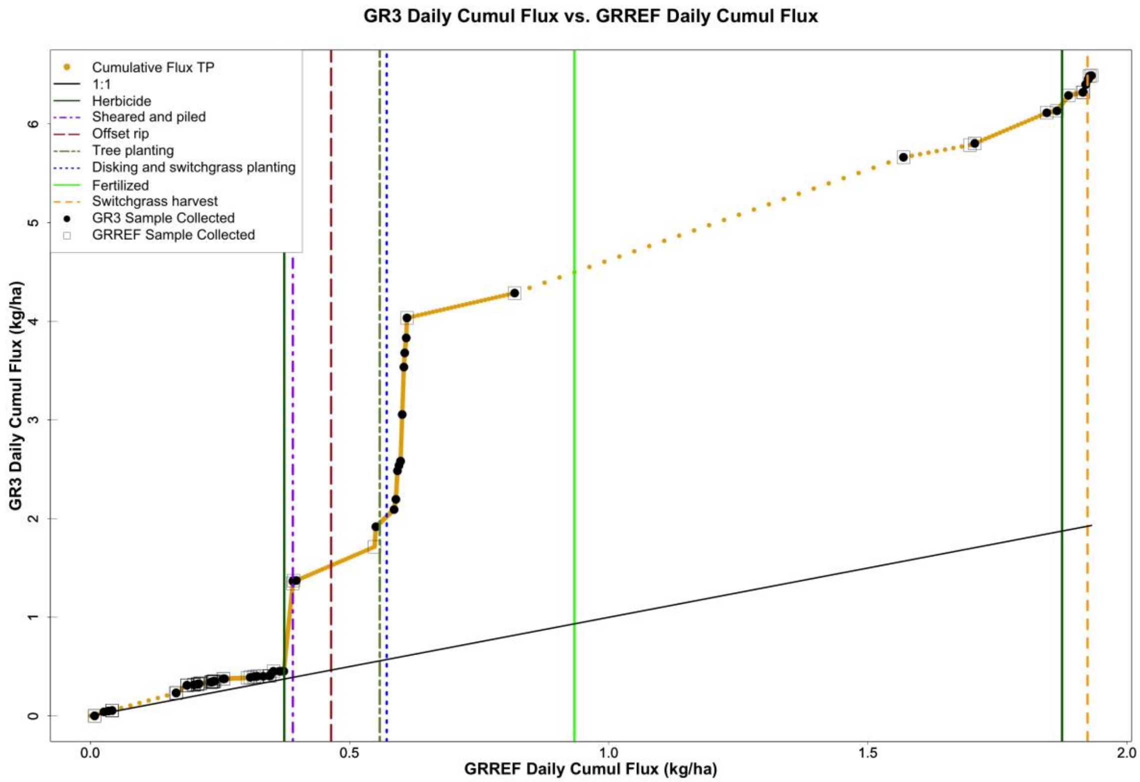

Figure G.123. Daily cumulative TP load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative TP load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

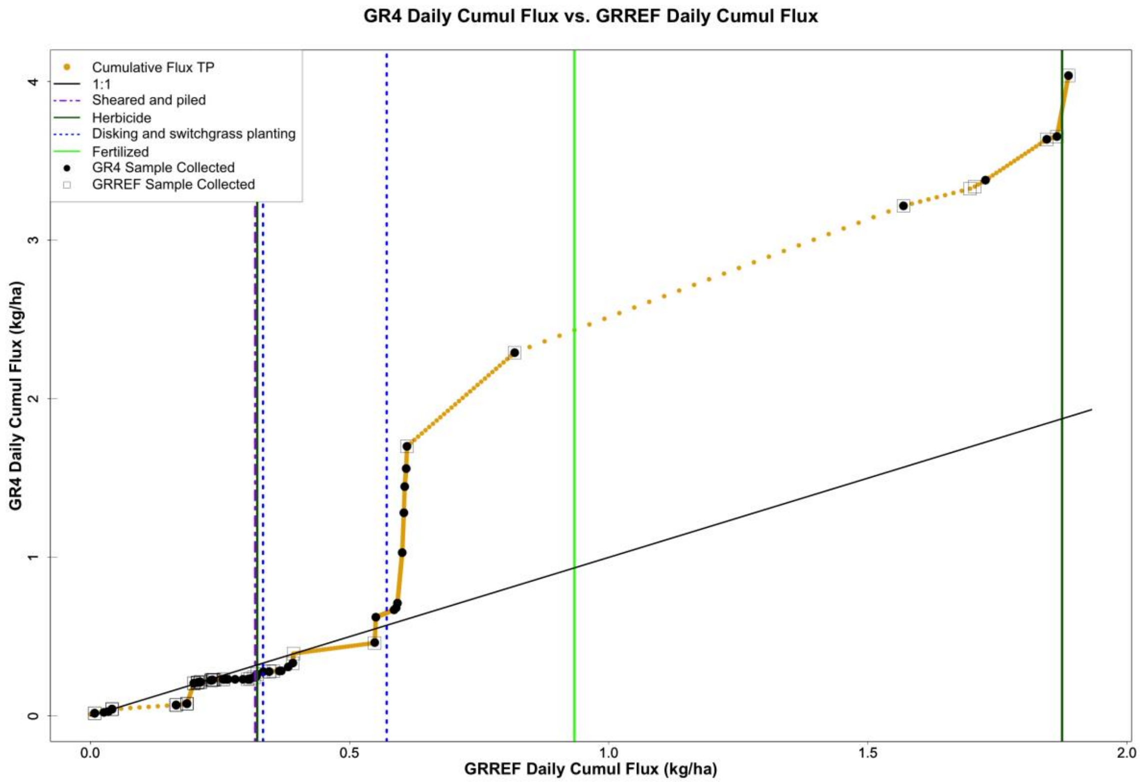

Figure G.124. Daily cumulative TP load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative TP load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

G.7 Phosphate (PO_4^{3+}-P)

Cumulative load over time with hydrograph (2011-2014)

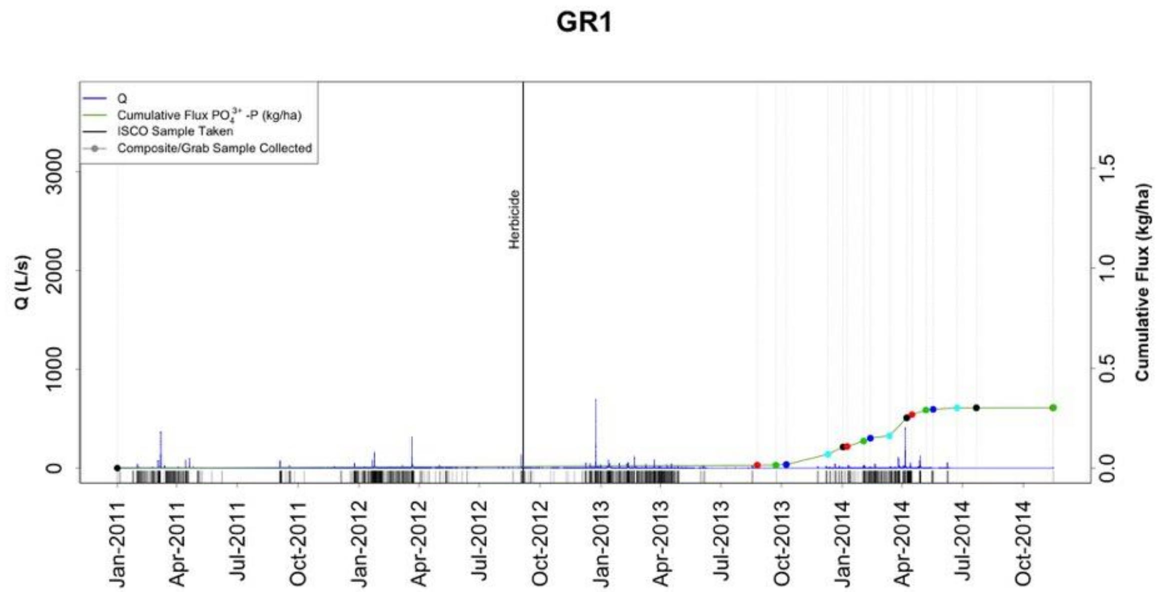

Figure G.125. Cumulative PO_4^{3+}-P flux over time (Jan 2011 to Nov 2014) in watershed GR1, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

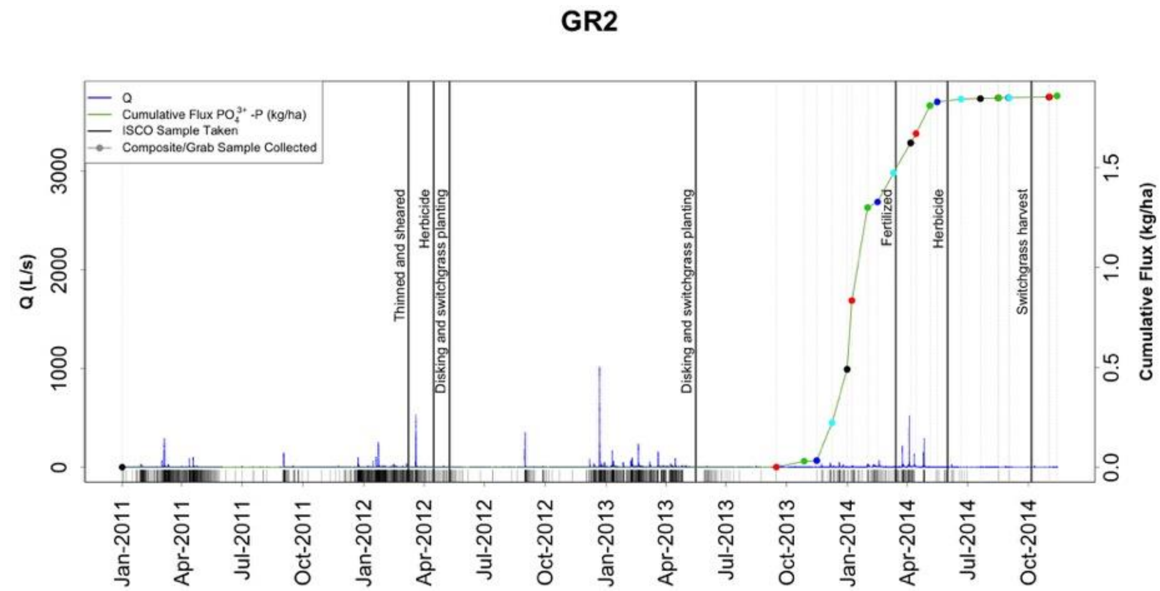

Figure G.126. Cumulative PO_4^{3+}-P flux over time (Jan 2011 to Nov 2014) in watershed GR2, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

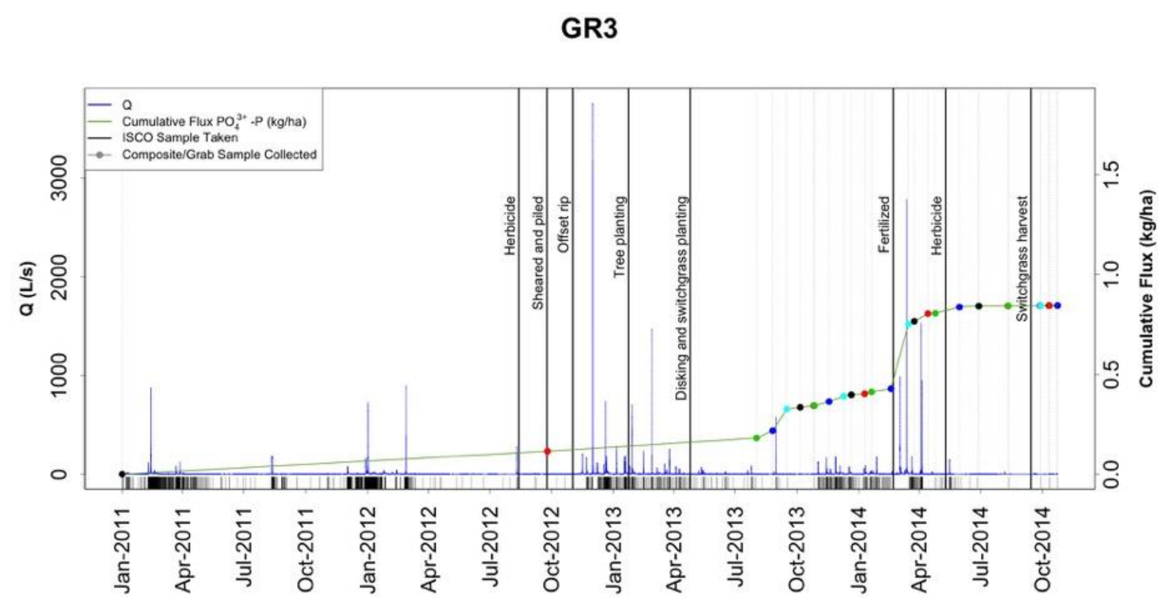

Figure G.127. Cumulative PO_4^{3+}-P flux over time (Jan 2011 to Nov 2014) in watershed GR3, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

GR4

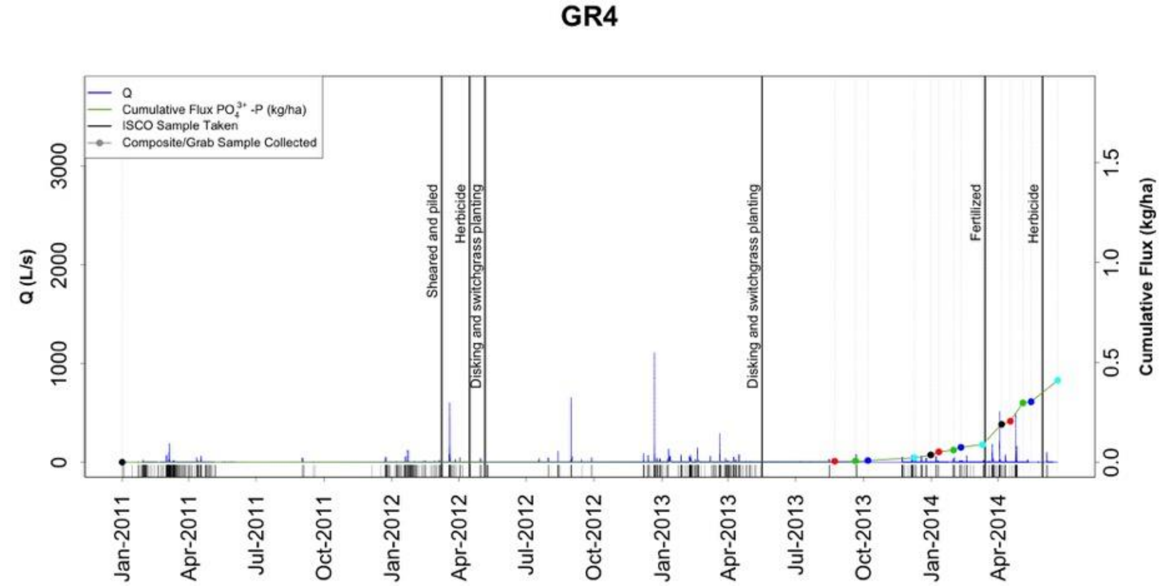

Figure G.128. Cumulative PO_4^{3+}-P flux over time (Jan 2011 to Nov 2014) in watershed GR4, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

GRREF

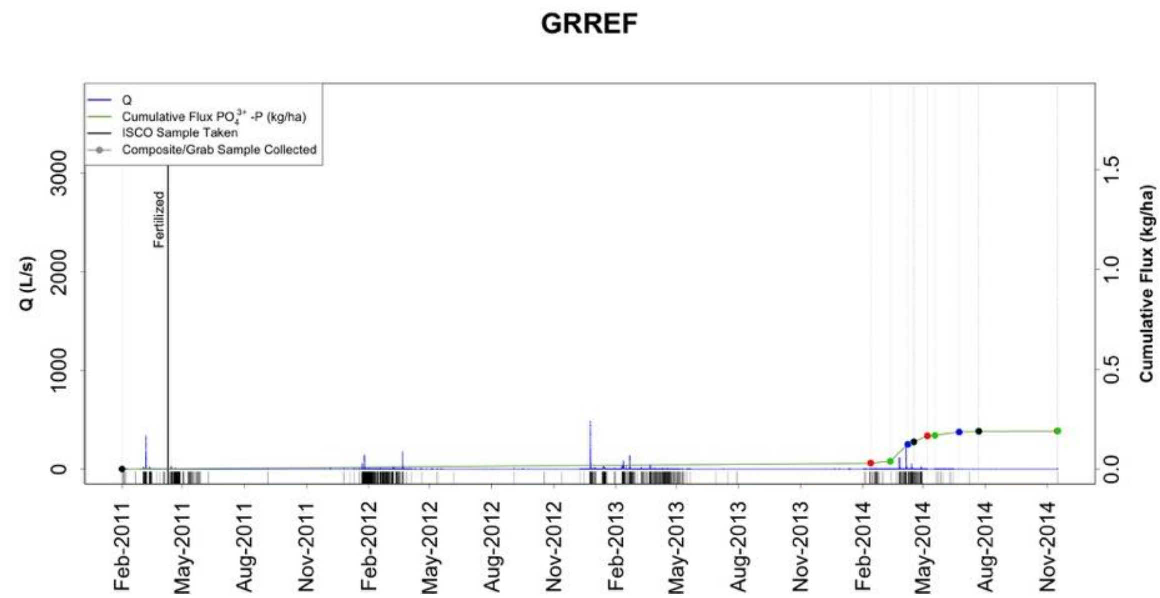

Figure G.129. Cumulative PO_4^{3+}-P flux over time (Jan 2011 to Nov 2014) in watershed GRREF, Green County, Alabama, with hydrograph and operations shown on vertical lines. Short vertical lines at bottom of plot indicate when a sample was taken by the automatic composite sampler.

Cumulative load versus cumulative volume (2011-2014)

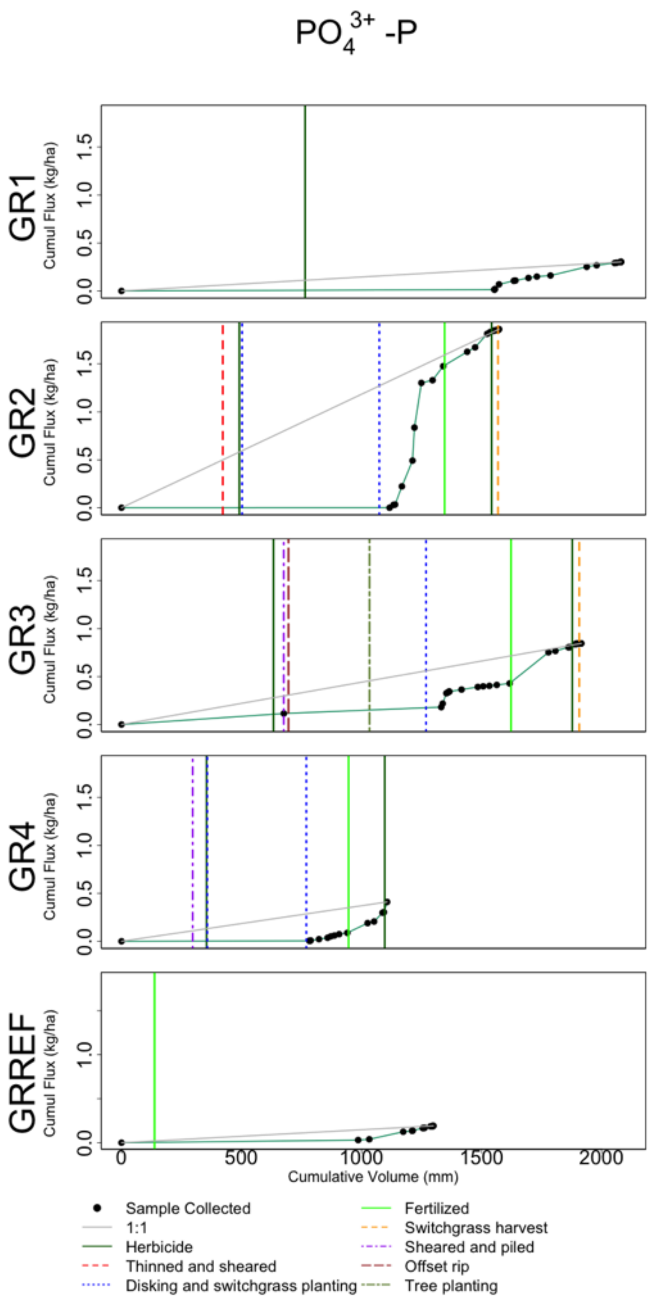

Figure G.130. Cumulative PO_4^{3+}-P flux (kg ha^{-1}) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

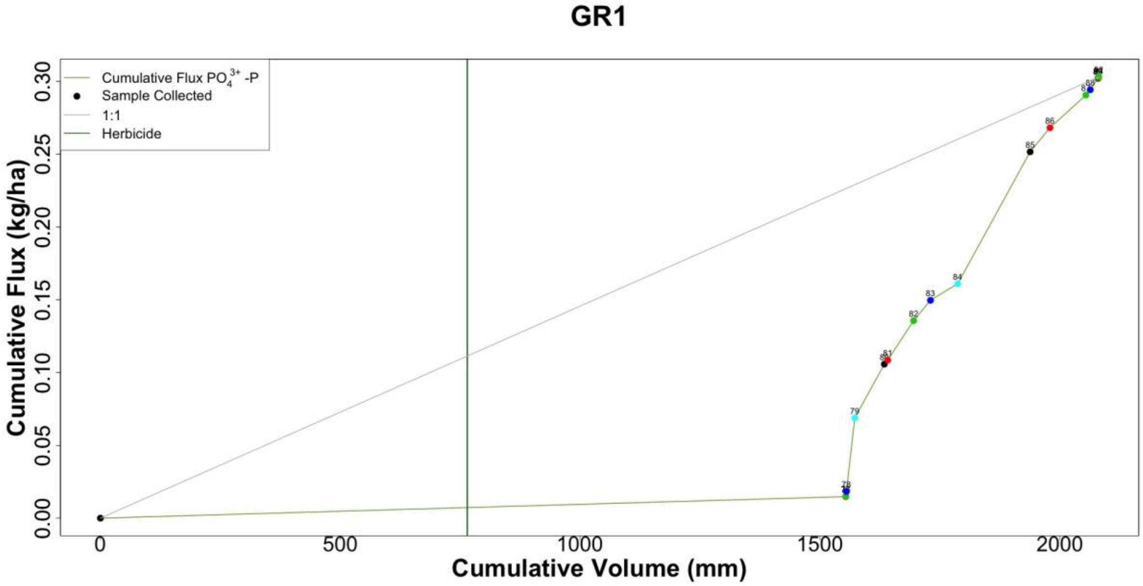

Figure G.131. Cumulative PO_4^{3+}-P load (kg ha^{-1}) of control watershed (GR1) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

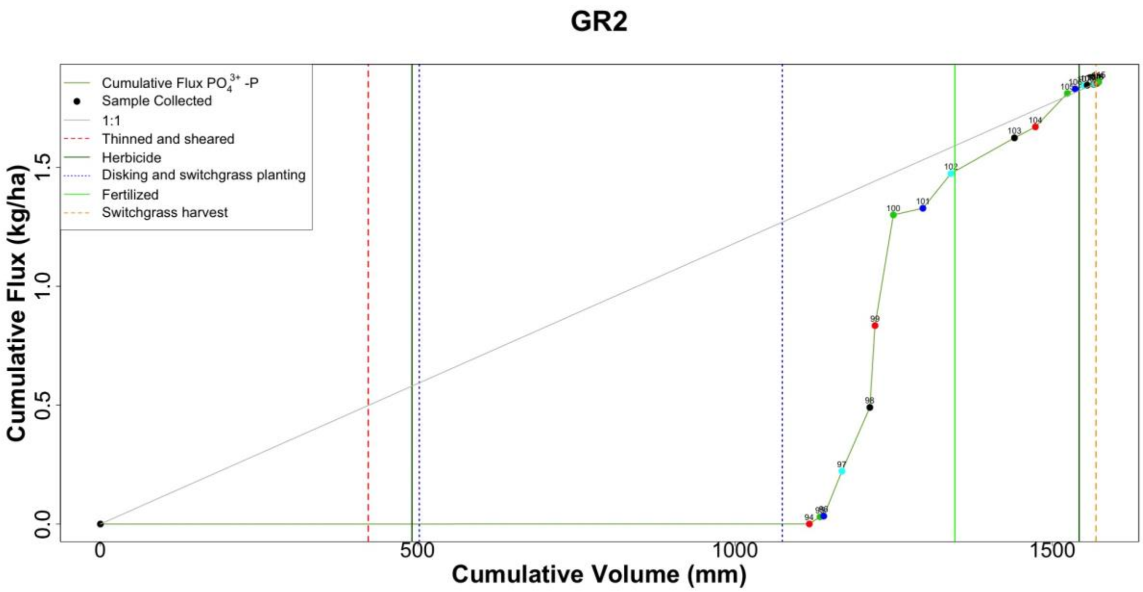

Figure G.132. Cumulative PO_4^{3+}-P load (kg ha^{-1}) of intercropped/thinned watershed (GR2) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

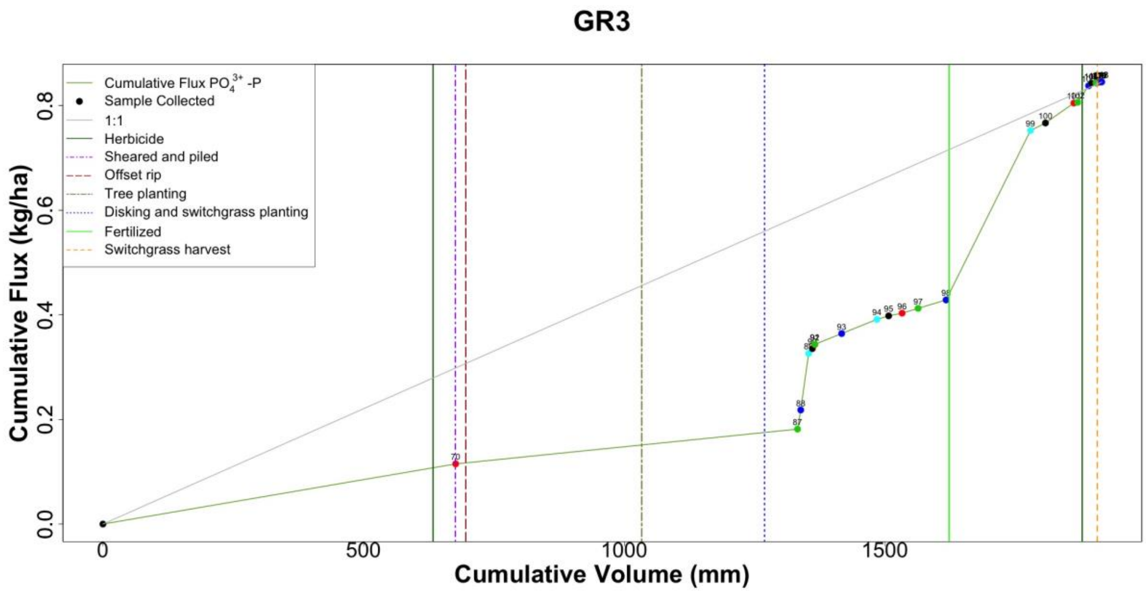

Figure G.133. Cumulative PO_4^{3+}-P load (kg ha^{-1}) of intercropped/replanted watershed (GR3) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

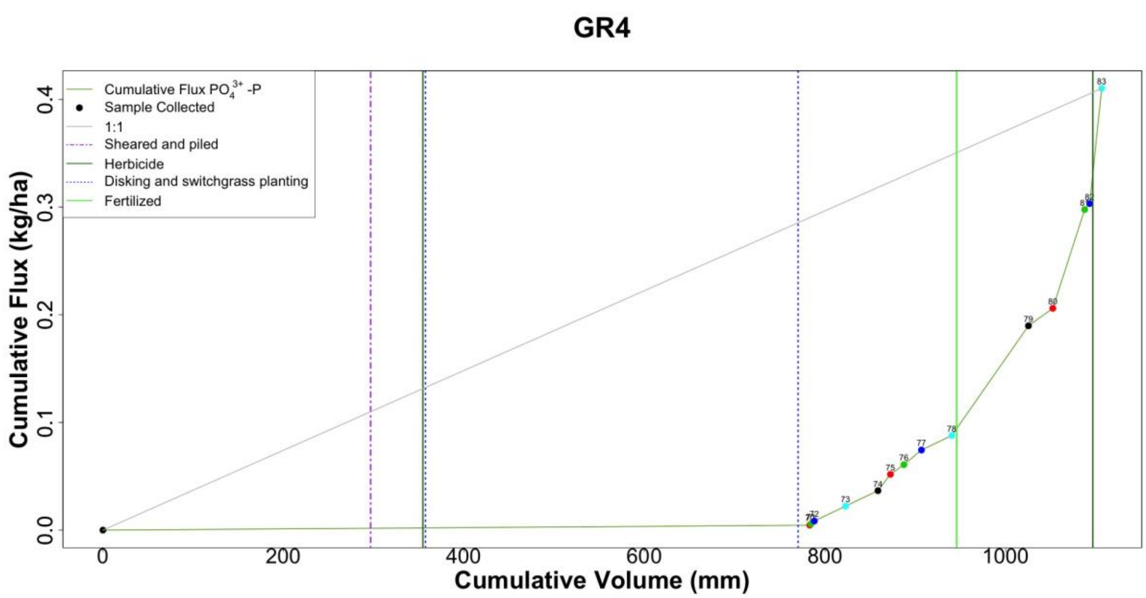

Figure G.134. Cumulative PO_4^{3+}-P load (kg ha^{-1}) of switchgrass watershed (GR4) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

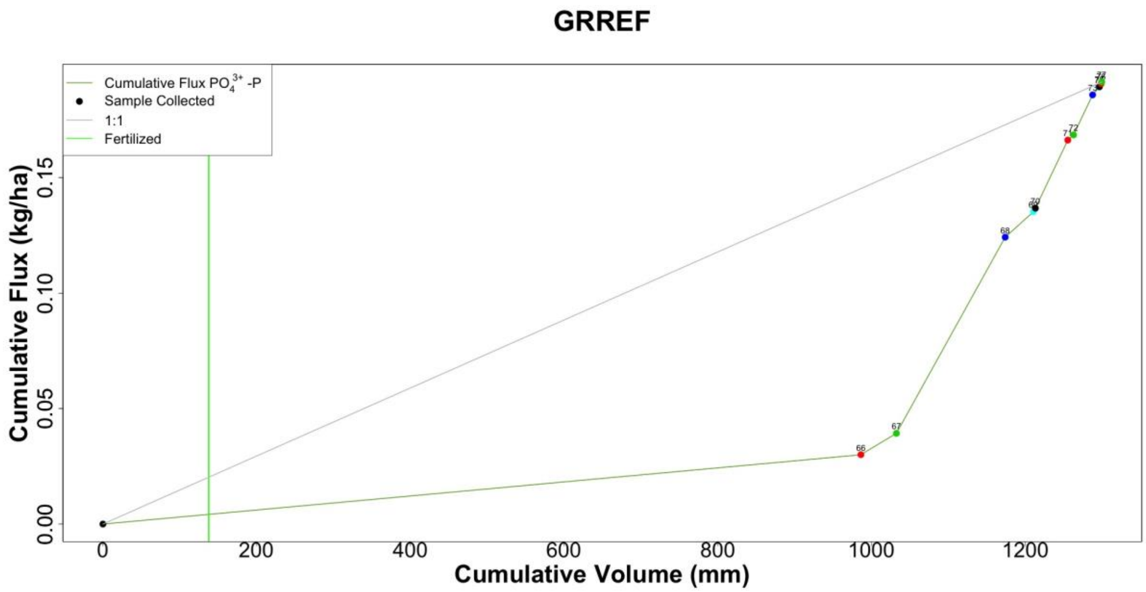

Figure G.135. Cumulative PO_4^{3+}-P load (kg ha^{-1}) of mature pine reference watershed (GRREF) as a function of cumulative flow volume (mm) during Jan 2011 to Nov 2014.

Cumulative load: treatment versus control watershed (GR1) (2011 to 2014)

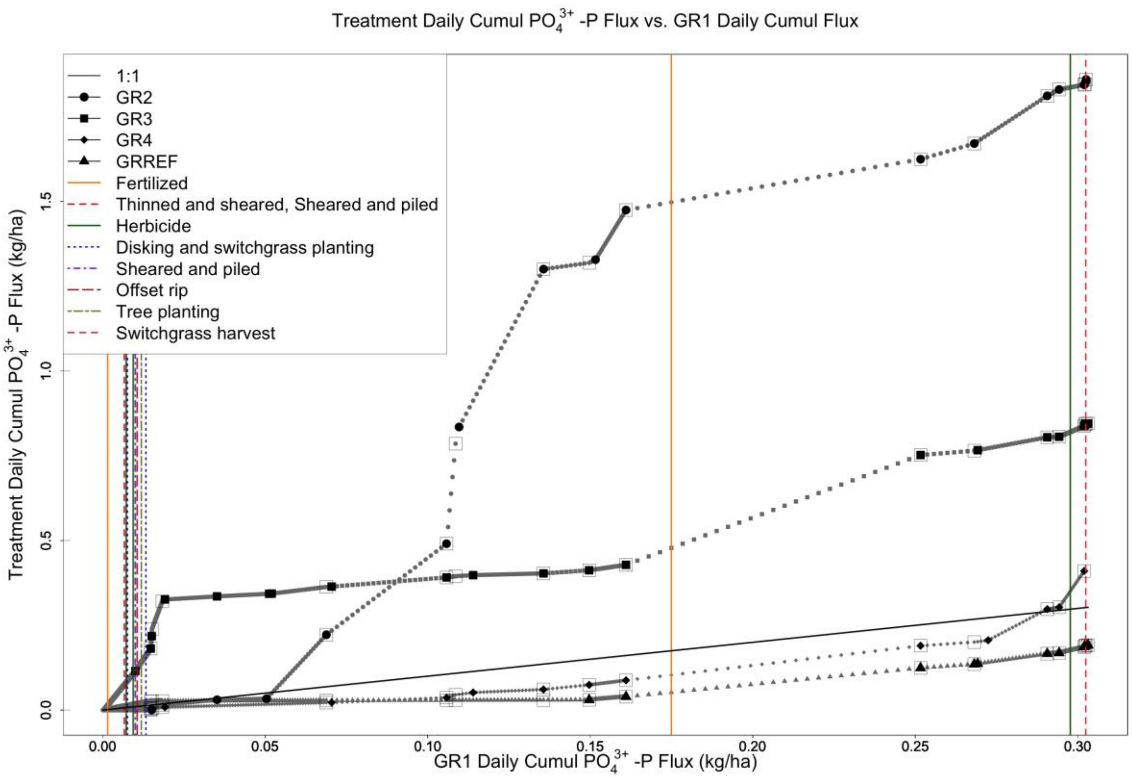

Figure G.136. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of all watersheds (GR2, GR3, GR4, GRREF) as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

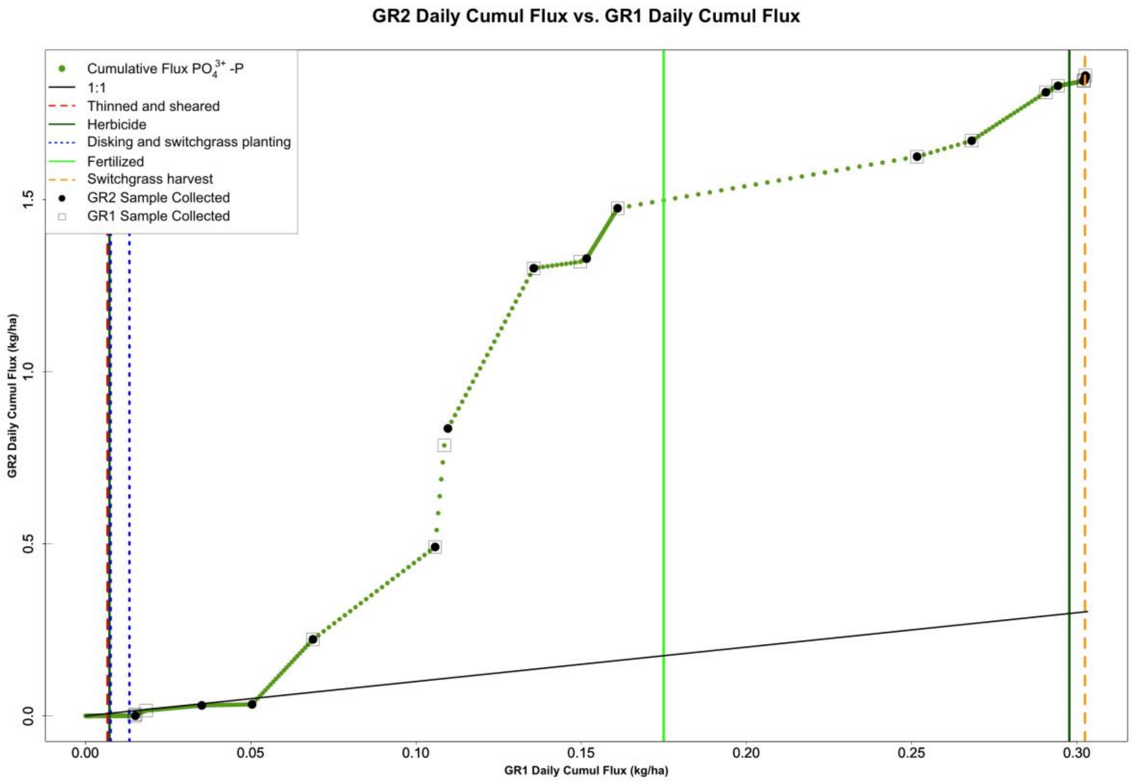

Figure G.137. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

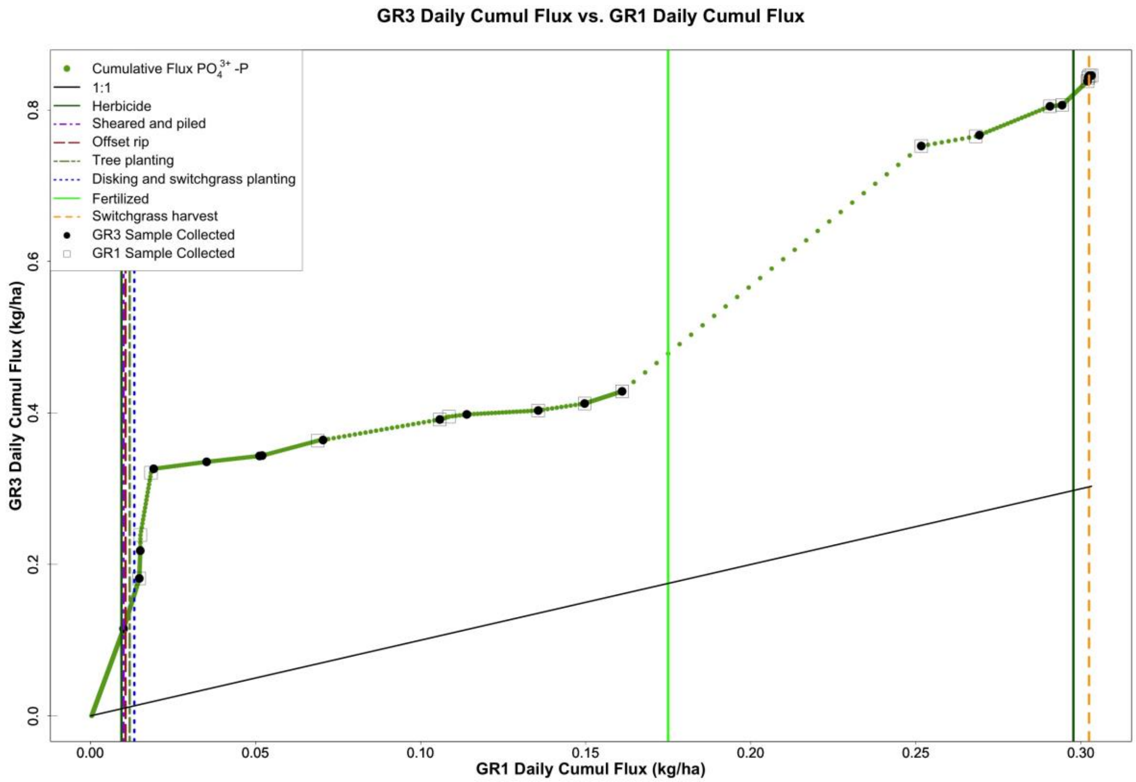

Figure G.138. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

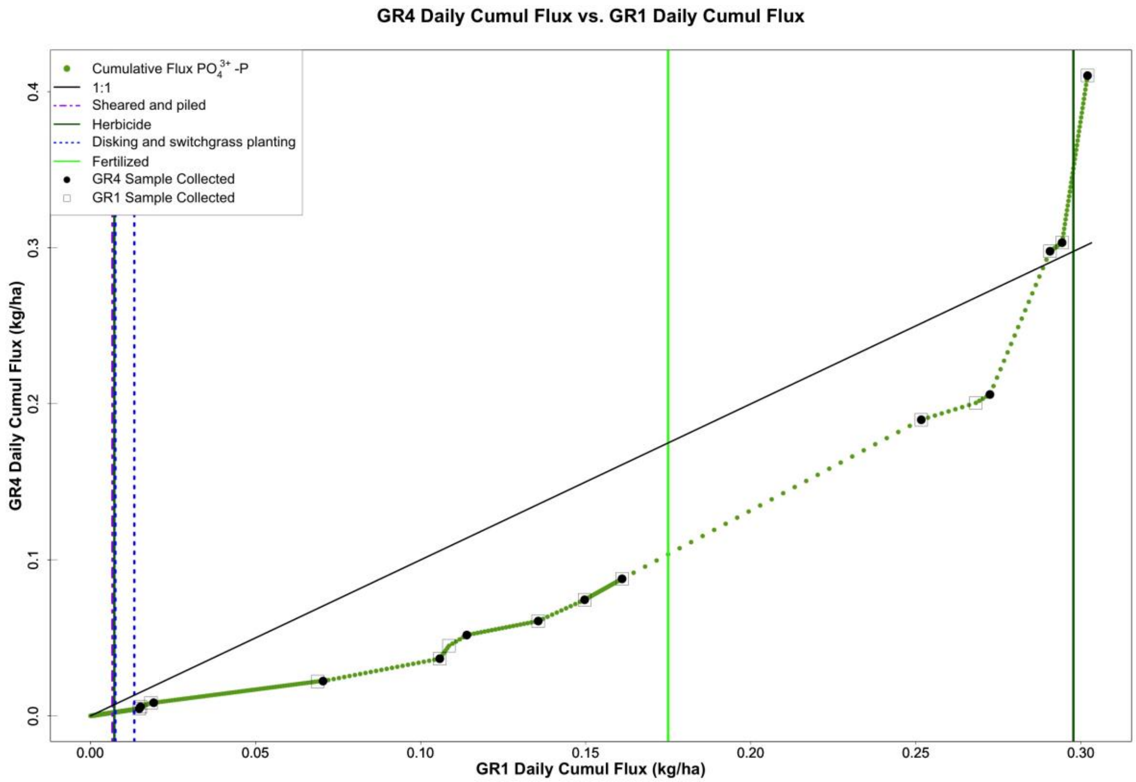

Figure G.139. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

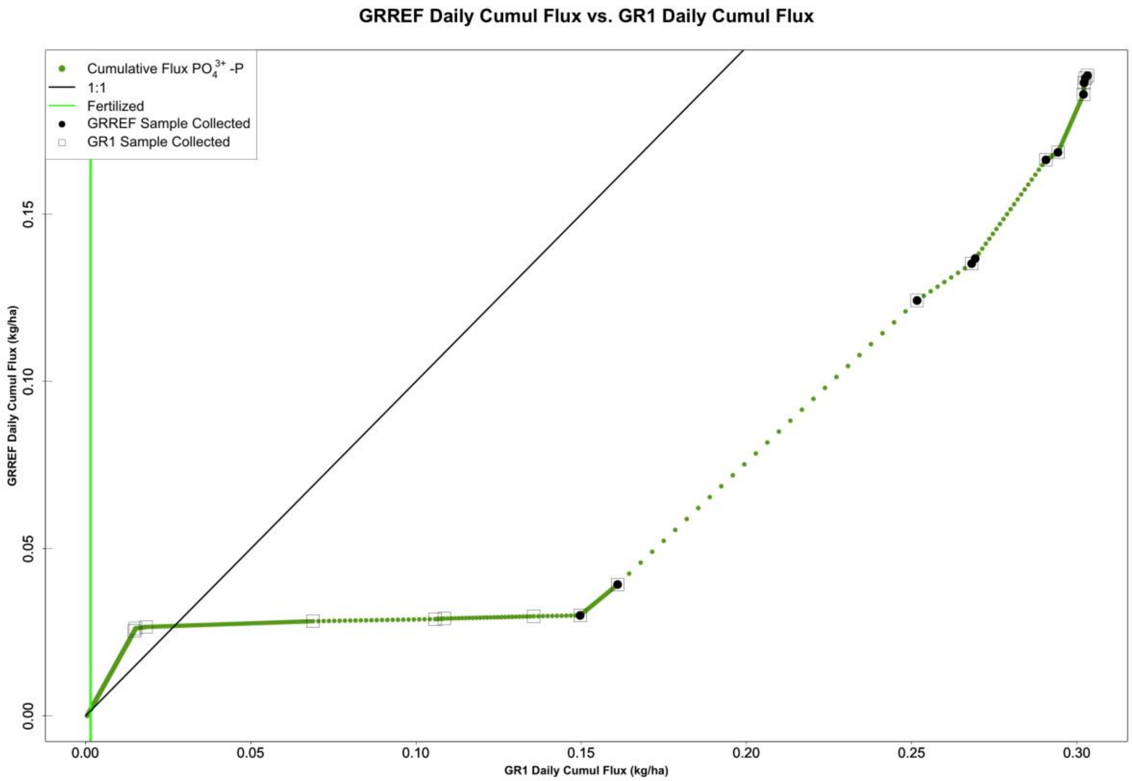

Figure G.140. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of watershed GRREF as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of control watershed (GR1) from Feb 2011 to Nov 2014.

Cumulative load: treatment versus mature reference watershed (GRREF) (2011 to 2014)

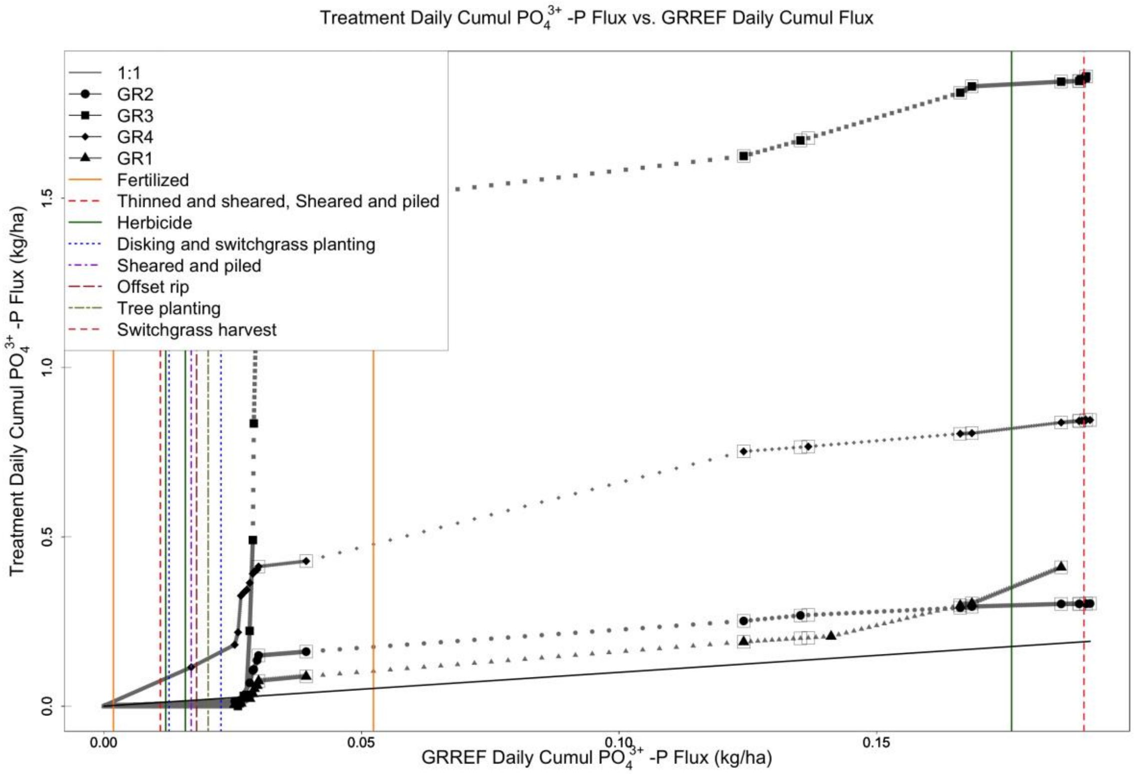

Figure G.141. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of all watersheds (GR1, GR2, GR3, GR4) as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

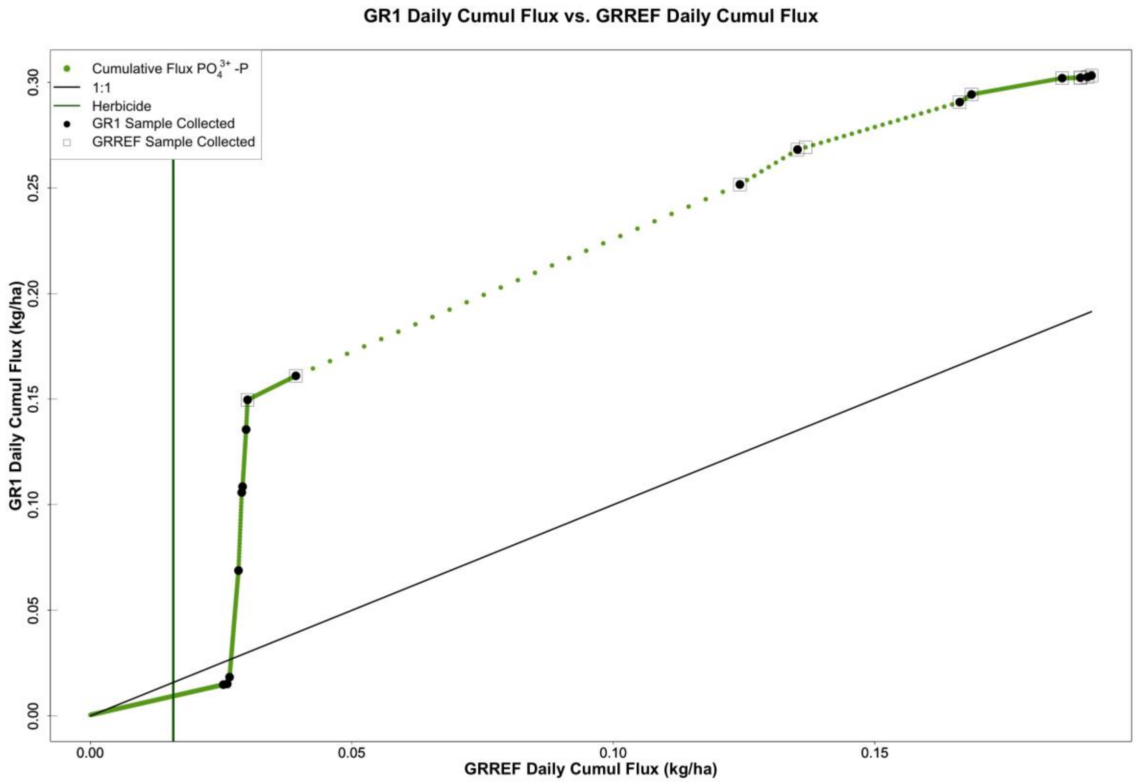

Figure G.142. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of watershed GR1 as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

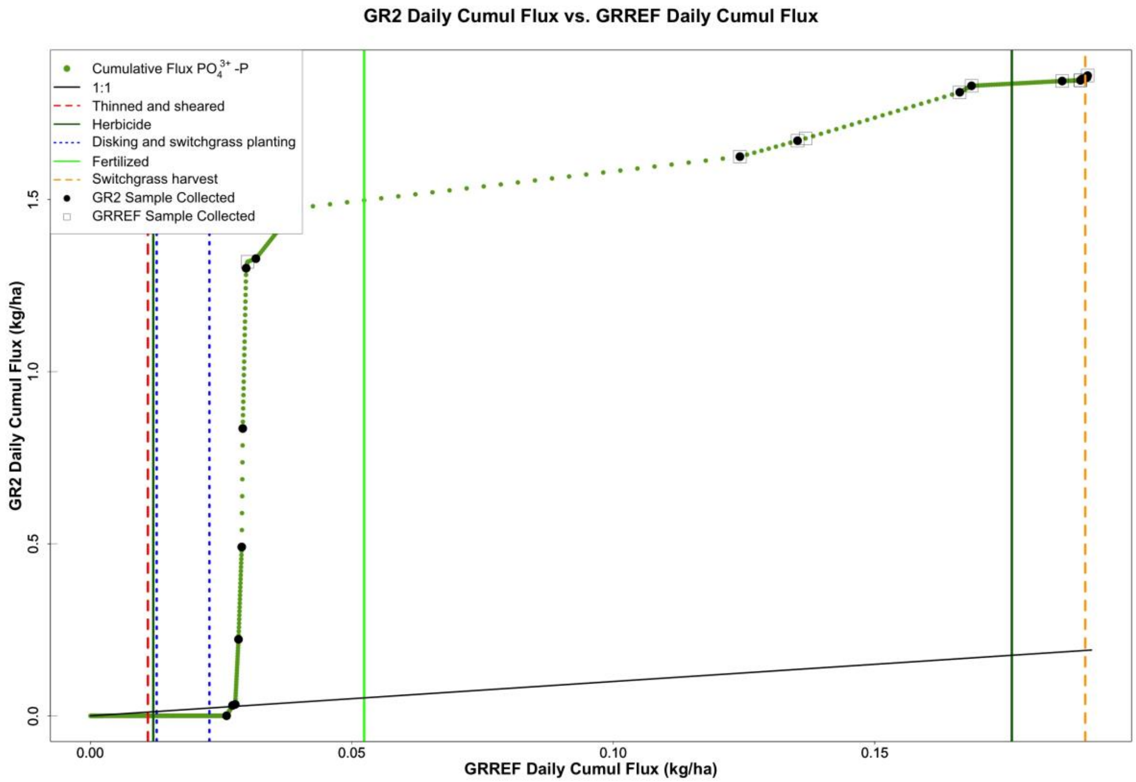

Figure G.143. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of watershed GR2 as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

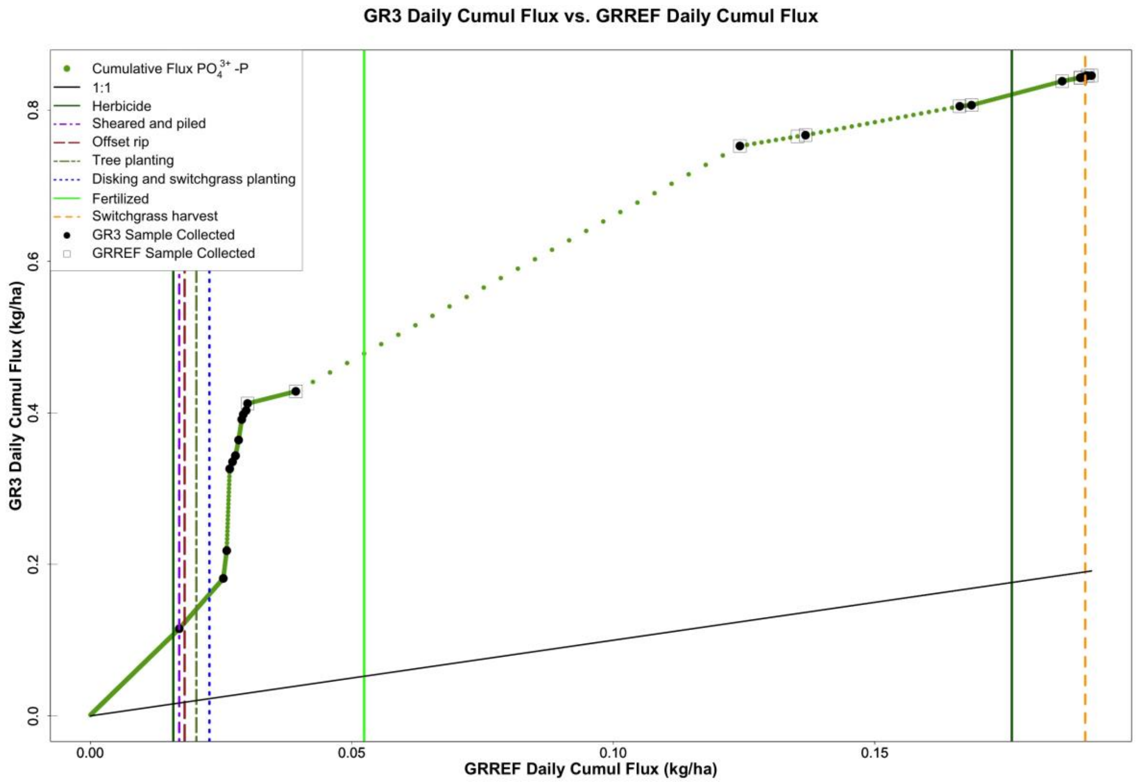

Figure G.144. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of watershed GR3 as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

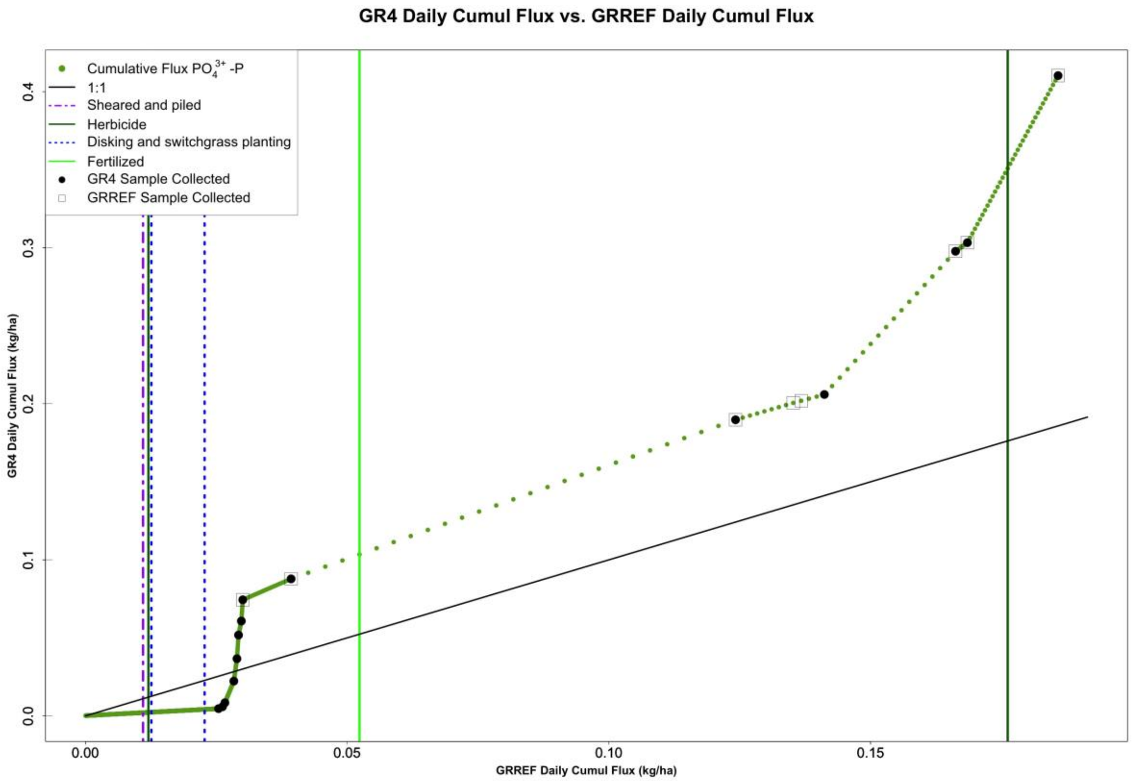

Figure G.145. Daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of watershed GR4 as a function of daily cumulative PO_4^{3+}-P load (kg ha^{-1}) of mature pine reference watershed (GRREF) from Feb 2011 to Nov 2014.

APPENDIX H: APEX Model

H.1 Input values and equations

Table H.1. Final input values and equations used in the model for each watershed (GR1, GR2, GR3, GR4 [calibration and validation]).

		GR1	**GR2**	**GR3**	**GR4-Cal**	**GR4-Val**
Parameter File						
Runoff curve number initial abstraction	PARM 20	0.30	0.20	0.40	0.20	0.20
Exponential coefficient used to account for rainfall intensity on curve number	PARM 25	1.7	0.0	1.5	0.0	0.0
SCS curve number index coefficient	PARM 42	1.6	1.5	1.5	2.5	2.5
Subsurface flow factor	PARM 90	100	85	70	100	100
Control File						
PET equation code	IET	Penman-Monteith (0)	Penman-Monteith (0)	Penman-Monteith (0)	Penman-Monteith (0)	Penman-Monteith (0)
Runoff estimation methodology	INFL	CN estimate of Q	CN estimate of Q	CN estimate of Q	CN estimate of Q	CN estimate of Q
Duration of antecedent period for rainfall and PET accumulation to drive water table	IWTB	15	15	15	15	15
Exponent in watershed area flow rate equation	QCF	0.5	0.5	0.5	0.5	0.5
Floodplain saturated hydraulic conductivity	FPSC	30	30	30	30	30
Maximum groundwater storage (mm)	GWSO	0	0	0	0	0
Groundwater residence time	RFTO	0	0	0	0	0

Table H.1. Continued.

Return flow/ (return flow + deep percolation)	RFPO	0.99	0.99	0.99	0.99	0.99
Equation for water erosion	DRV	3	3	3	3	3
Operation Schedule						
Time from planting to maturity (Pine trees)	XMTU	20	20	15	15	15
Potential heat units	OPV1	RNGE= 4500 SWCH= NA	RNGE= 4500 SWCH= 4000	RNGE= 1000 SWCH= 4000	RNGE= 4500 SWCH= 1000	RNGE= 4500 SWCH= 3000
Land use number or 2 Condition SCS Runoff Curve number	OPV2	Pine: 27-29	Pine = 27-29 RNGE= 24 SWCH= 24	Pine = 27-29 RNGE= 24, 29 SWCH= 28	Pine= 27-29 RNGE= 29 SWCH = 24	Pine = 27-29 RNGE= 23 SWCH= 23
Plant population (ha^{-1})	OPV5	Pine = 1077 RNGE = 500 SWCH = 30		Pine= 1077 RNGE= 500 SWCH= 30	Pine= 1077 RNGE= 500 SWCH= 30	Pine= 1077 RNGE= 30 SWCH= 30
Soil File						
Soil hydrologic group	HSG	3	3	3	3	3
Maximum groundwater storage	GWMX	0	0	0	0	0
Groundwater residence time (days)	RFTT	30	30	30	30	30
Return flow/ (return flow + deep percolation)	RFPK	0.99	0.99	0.99	0.99	0.99
Crop File						
Radiation use efficiency (SWCH)	WA	NA	45	45	12	12
Fraction of growing season when LAI declines (SWCH)	DLAI	NA	0.4	0.4	0.6	0.6

H.2 Measured and Predicted Annual Streamflow

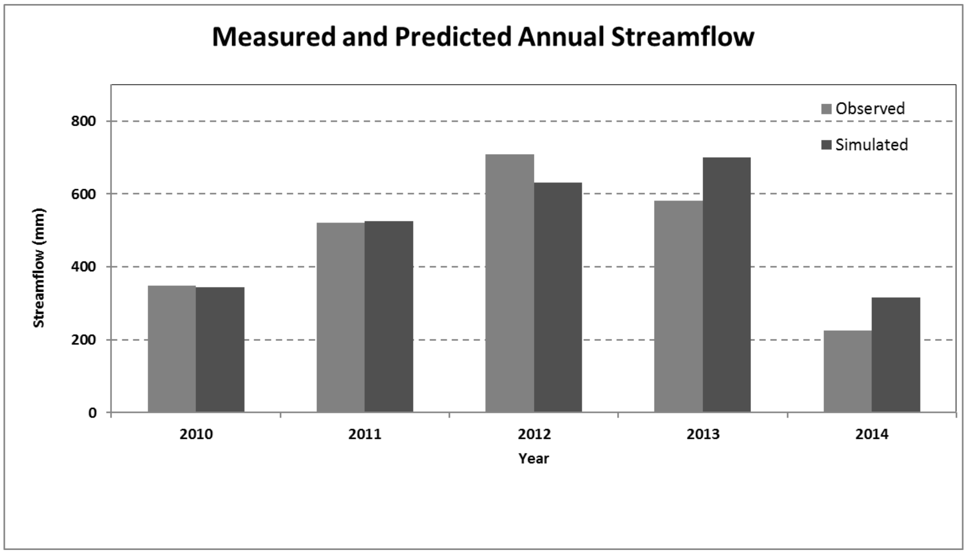

Figure H.1. Measured and predicted annual streamflow (mm) from watershed GR1 from March 4 2010 through December 1 2014.

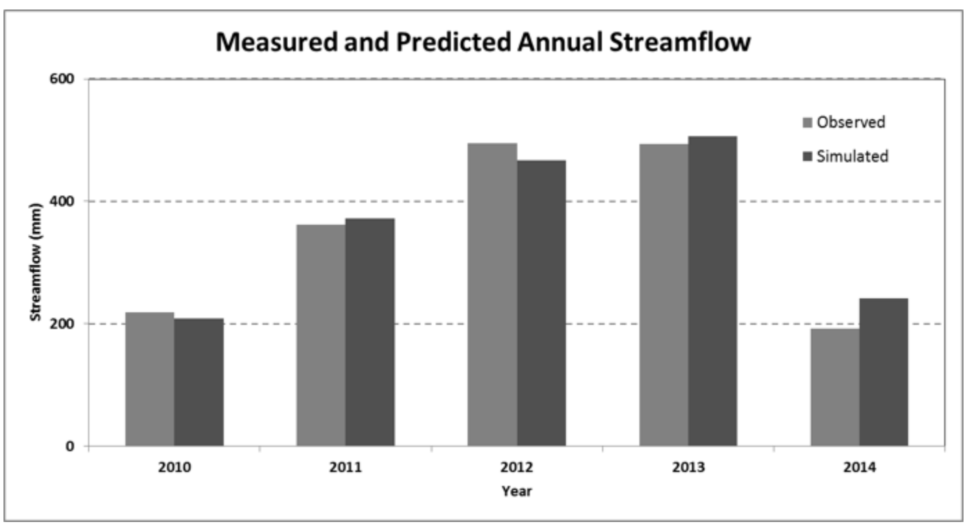

Figure H.2. Measured and predicted annual streamflow (mm) from watershed GR2 from March 4 2010 through December 1 2014.

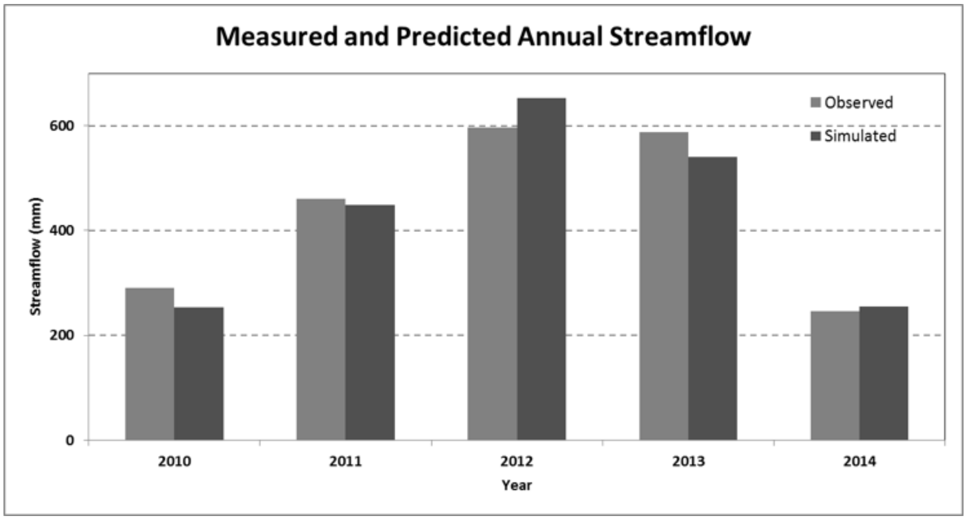

Figure H.3. Measured and predicted annual streamflow (mm) from watershed GR3 from March 4 2010 through December 1 2014.

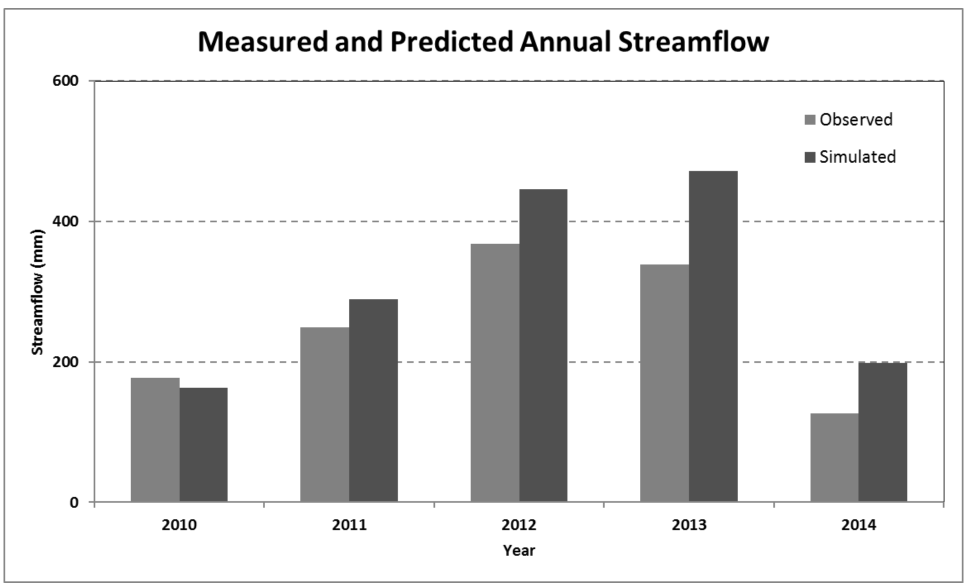

Figure H.4. Measured and predicted annual streamflow (mm) from watershed GR4 from March 4 2010 through December 1 2014.

H.3 Predicted and Measured Daily Flow Plots

Young pine control watershed

Calibration

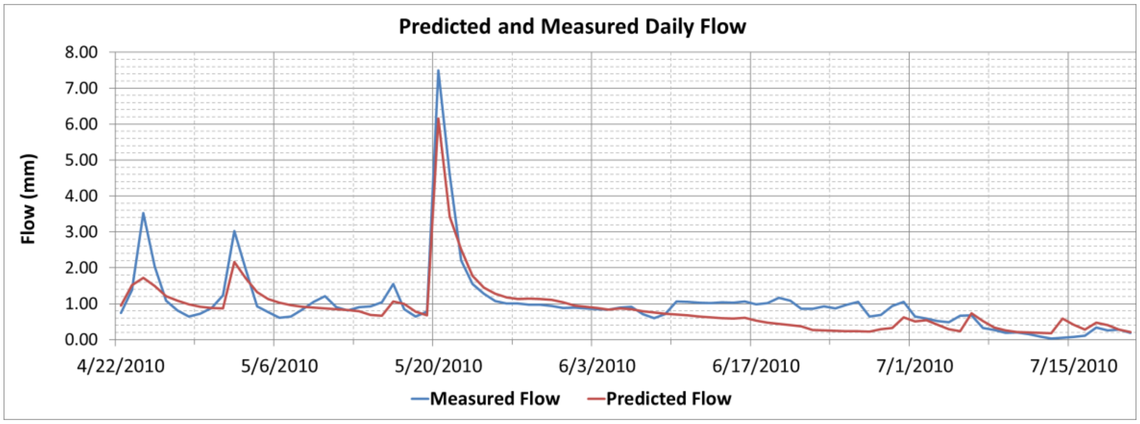

Figure H.5. Time series plot for predicted and measured flow from April through July 2010 (calibration period) for watershed GR1 (young pine control).

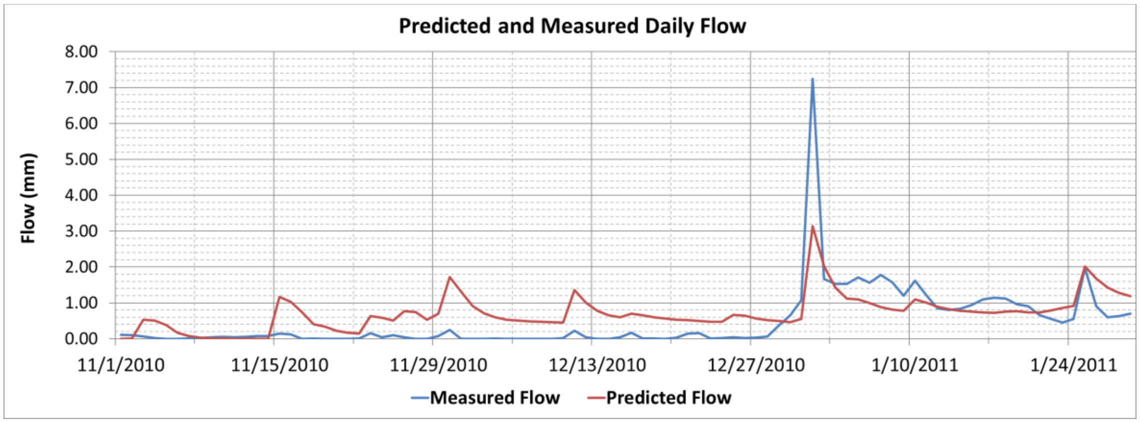

Figure H.6. Time series plot for predicted and measured flow from Nov 2010 through Jan 2011 (calibration period) for watershed GR1 (young pine control).

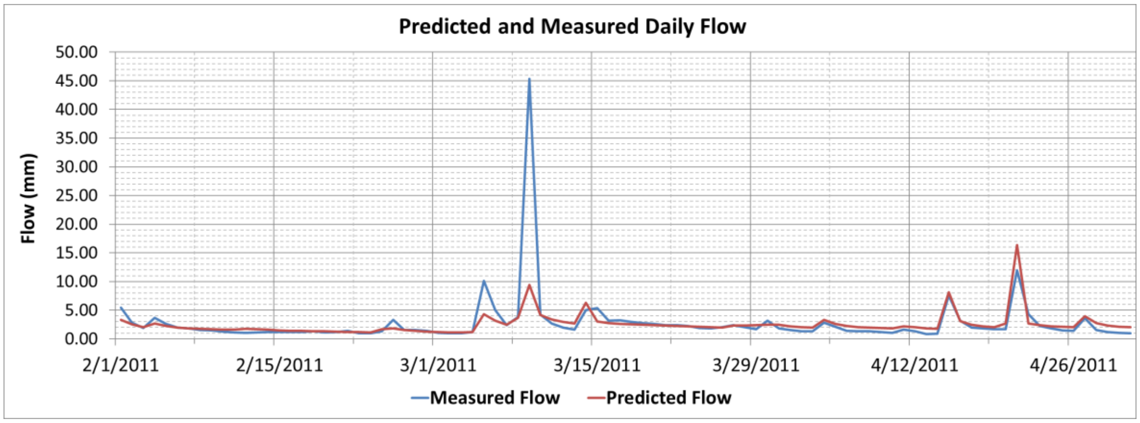

Figure H.7. Time series plot for predicted and measured flow from Feb through May 2011 (calibration period) for watershed GR1 (young pine control).

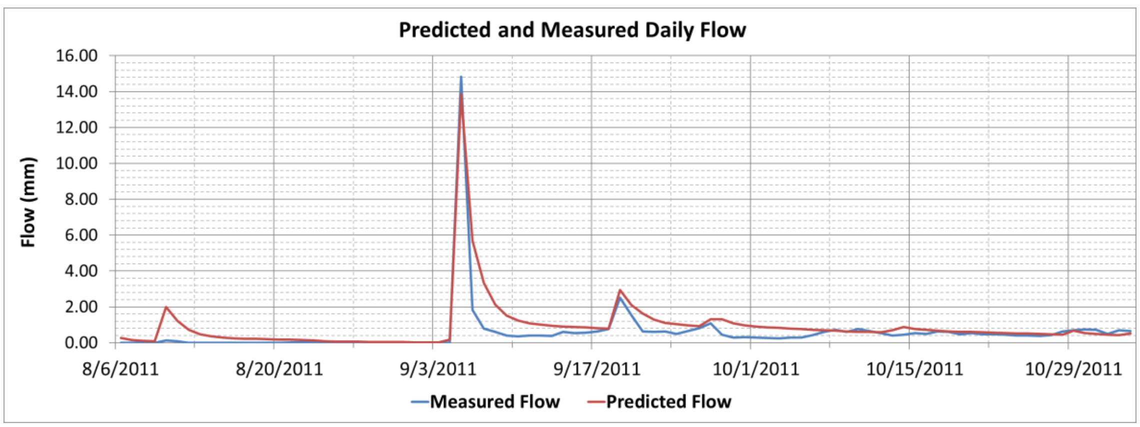

Figure H.8. Time series plot for predicted and measured flow from Aug through Oct 2011 (calibration period) for watershed GR1 (young pine control).

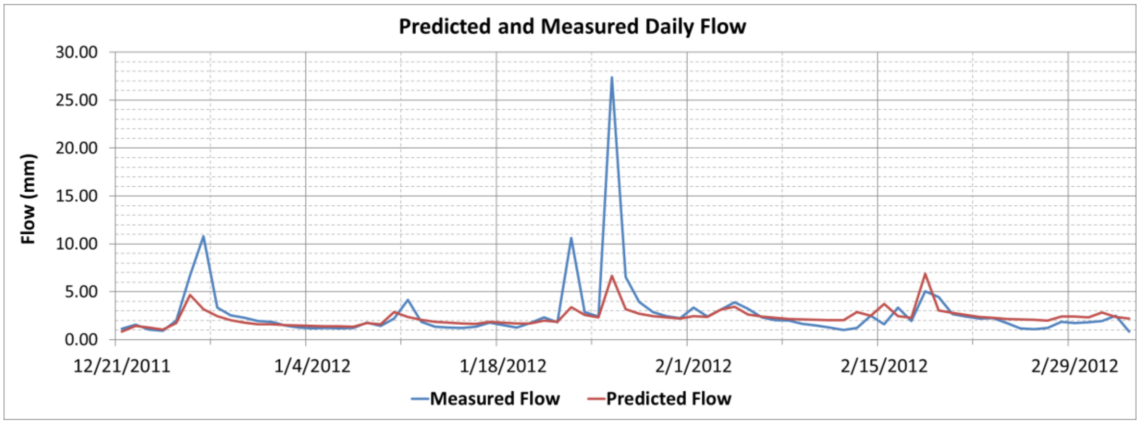

Figure H.9. Time series plot for predicted and measured flow from Dec 2011 through Feb 2012 (calibration period) for watershed GR1 (young pine control).

Validation

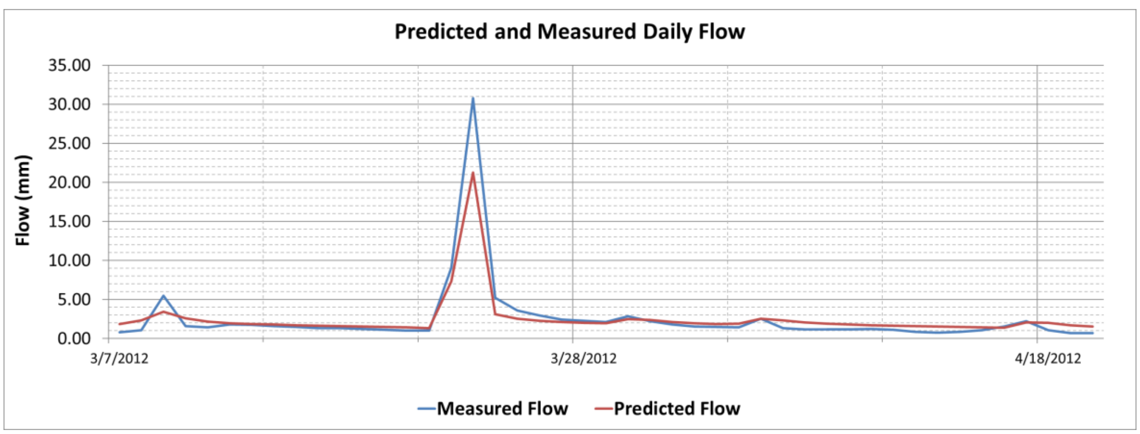

Figure H.10. Time series plot for predicted and measured flow from Mar through Apr 2012 (validation period) for watershed GR1 (young pine control).

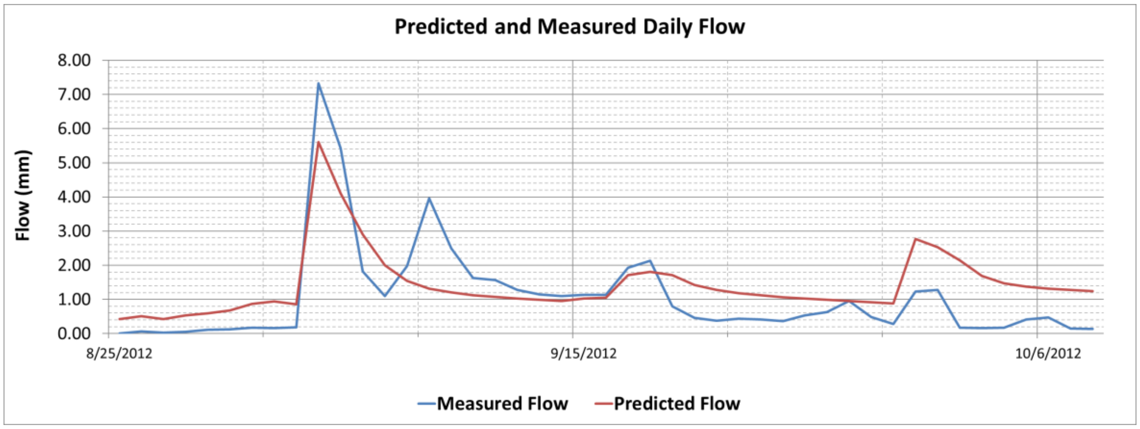

Figure H.11. Time series plot for predicted and measured flow from Aug through Oct 2012 (validation period) for watershed GR1 (young pine control).

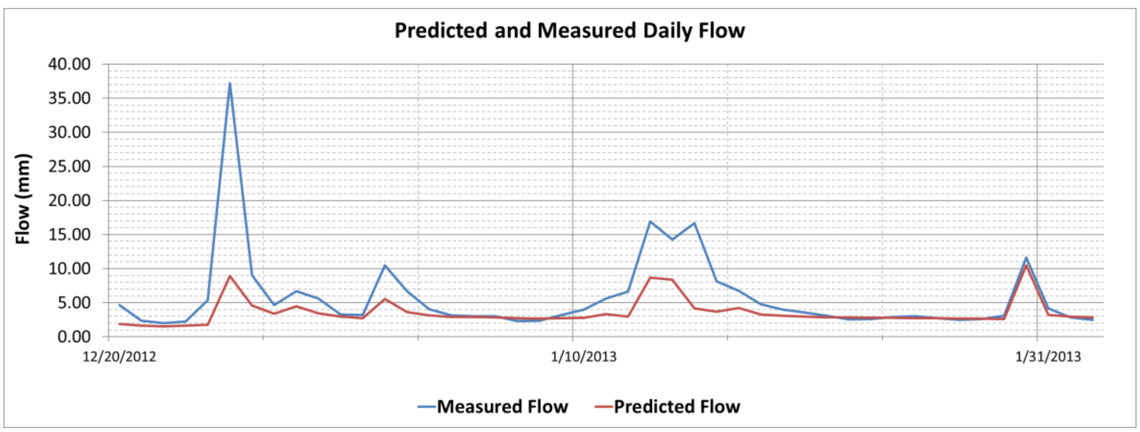

Figure H.12. Time series plot for predicted and measured flow from Dec 2012 through Jan 2013 (validation period) for watershed GR1 (young pine control).

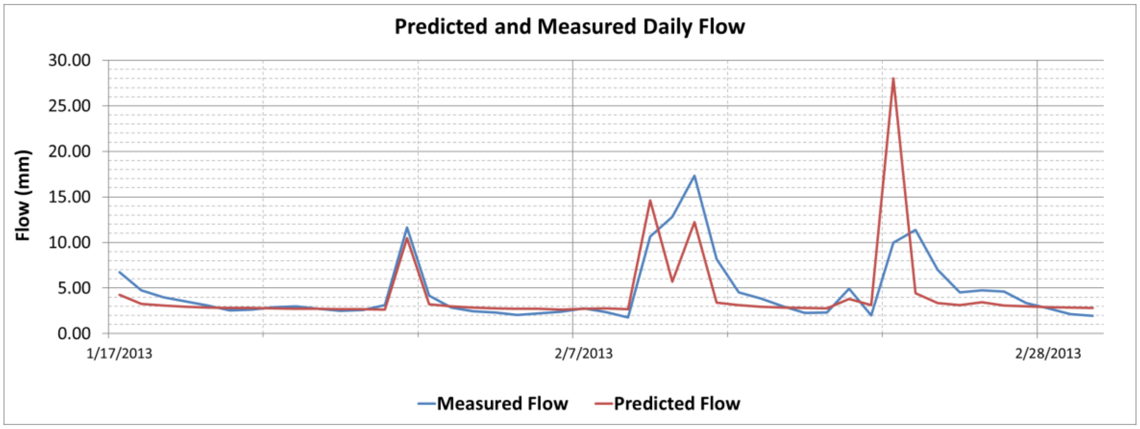

Figure H.13. Time series plot for predicted and measured flow from Jan through Feb 2013 (validation period) for watershed GR1 (young pine control).

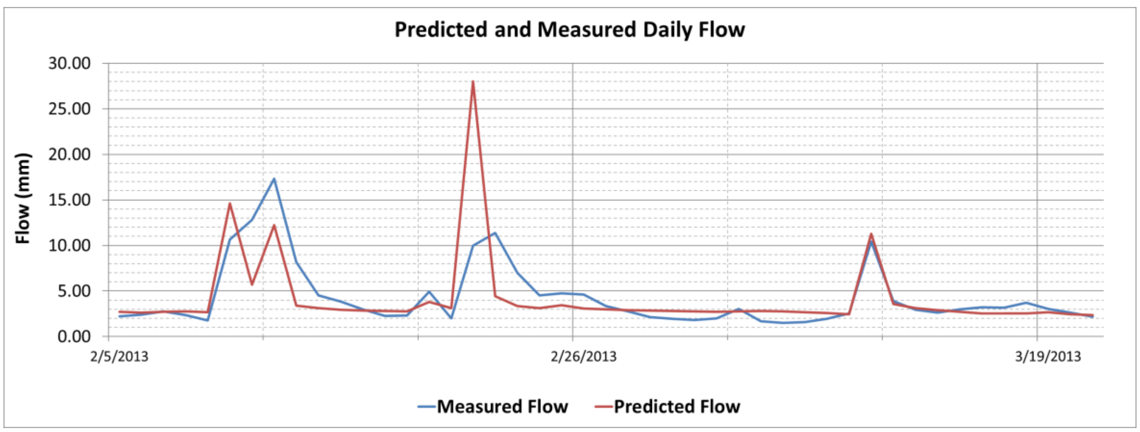

Figure H.14. Time series plot for predicted and measured flow from Feb through Mar 2013 (validation period) for watershed GR1 (young pine control).

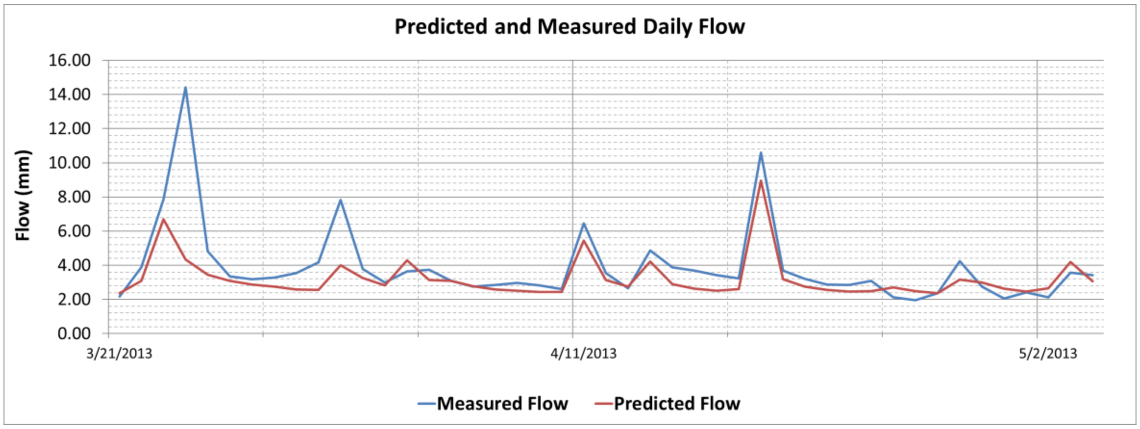

Figure H.15. Time series plot for predicted and measured flow from Mar through May 2013 (validation period) for watershed GR1 (young pine control).

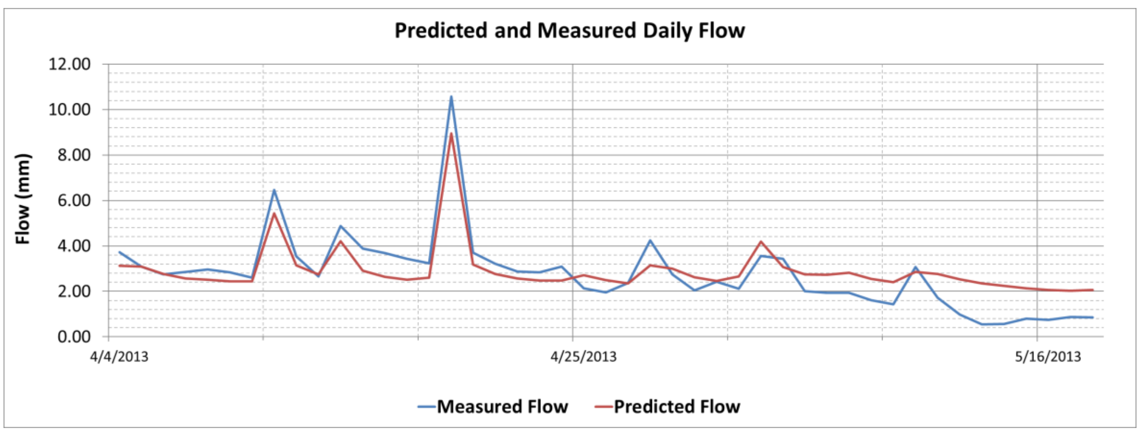

Figure H.16. Time series plot for predicted and measured flow from Apr through May 2013 (validation period) for watershed GR1 (young pine control).

Intercropped-Thinned Watershed

Calibration

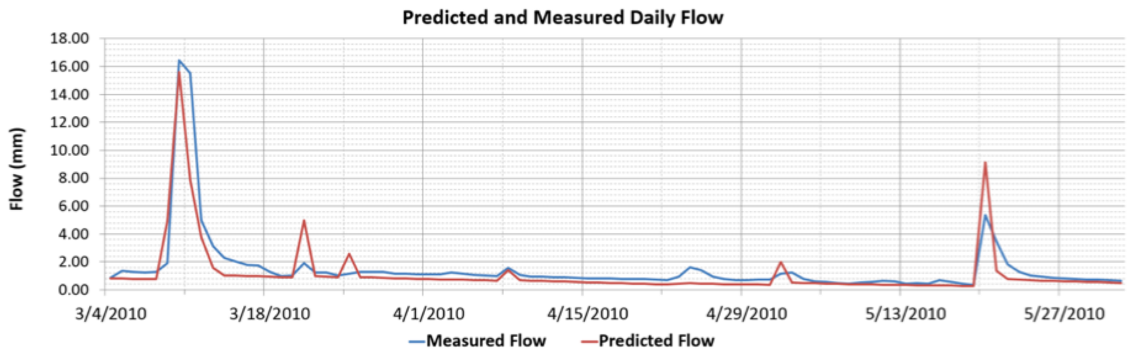

Figure H.17. Time series of measured and predicted outflow from watershed GR2 (thinned, intercropped) during calibration period (March to May 2010).

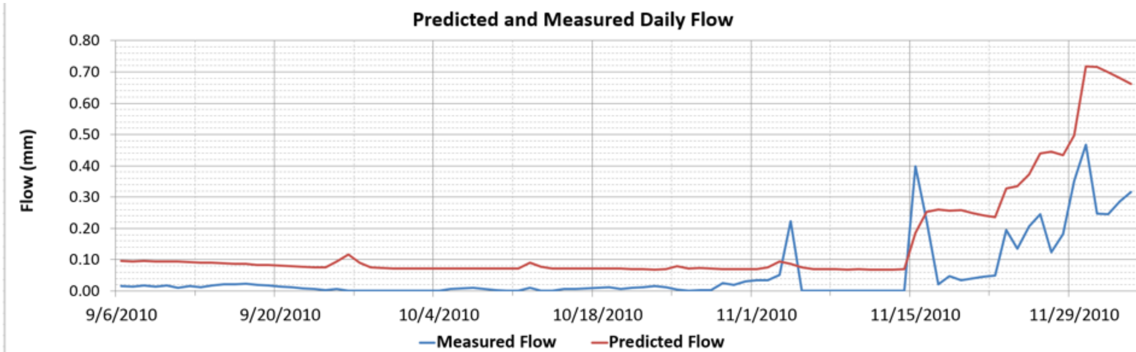

Figure H.18. Time series of measured and predicted outflow from watershed GR2 (thinned, intercropped) during calibration period (September to November 2010).

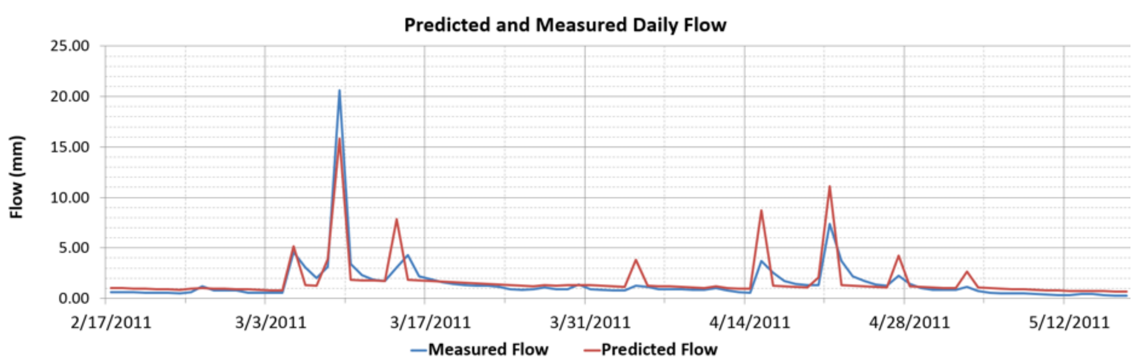

Figure H.19. Time series of measured and predicted outflow from watershed GR2 (thinned, intercropped) during calibration period (February to May 2011).

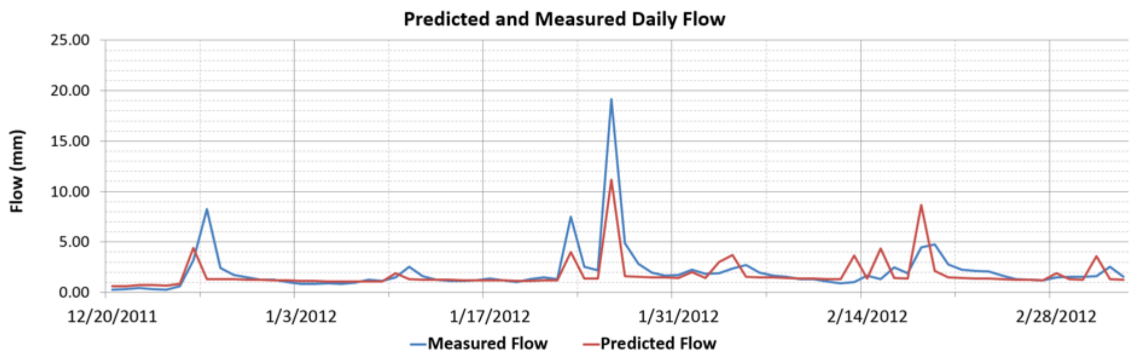

Figure H.20. Time series of measured and predicted outflow from watershed GR2 (thinned, intercropped) during calibration period (December 2011 to February 2012).

Validation

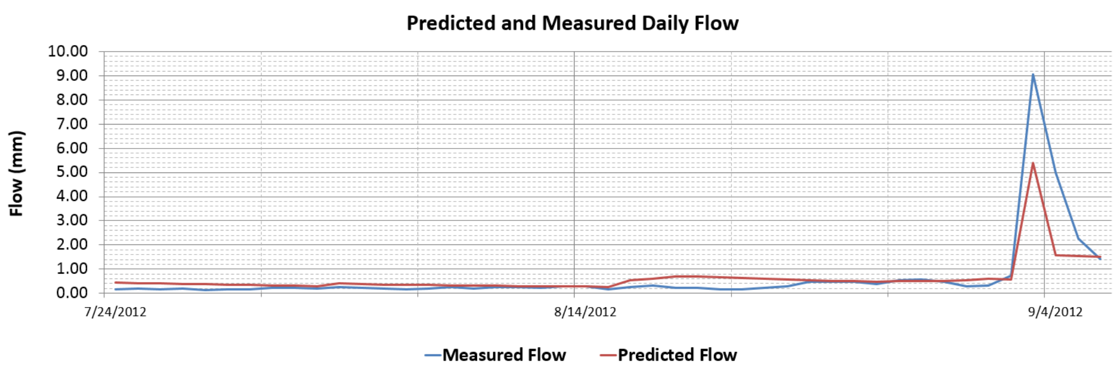

Figure H.21. Time series of measured and predicted outflow from watershed GR2 (thinned, intercropped) during validation period (July to September 2012).

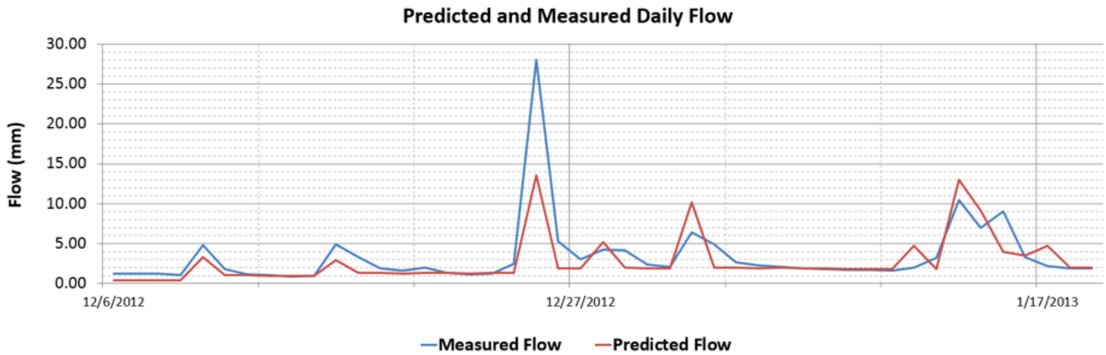

Figure H.22. Time series of measured and predicted outflow from watershed GR2 (thinned, intercropped) during validation period (July to September 2012).

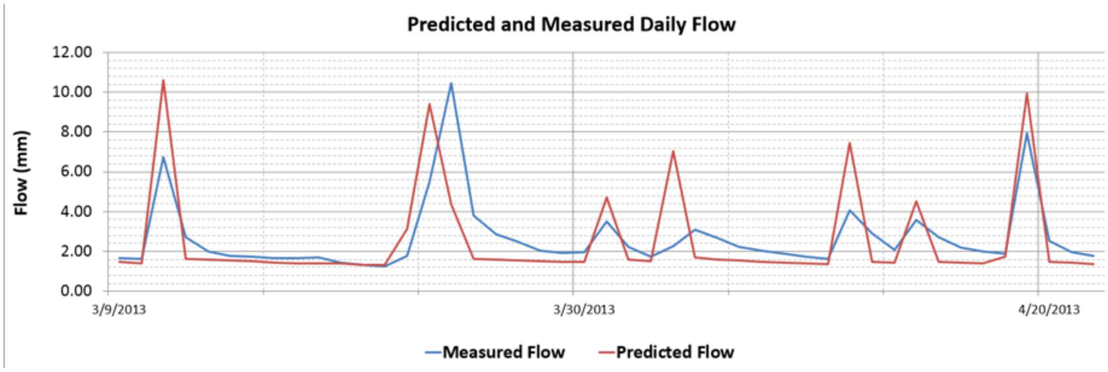

Figure H.23. Time series of measured and predicted outflow from watershed GR2 (thinned, intercropped) during validation period (March to April 2013).

Intercropped-Replanted Watershed

Calibration

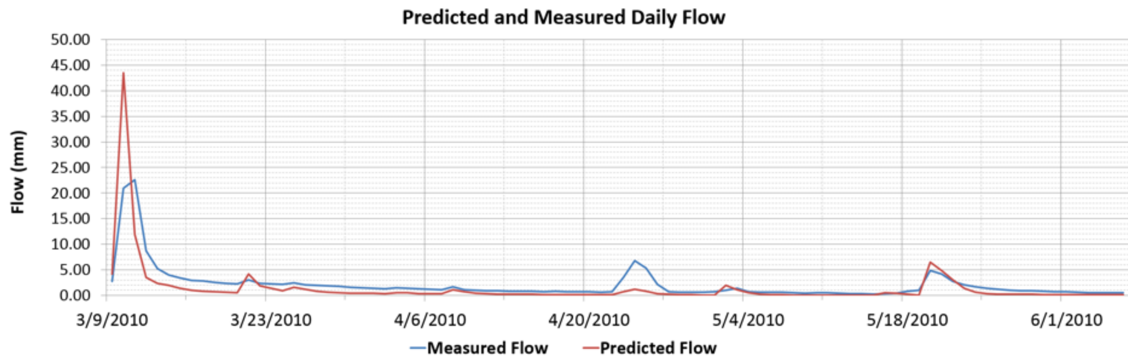

Figure H.24. Time series of measured and predicted outflow from watershed GR3 (intercropped, replanted) during calibration period (March to June 2010).

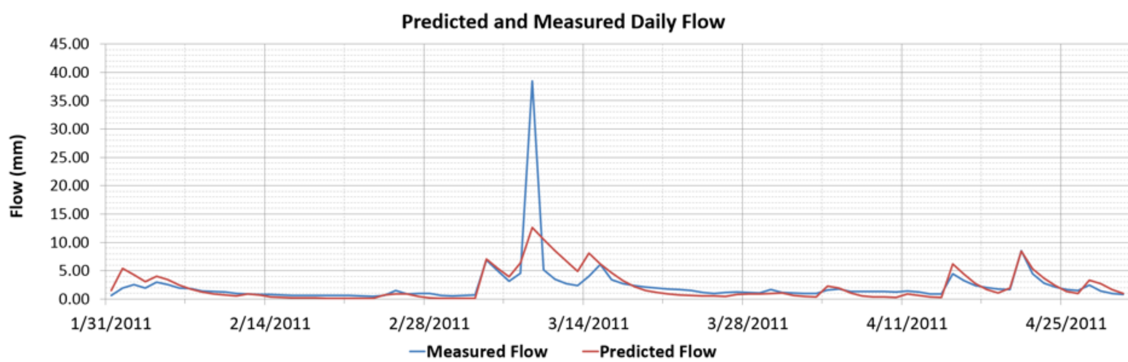

Figure H.25. Time series of measured and predicted outflow from watershed GR3 (intercropped, replanted) during calibration period (January to April 2011).

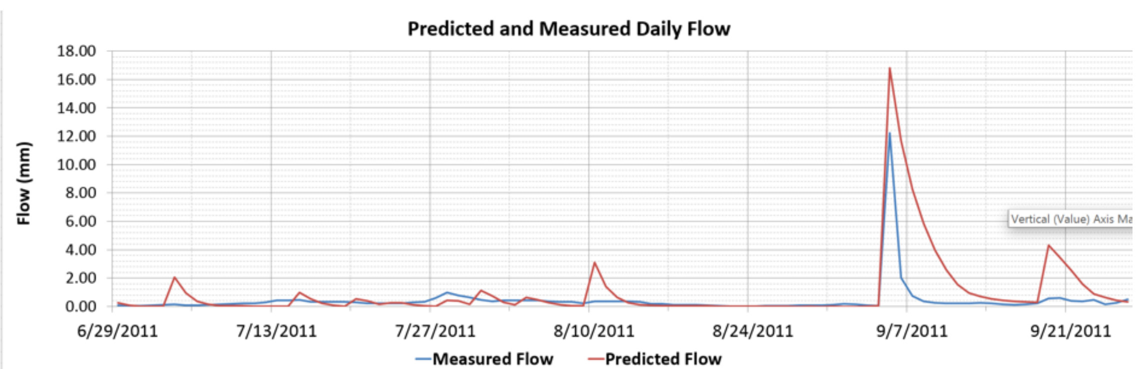

Figure H.26. Time series of measured and predicted outflow from watershed GR3 (intercropped, replanted) during calibration period (June to Sept 2011).

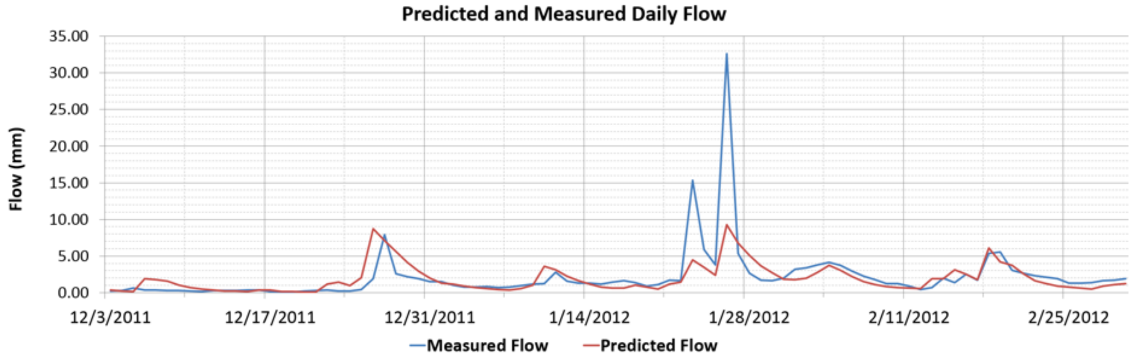

Figure H.27. Time series of measured and predicted outflow from watershed GR3 (intercropped, replanted) during calibration period (Dec 2011 to Feb 2012).

Validation

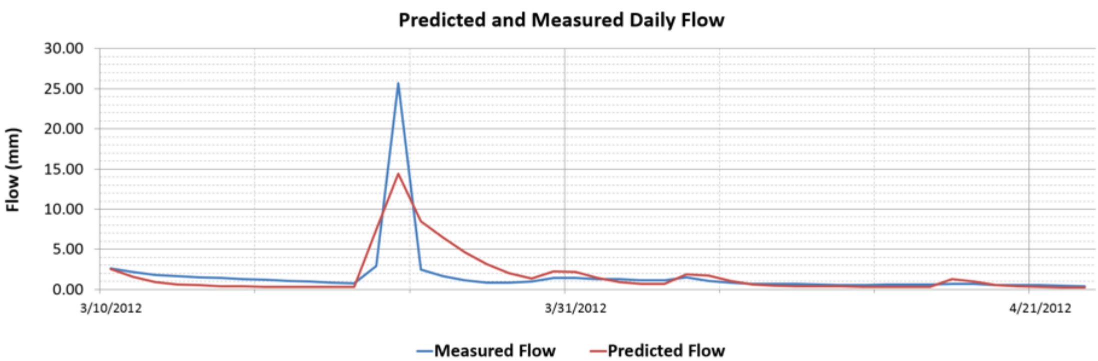

Figure H.28. Time series of measured and predicted outflow from watershed GR3 (intercropped, replanted) during validation period (Mar to Apr 2012).

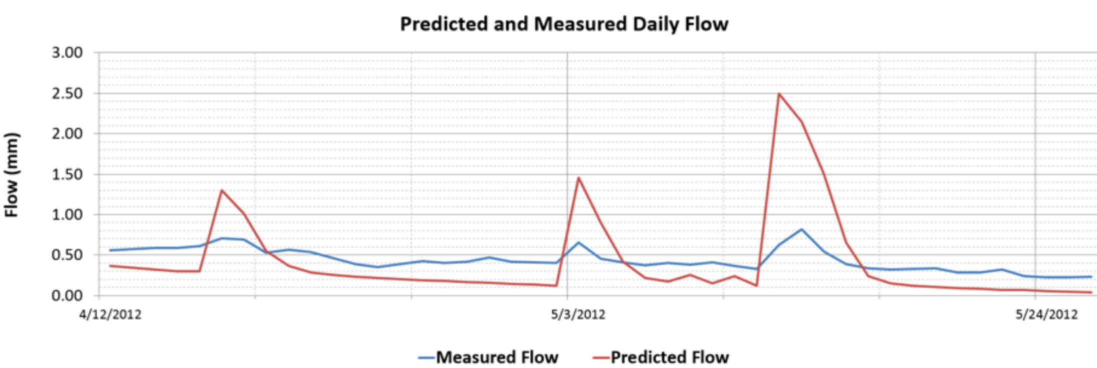

Figure H.29. Time series of measured and predicted outflow from watershed GR3 (intercropped, replanted) during validation period (Apr to May 2012).

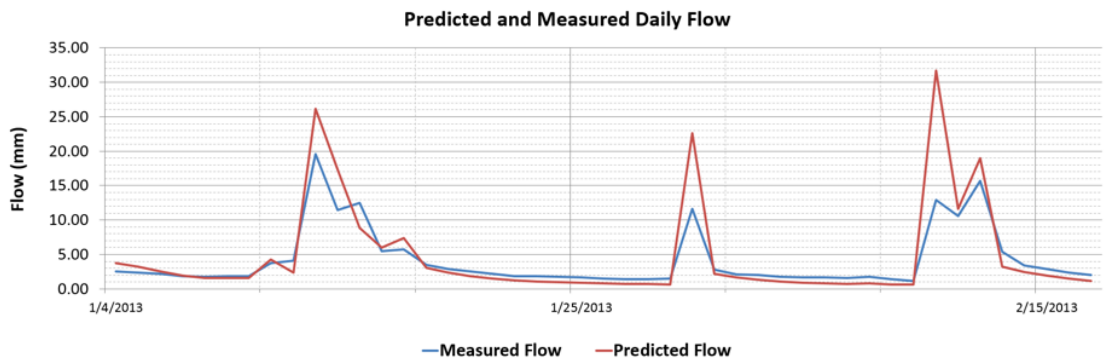

Figure H.30. Time series of measured and predicted outflow from watershed GR3 (intercropped, replanted) during validation period (Jan to Feb 2013).

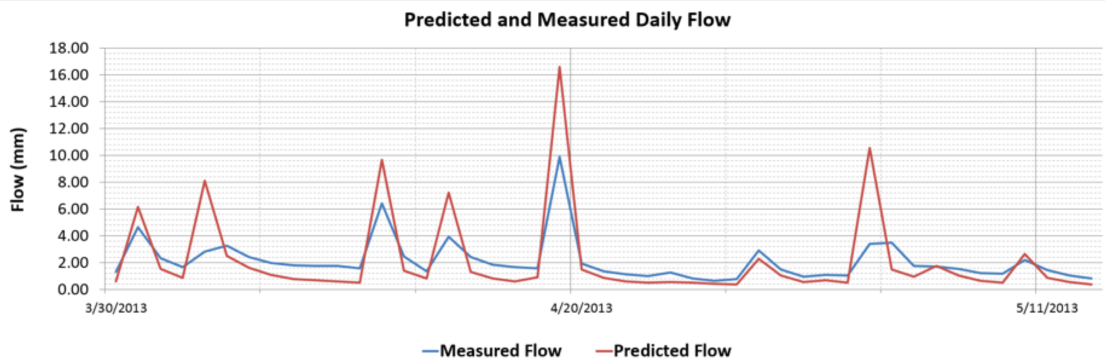

Figure H.31. Time series of measured and predicted outflow from watershed GR3 (intercropped, replanted) during validation period (Mar to May 2013).

Switchgrass Watershed

Calibration

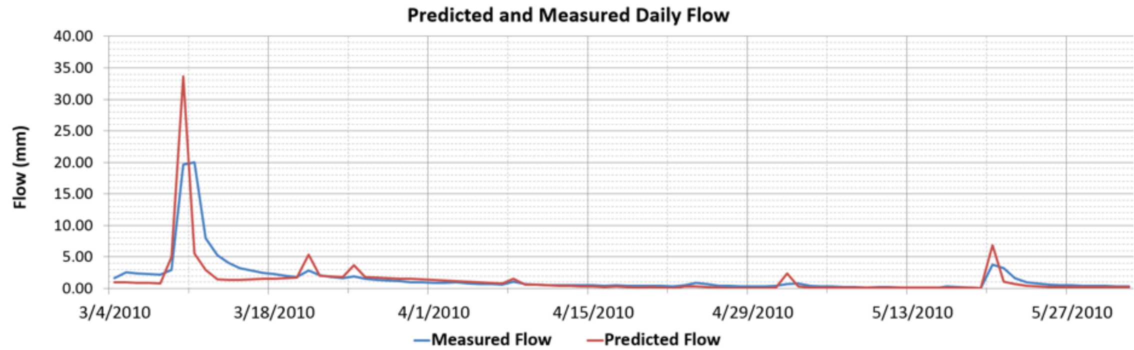

Figure H.32. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during calibration period (Mar to May 2010).

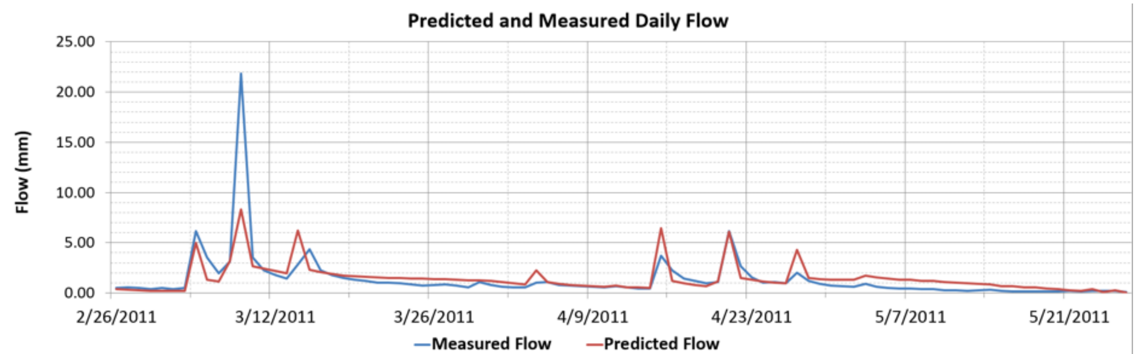

Figure H.33. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during calibration period (Feb to May 2011).

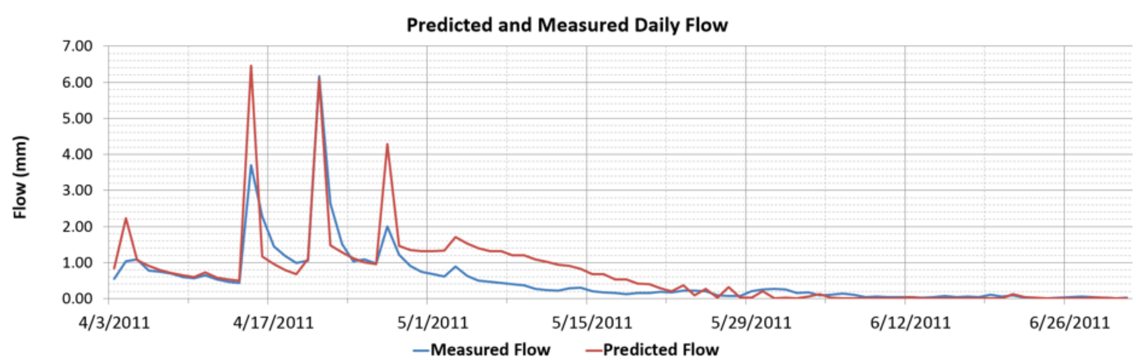

Figure H.34. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during calibration period (Apr to June 2011).

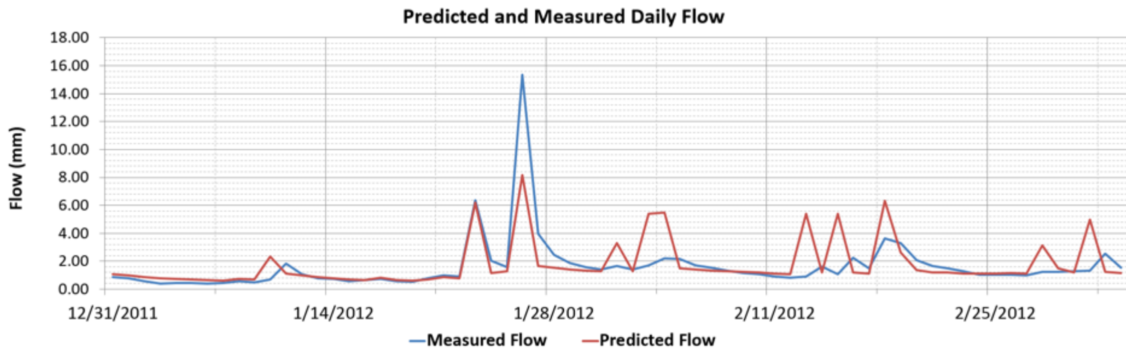

Figure H.35. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during calibration period (Dec 2011 to Feb 2012).

Validation

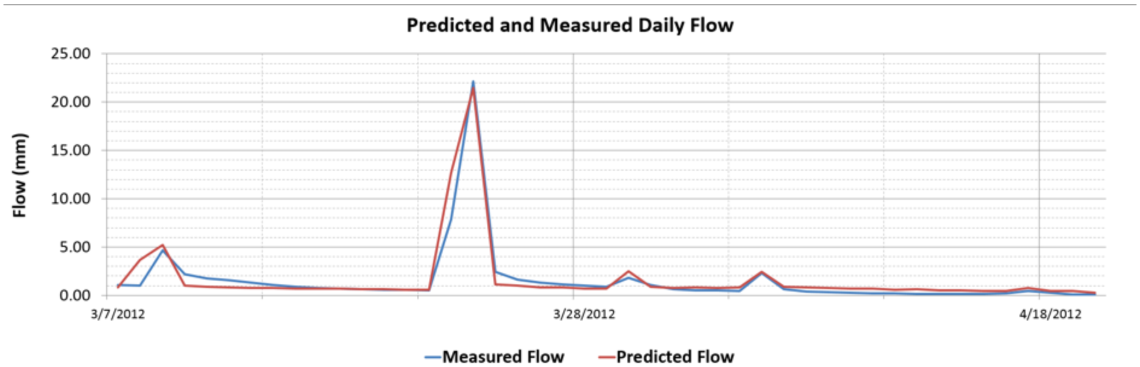

Figure H.36. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during validation period (Mar to Apr 2012).

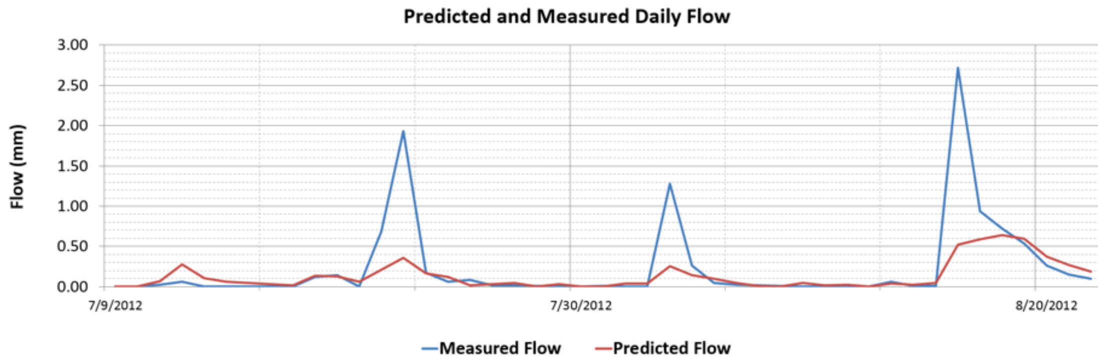

Figure H.37. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during validation period (Jul to Aug 2012).

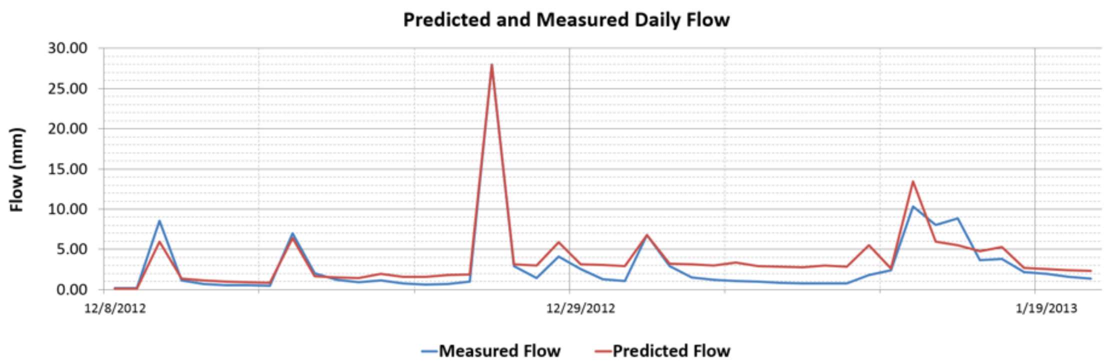

Figure H.38. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during validation period (Dec 2012 to Jan 2013).

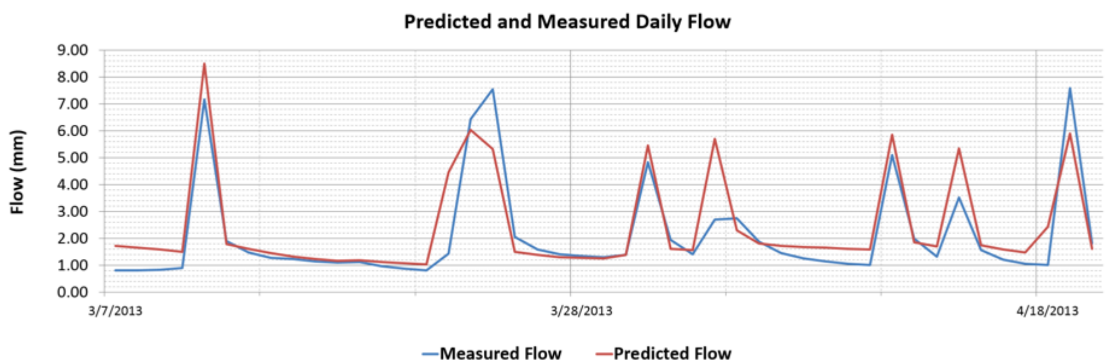

Figure H.39. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during validation period (Mar to Apr 2013).

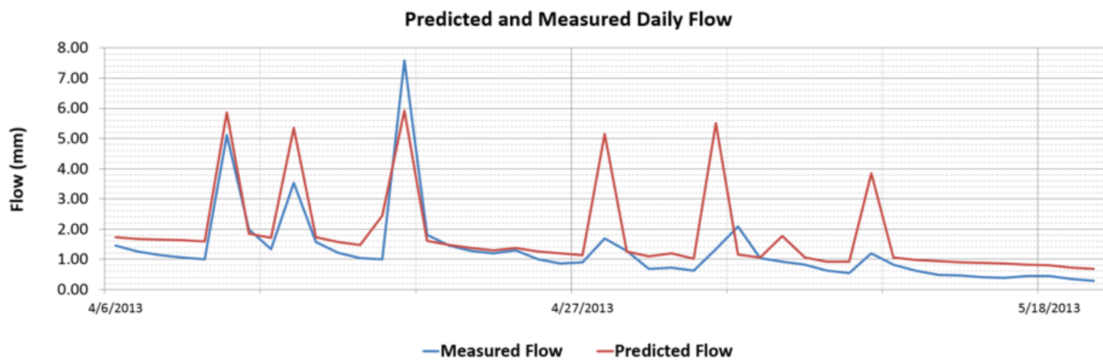

Figure H.40. Time series of measured and predicted daily outflow from watershed GR4 (switchgrass) during validation period (Apr to May 2013).

H.4 Sediment Calibration

The equation for water erosion (set in the Control file) which affects sediment yield was the MUSS Small Watershed MUSLE out of the eight available options. The main parameters that influenced sediment output were soil parameters. The following soil inputs were adjusted for calibrating sediment output: sand, silt, and the organic carbon (WOC) contents in the top soil layer. Reducing WOC and increasing sand and silt (more so silt content) increased the soil erodibility factor (EK), therefore increasing sediment output. Various combinations of sand, silt, and WOC were tested to increase EK. Final values for sand, silt, and WOC were 30, 60, and 0.1, respectively. Simulated cumulative sediment loads (kg ha^{-1}) from each watershed (GR1, GR2, GR3, GR4) are shown in Figure H.41 along with the measured and predicted loads and percent differences for each year (Table H.2).

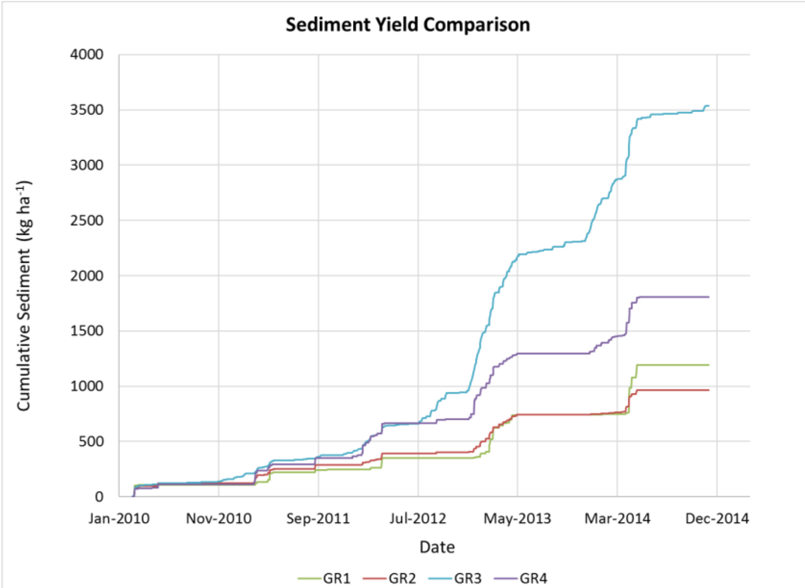

Figure H.41. Simulated cumulative sediment load (kg ha^{-1}) for entire study period (Mar 2010- Dec 2014) for all watersheds (GR1, GR2, GR3, GR4).

Table H.2. Measured and predicted sediment loads from each watershed (GR1, GR2, GR3, GR4).

		Sediment		
		Measured	**Predicted**	**% Difference**
Watershed	**Year**	(kg ha^{-1})	(kg ha^{-1})	
GR1	1	NA	NA	NA
	2	394	154	-61%
	3	681	361	-47%
	4	312	122	-61%
	5	347	447	+29%
GR2	1	NA	NA	NA
	2	497	207	-58%
	3	1435	299	-79%
	4	7259	133	-98%
	5	2367	204	-91%
GR3	1	NA	NA	NA
	2	252	339	+35%
	3	1899	1296	-32%
	4	2474	1025	-59%
	5	1857	631	-66%
GR4	1	NA	NA	NA
	2	96	438	+356%

	3	814	632	-22%
	4	590	275	-53%
	5	485	355	-27%

APPENDIX I: Flow Calculations for V-Notch Weir

The flow (Q) for each watershed was calculated based on the following equations (Villemonte, 1947):

$$Q = 4.2h_u^{2.5} \quad \text{(I.1)}$$

where Q is flow in $ft^3\ s^{-1}$, h_u is the head (ft) above the v-notch upstream, h_d is the head (ft) above the v-notch downstream

I.1 Unsubmerged flow

If h_u>0 and h_u<w_d, then

$$Q = \left(4.2h_u^{2.5}\right) * 28.317 \quad \text{(I.2)}$$

where Q is flow in L s^{-1}, w_d is the depth of the weir, and 28.317 is a conversion factor.

If h_u>w_d, then

$$Q = \left\lfloor 4.2h_u^{2.5} - (h_u - w_d)^{2.5} \right\rfloor * 28.317$$

(I.3)

I.2 Submerged flow

If h_d>0 and h_u<w_d, then

$$Q = \left\lfloor Q_1 \left(\left(1 - \frac{h_d}{h_u} \right)^{2.5} \right)^{0.385} \right\rfloor * 28.317$$

(I.4)

where $Q_1 = 4.2h_u^{2.5}$ (I.5)

If $h_d>0$ and $h_u>w_d$, then

$$Q = \left[Q_2 \left(\left(1 - \frac{h_d}{h_u} \right)^{2.5} \right)^{0.385} \right] * 28.317 \tag{I.6}$$

where $Q_2 = 4.2 * h_u^{2.5} - \left(h_u - w_d\right)^{2.5}$ (I.7)

If either $h_u<0$ or both $h_u<0$ and $h_d<0$, then Q=0. If both $h_u>0$ and $h_d>0$ and $h_d>h_u$, then the flow will be submerged and negative and the equations for submerged flow will be adjusted as follows (keeping the same conditions listed above for the two different cases of submerged flow):

If $h_d>h_u$ and $h_d>0$ and $h_u<w_d$, then

$$Q = \left[-Q_1 \left(\left(1 - \frac{h_u}{h_d} \right)^{2.5} \right)^{0.385} \right] * 28.317 \tag{I.8}$$

where $Q_1 = 4.2 h_u^{2.5}$ (i.e., equation I.5)

If $h_d>h_u$ and $h_d>0$ and $h_u>w_d$, then

$$Q = \left[-Q_2 \left(\left(1 - \frac{h_u}{h_d} \right)^{2.5} \right)^{0.385} \right] * 28.317 \tag{I.9}$$

where $Q_2 = 4.2 * h_u^{2.5} - \left(h_u - w_d\right)^{2.5}$ (i.e., eq. I.7)

I.3 Reference

Villemonte, J. R. 1947. Submerged weir discharge studies. *Engineering News-Record* 139(26): 54-56.