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Optimizing edge-of-field water quality monitoring methods to determine the effects of best management practices on nutrient and sediment runoff

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This study investigates the impact on water quality of combined agricultural best management practices cover crop and minimum tillage, alongside an examination of techniques used to collect those samples. Edge-of-field (EOF) water quality samples were collected from 11 working farms during a two-year paired field experiment. Results showed significant reductions in nutrient concentrations, increased discharge, and mixed findings regarding nutrient mass transport post-treatment. A suite of EOF collection techniques were compared using in-situ automated water sampling systems sampling the same runoff events. Sampling protocols influenced nutrient concentrations in composite samples, but unexpected variance in velocity sensors affected measured discharge, making it challenging to confidently attribute differences in nutrient loading estimates to sampling protocol. The findings provide regionally specific evidence for mitigating on-farm nutrient enrichment in the Lower Mississippi Alluvial Valley and enhancing monitoring techniques.

DEDICATION

I would like to dedicate this work to my family. Thank you for believing in me even when I didn’t believe in myself. I could not imagine where I would be without you.

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Many individuals were instrumental in carrying out this work. Beau, thank you for all of your support. I am indebted to you for your assistance, both in the lab and the field. Dr. Baker, thank you for giving me the opportunity to explore how we can make a difference. Your patience, diligence, and positive attitude are virtues to aspire to. I am better because of it. And thank you to all the team members along the way: Andrew, Josh, Madison, and Mason. Lastly, without the assistance of the team at Delta F.A.R.M. this work would never have happened. Thank you all.

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CHAPTER I

INTRODUCTION

1.1 Overview

Across the globe, increasing human populations and commensurate increases in pressure on natural ecosystems are driving changes to climate, biodiversity, and water resources (IPBES, 2019; Secretariat of the Convention on Biological Diversity, 2010). Increasing demand for food and energy crops produced on a stable amount of arable land has led to an intensification that often comes at an environmental cost to soil and water quality (Molden, 2013; Wackernagel et al., 2002). However, increased production must not come at the cost of environmental degradation if there is to be continued expectation of sustained and even increased yields (Millennium Ecosystem Assessment, 2005). Thus, the need arises for improved agricultural management practices which meet the two-fold goals of environmental stewardship and continued or improved production.

The Mississippi River Basin is the epicenter of grain and fiber production in the United States (USGS, 2000). Cropland dominates the alluvial floodplain of the basin's lower reaches in Missouri, Arkansas, Mississippi, and Louisiana known as the Lower Mississippi Alluvial Valley (LMAV). Agriculture has been shown to be the principal driving factor of nutrient enrichment in waters of the Mississippi River and the Gulf of Mexico (Robertson & Saad, 2013; United States Environmental Protection Agency, 2000). Agricultural non-point source nutrient pollution is thus a major concern in the LMAV. Impacts from nutrient enrichment have been well documented and include eutrophication, harmful algal blooms, and loss of marine biodiversity (Diaz & Solow, 1999; Rabalais et al., 2002). While there are natural sources of nutrient loading to the Gulf of Mexico, it is widely recognized that agricultural nutrient runoff is the primary contributor to a seasonal area of oxygen deficient waters off the coast of Louisiana known as the hypoxic 'dead zone'(Rabalais et al., 2002; USGS, 2000).

Hypoxia in the Gulf of Mexico is a result of increases in human pressure upstream largely driven by nutrient rich effluent from agricultural runoff (Carpenter et al., 1998). In a simplistic view, there are limiting nutrients which prevent biological productivity. In marine ecosystems the limiting nutrient is nitrogen (N) when the ratio of N species to phosphorus (P) species is low, whereas freshwater aquatic ecosystem productivity is primarily linked to P availability, when the ratio of N to P is high. Excess P in lakes and streams promotes harmful algal blooms which threaten both fisheries and human health. Similarly, excess N in marine ecosystem leads to an overabundance of algae. Eutrophication and subsequent decomposition of excess algae leads to a low oxygen condition (< 2 mg/L) unsuitable for marine benthic communities (Rabalais et al., 2002). This seasonal shortage of oxygen can drive loss of biodiversity, economic losses to Gulf of Mexico fisheries, and can be especially troublesome for sessile creatures such as shellfish (Diaz & Solow, 1999; Rabalais et al., 2002). The increase in nutrient loading, in large part, is driven by non-point sources associated with agriculture and point sources such as wastewater treatment facilities (Carpenter et al., 1998; Diaz & Rosenberg, 1995). Developing solutions, or best management practices (BMPs), to keep nutrients on farms and out of waterways make sense from both an ecological and economic standpoint.

Management practices and tools for landowners are developed by a diverse group of agencies and organizations such as the United States Department of Agriculture (USDA), the

United States Environmental Protection Agency (USEPA), the United States Fish and Wildlife Service, and other non-government organizations like Delta F.A.R.M., the Rodale Institute, the Sierra Club, Ducks Unlimited, among others. With so many groups invested in multi-functional land use, it can be beneficial to develop cooperative landscape-scale initiatives that integrate stakeholder needs and leverage resources toward common goals. Toward this end, the federal government formed a multi-agency Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (hereafter Hypoxia Task Force, HTF) in 1998 led by a liaison from the USEPA to address an ever-increasing hypoxic zone in the northern Gulf of Mexico (Environmental Protection Agency, 1998).

The USEPA and the HTF, along with state-level stakeholders, have developed a framework for excess nutrient mitigation that identifies priority watersheds where numeric nutrient criteria are developed for specific categories of water uses (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2001; Stoner, 2011). The framework encourages states to develop total maximum daily loads (TMDL) that would collectively limit and reduce nutrient loading from these priority watersheds (Stoner, 2011). Part of the approach incentivizes landowners to voluntarily adopt sustainable BMPs in agricultural landscapes to reduce stream loading (FTN Associates, 2012). Management practices aimed at enhancing farm viability and improving the quality indicators of local and downstream habitats have encompassed various strategies. These include the preservation of natural vegetation, the adoption of edge-of-field (EOF) practices, the implementation of conservation tillage methods, and the effective management of on-farm nutrients.

Reductions to agricultural effluent nutrient concentrations will be necessary to mitigate ongoing nutrient enrichment in the northern Gulf of Mexico hypoxic zone. The Federal Water

Pollution Control Act, or “Clean Water Act”, has gone a long way towards improving adverse anthropogenic impact on our public waters (33 U.S.C. §§1251-1387). Yet, this legislation is much less effective at managing non-point source pollution, such as that contributed by excess fertilizer runoff from agriculture. Successful improvements to this diffuse problem will come through adoption of on-farm management practices that, while improving environmental outcomes, do not impede farm profitability.

Reducing nutrient transport by using a reduced tillage approach and cover crops during the fallow season may represent a successful complement to effective on-farm nutrient management in reaching nutrient loading reduction goals (Hanrahan et al., 2021). Effective nutrient management would reduce loss of mineral fertilizer from inappropriate rates or timing of application. Managers have sought to keep these valuable inputs in place rather than being lost to effluent that ultimately contaminates marine and aquatic ecosystems. Double cropping in areas where bare soil would be exposed during the fallow season has also been shown to mitigate soil erosion, reduce runoff of soil bound nutrients, and nitrate loss (Kaspar et al., 2012; Reba et al., 2020; Sharpley et al., 2006).

Using cover crops during the fallow season has been shown to reduce soil erosion (Lu et al., 2000). Further, no-till or reduced tillage when coupled with fallow season cover crop has shown promise to improve both soil health and fertility, but also to help mitigate downstream nutrient enrichment (Boselli et al., 2020; Dabney et al., 2001). This is especially important in the midsouth during the mid to late spring rainy season where residual P from fall fertilization remains on or near the exposed soil surface. Mineral P tends to be sediment bound and it is expected that the cover crop-reduced tillage treatment will significantly slow soil erosion rates through various mechanisms and, by extension, P loading (Sharpley et al., 2006). There are, however, mixed results that suggest cover crops can actually increase transport of soluble P (Blanco-Canqui, 2018; Her et al., 2017). There is no expectation that mechanical binding of soils will reduce leaching of soluble nutrients N and orthophosphate (OP). In the watersheds studied by Jarvie et al. (2017), the adoption of widespread no-till and reduced tillage practices resulted in an observed increase in the transport of soluble reactive P. This increase is believed to be attributed to a larger pool of labile P in residues. Phosphorus bioaccumulates in cover crop biomass which eventually leads to greater stratification in the upper layer of the soil (Sharpley, 2003).

Cover crops are expected to uptake nitrate (NO_3^-) during the fallow season by assimilating nutrients for photosynthesis, thereby reducing availability for transport in effluent (Blanco-Canqui, 2018; Thorup-Kristensen et al., 2003). This uptake of residual fertilizer can provide positive benefits for downstream water quality and provides a store of slowly released bioavailable N during subsequent decomposition (Christopher et al., 2021). Given reduced nutrient transport, this could alleviate some of the need for exogenous N inputs on fields, thereby increasing farm profitability. Leguminous cover crop species provide an added benefit late in their life cycle by fixing atmospheric N via symbiotic bacterium in root nodules (Liu et al., 2011). This fixed N is used by the leguminous cover species and would be made available to a subsequent cash crop through decomposition (Liu et al., 2011). Additionally, available soluble NO_3^- has been documented to decrease while the cover crop stand is growing and reductions have been shown to be correlated with stand biomass (Christopher et al., 2021).

Most efforts to ascertain the efficacy of cover crop-reduced tillage management practices have been carried out in the upper Mississippi Alluvial Valley where cropping systems are similar, but soil types, hydrology, and topography are markedly different than the LMAV

(Hanrahan et al., 2021; Williams et al., 2016). In the Midwest, where the majority of cover crop water quality studies have taken place, subsurface tile drainage is increasingly common and has been shown to have a significant effect on nutrient transport (Dinnes et al., 2002; King et al., 2016). This practice is practically nonexistent in the low-grade slopes of the LMAV. There have been limited studies that focus specifically on conservation efficacy in the LMAV (Kröger et al., 2012). Given the different nature of surface runoff nutrient transport (King et al., 2018), an examination of the effect of cover crop-reduced tillage BMPs on water quality in the LMAV is prudent. Edge-of field water quality monitoring of BMPs, including cover crop-reduced tillage, is ongoing by the University of Arkansas and the Arkansas Discovery Farms program (Sharpley et al., 2015). The question remains if nutrient reduction goals are achievable through these BMPs in the silt/clay loam soils of the LMAV, a region that has predominantly surface runoff drainage and mild winters (2 ºC - 13 ºC) characterized by heavy fallow season rainfall (~ 5 in/mo) (Arguez et al., 2012). This study used a field-scale, paired-field experiment to test the efficacy of cover crop-reduced tillage BMPs at reducing nutrient transport in effluent measured at the edge-of-field.

The scope of agricultural edge-of-field water quality data are rather limited (Harmel et al., 2018). Water quality sampling is typically carried out to collect composite samples that are representative of entire runoff hydrographs (Aryal et al., 2018). Several means of achieving composite samples exist, from collecting aliquots based on time-series to flow-weighted designs. It is important to understand the implications of how the sampling protocol is designed if nutrient concentration data collected at the edge-of-field with composite samplers are to be used for estimating nutrient loading to waterways (Harmel et al., 2006). This would be especially true when using data collected at edge-of-field monitoring stations to inform models that estimate landscape-wide application effects of BMPs. The paired-field test is robust against potential differences among these sampling approaches, in so much as the same approach is used on both experimental fields. However, it was not clear that different sampling protocols will yield a similar event mean concentration (EMC) for individual runoff events. This study aimed to examine differences in event mean nutrient and sediment concentrations collected with three different composite sample collection methodologies: volumetric flow-weighted, volumetric Δ flow rate, and time-series.

1.2 Research Question

Understanding BMP effects relative to water quality and specific to soil type and physiographic region is essential to understanding how and where these practices should be implemented. Given the limited resources available to producers, sponsored BMP applications should be made in a manner that most efficiently produces desired outcomes using the best available knowledge (Stoner, 2011). If cover crops and reduced tillage yield less return on investment than other conservation practices such as grassed buffers or sedimentation pools, producers and landowners should be informed of likely outcomes when approaching the decision-making process.

In an effort to investigate the impact on nutrient transport, this study examined effects of two combined conservation practices, fallow season cover crop and reduced tillage, on water quality indicators. Further, it provides a methodological examination of automated EOF water quality sampling collection techniques used to measure event mean nutrient concentrations.

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CHAPTER II

INVESTIGATION OF NUTRIENT AND SEDIMENT EFFLUENT REDUCTION ASSOCIATED WITH COVER CROP – REDUCED TILLAGE BEST MANAGEMENT PRACTICES

2.1 Introduction

Nutrient transport from agricultural landscapes has become a principal driver of Gulf of Mexico hypoxia (Goolsby et al., 1999; Robertson & Saad, 2013). Reducing nutrient loading to waterways is essential from both an on-farm economic perspective as well as environmental and wildlife habitat perspective. Most farms operate on low margins and use exogenous nutrients, which represent a significant operating expense for farmers (Foreman, 2014; Hoppe, 2014). Thus, developing improved management strategies to address nutrient use-efficiency, nutrient runoff, and soil erosion is a priority for landowners and agencies alike. Cover crops and reduced tillage are practices that have shown promise in mitigating nutrient enrichment and soil erosion (Dabney et al., 2001; Sharpley et al., 2006).

The USDA- Natural Resources Conservation Service (NRCS) provides financial and technical support to farmers implementing conservation practices. The Agriculture Improvement Act of 2018 or “farm bill” provides financial incentives to producers seeking to improve environmental outcomes through various practices designed to limit transport of nutrients and sediments from agricultural landscapes. Cover crop (practice 340) and reduced tillage (practice 345) are both supported activities for which eligible producers can receive technical and financial assistance from the USDA-NRCS Environmental Quality Incentives Program (EQIP). The effectiveness of these practices in controlling nutrient transport shows significant variation, which could be attributed to landscape heterogeneity. For instance, the movement of soluble nutrients through soil macropores exhibits substantial variability across different soil series (Blanco-Canqui, 2018; Christopher et al., 2021; Jarvie et al., 2017).

Though it is widely accepted that cover crops have potential for reducing nutrient transport, there is presently no scientific consensus as to their efficacy. In a similarly structured study, Aryal et. al (2018) found significant concentration reductions in suspended sediment, PO_4, and NO_3^- following application of fallow season cover crop. However, Blanco-Canqui's (2018) review found significant reductions in nutrient transport in less than 25% of 13 studies. Cover crop efficacy for reduction of soil erosion and sediment transport is well documented and accepted (Blanco-Canqui et al., 2013; Grabber & Jokela, 2013; Siller et al. 2016). While there is research in the LMAV regarding use of BMPs (Baker et al., 2018; Lizotte & Locke, 2018; Reba et al., 2013), most studies related to cover crop implementation have taken place in the Midwest (Christopher et al., 2021; Dougherty et al., 2020) where soil type, climate (particularly in annual rainfall and winter temperatures), and hydrology are markedly different. Thus, there is a need to evaluate the efficacy of cover crop- reduced tillage practices in reducing both nutrient and sediment transport in the LMAV.

This study aims to ascertain the effects on water quality of two combined conservation practices, fallow season cover crop and reduced tillage. Paired treatment-control fields outfitted with automated water sampling equipment allowed us to examine field-scale treatment effects on storm runoff water quality from working row-crop farms in the LMAV. There is an expectation that sediment transport will be reduced by the cover crop- reduced tillage treatment, whereas there is no expectation of nutrient transport reductions. These hypotheses are framed as such:

> H_0: Cover crop – reduced tillage treatment will not change sediment and nutrient concentrations and loads relative to runoff from control sites when measured at the field scale
>
> H_a: Cover crop – reduced tillage treatment will either reduce or increase sediment and nutrient concentrations and loads relative to runoff from control sites when measured at the field scale.

The paired field study design allows for a simple statistical test of these hypotheses as well as comparative inference via effect size relative to the untreated fields. Further, this study aims to inform management decisions when choosing voluntary conservation practices in a concerted effort to mitigate agricultural non-point source nutrient runoff.

2.2 Materials and Methods

2.2.1 Study Area

Water quality samples were collected from 22 paired treatment-control fields on 11 working row-crop farms from winter 2018 through spring 2020. Participating farms were located in the Mississippi Delta region of the LMAV. Geographic distribution of experimental field sites covered a large section of the Delta ranging from the most northern farm in Clarksdale, MS to Rolling Fork, MS in the south. See Figure 2.1 for illustration of sample sites.

The Delta has soil types that generally consist of high clay composition and exceedingly low-grade slopes (Soil Survey Staff, 2006). Soil series include Dundee, Forestdale, Sharkey, and Alligator. They are principally derived from river alluvium and are considered poor to very poorly drained. Study sites were intentionally selected across a large geographic area to account for natural variation in major soil types in the study results. Thus, results should be considered as typical for the Delta ecoregion and any of its predominant soil types.

This project expands on the work by Badon *et al.* (2022), which was carried out in collaboration with Delta F.A.R.M..

2.2.2 Management Techniques

Experimental fields were established and agronomically managed by partner non-profit organization Delta F.A.R.M.. Treatment fields were managed under the same agronomic system as control fields, except that following harvest, fallow season cover crops and minimum tillage (CCMT) were used. Cover crop blends employed included a typical two-way blend of grass (oats [*Avena sativa* L.], triticale [*Triticosecale rimpaui* C. Yen & J.L. Yang]), legume (vetch [*Vicia villosa* Roth] and clover [*Trifolium michelianum* Savi]), and a brassica species (radish [*Raphanus sativus* L.]). An adaptive management approach was taken with regard to planting method and cover crop species ratio. Seed was typically drilled at a rate of ~ 50 lb ac^{-1} consisting mostly of grasses (80% – 90%) with relatively higher legume rates planted prior to corn cash crop (20 % vs 10 %). Brassicas typically constituted a very small percentage of seed mixes (2% - 5 %). Cover crop seed was also aerially seeded if wet field conditions dictated. Seeding rates were 20% – 40% higher for aerial application, dependent on species. This method is less preferred to no-till drill application as stand establishment is typically inferior. See Table 2.1 for description of cover crop blend proportion and seeding rate. Cover crop planting occurred in October following corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] cash crop and November following the single cotton (*Gossypium hirsutum*) site-year. Chemical cover crop termination occurred ~4 weeks prior to cash crop planting (March for corn fields, April for soybean and cotton fields).

Control fields were managed by individual farm owner/managers using prevailing management practices (farmer best management-FBM). All fields except one site-year were planted in the typical corn-soybean rotation. One site-year was planted in cotton, which has a characteristic later planting and harvest date. Cover crop was planted around 30 days later at this site-year. Control fields were left fallow during the winter season and underwent more frequent tillage events, including post-harvest disking, cultivating, bed forming, and subsoiling if conditions dictate. Cover crop-reduced tillage treatment fields were limited to bed hipping and cultivating furrows. See Badon *et al.* (2022) for a complete description of minimal tillage practice.

2.2.3 Water Quality Monitoring

Field-scale water quality samples were collected at 11 farms with established paired treatment and control fields. Agricultural water management in the region is characteristic of engineered surface water drainage that includes precision land leveling, the building of pads around fields, and growing crops on beds such that furrow irrigation and drainage to field pipes is possible. Field drainage pipes convey water to drainage ditches that connect to downstream water bodies. See Omer *et al.* (2018) for a complete description of prevailing regional specific water management techniques. Fields were equipped with field pads and either standard or slotted outflow pipes (Kröger et al., 2013). At 10 paired study sites, fields were one large field divided with an earthen berm to establish two hydrologically distinct drainages. At one site, two separate, yet directly adjacent fields that met the same soil type and single outflow structure criteria were chosen.

Each treatment and control field pair was outfitted with automated water sampling units designed to collect flow-weighted composite samples from surface runoff. Each sampling unit consisted of an automatic water sampler, ultrasonic velocity meter, wireless telemetry, housing, and electrical system. Ultrasonic velocity meters (Starflow or Starflow QSD) were mounted in outflow culverts to record discharge and activate automatic water samplers (Hach as950 or sd900, Loveland, CO, USA). Velocity meters depend on laminar flow in outflow pipes to correctly measure water velocity. To maintain sensor data integrity, mounting points were located sufficiently far from the inlet of the pipe to avoid water turbulence entering the outflow pipe. Water velocity was continuously recorded throughout the project period and logged in five-minute intervals. Water sampling systems used either of two different flow-weighted sampling schemes to collect composite runoff samples. Six farms used a volumetric design set to collect 100ml aliquots for every 1000 L of measured discharge. Five farms used a flow-weighted design which used a change in flow rate sampling scheme (Δ flowrate) where once a runoff event began, the sampler would contribute one 100 ml aliquot to the composite every 1 L s^{-1} change in flow rate. In all cases, both samplers at each site used the same collection protocol. Composite samples were used to estimate event mean nutrient concentrations which were in turn used to estimate event-based stream loading estimates.

Water samples were collected by and transported to the Water Quality laboratory at Mississippi State University for analysis. Off-site telemetry equipment notified the sampling crew of sample events in real time via text message and KTS Wireless web interface MyFarm (KTS Wireless, Lake Mary, FL), such that samples were collected within 24 - 48 hours of rainfall events. The telemetry equipment also transmitted logged water velocity measures to an offsite web server where the data were later retrieved for analysis. Sample analysis or acid preservation of samples was performed no more than 72 hours after rainfall events.

2.3 Analysis

2.3.1 Water Sample Analysis

Water quality indicators analyzed included turbidity (TUR), total suspended solids (TSS), total nitrogen (TN), nitrate-nitrite nitrogen (NO_3^- - NO_2^-- N), total kjeldahl nitrogen (TKN), total phosphorus (TP), and orthophosphate (OP). All methods met standards outlined in the Code of Federal Regulations title 40 section 136 concerning analysis of environmental pollutants.

Turbidity was measured with Hach 2100Q portable turbidimeter (Hach, Loveland, CO). Hach method 8195 compares the intensity of light scattered by a sample with that of a standard reference in suspension. Turbidity was reported in nepholometric turbidity units (NTU).

Total suspended solids concentration was determined following American Public Health Association method 2540 D (APHA, 2005). Samples were filtered through prepared and weighed fiberglass filters under vacuum. The sediment and filters were then dried to constant weight and weighed. Subtracting the initial weight of the washed and dried filter multiplied by the sample volume yields total suspended solid concentration (Eq. 2.1).

$$(final\ weight - initial\ weight\ (mg)) * \left(\frac{1000}{sample\ volume\ in\ ml}\right) = TSS\ mg/l \qquad (2.1)$$

Nitrogenous species TN, NO_3^--NO_2^-- N, and TKN were analyzed with Hach simplified TKN TNTplus tests kits using USEPA approved Hach method 10242 (Hach, Loveland, CO). Total nitrogen is measured by acid digestion to nitrate then indicated spectrophotometrically. This value is compared to an undigested sample to measure the amount of nitrogen that is oxidized. This difference indicates the amount of total kjeldahl nitrogen present in samples (Eq. 2.2).

$$Total\ N = TKN + NO_3^- + NO_2^- \rightarrow Total\ N - NO_3^- - NO_2^- = TKN \tag{2.2}$$

Total phosphorus was analyzed using Hach TNT843-845 chemistry kits using USEPA approved Hach method 10209 (Hach, Loveland, CO). This uses the ascorbic acid method followed by spectrophotometry. Dilute P solution is first treated with sulfuric acid hydrolysis to break down inorganic polyphosphates and then reacted with ammonium molybdate and potassium antimony tartrate in an acid medium to form a complex that is then reduced with ascorbic acid. This reduction indicates TP concentration as a blue color that is measured colorimetrically with a spectrophotometer at 650nm.

Orthophosphate constituent was analyzed using Lachat Flow Injection Analyzer (FIA) 8500 Series 2 (Lachat Instruments, Loveland, Colorado, United States). Samples are first filtered with 0.45μ cellulose filter then preserved with H_2SO_4. Dilute phosphorus solution is reacted with ammonium molybdate and potassium antimony tartrate in an acid medium to form a complex that is then reduced with ascorbic acid. This reduction indicates OP concentration with a blue color that is measured colorimetrically with a spectrophotometer at 880nm.

Discharge hydrographs using data from Starflow-QSD ultrasonic velocity meters were characterized using program R and Microsoft Excel. Post-processing of discharge data were carried out manually and event-wise. Occasionally it was necessary to estimate discharge using depth readings and a discharge rating curve. To estimate the discharge in cases where only velocity data were missing, a power regression analysis was conducted specifically for those events. Discharge values were omitted rather than estimated in the case of extrapolation. Total discharge was measured and normalized by field area of the study site. Event-based nutrient loading was calculated by multiplying effluent event mean concentration and total discharge.

Quality assurance measures included respective sample holding times and lab standard recovery of <± 10%. In the event lab standards were not met, sample values were omitted then imputed with R package mice using random forest imputations (van Buuren & Groothius-Oudshoorn, 2011). Values that were less than analysis method detection limits were imputed using R package zCompositions (Palarea-Albaladejo & Martin-Fernandez, 2015). This package provides functionality to impute left-censored data with maximum-likelihood model parameter estimation.

2.3.2 Data Analysis

Paired sample concentrations and loads were first checked for assumptions of normality using the Shapiro-Wilk test and for homogeneity of variance using Levene's test. It was expected that most water quality data indicators would violate the normality assumption; this was confirmed during preliminary data exploration. All further analysis was carried out using non-parametric methods. Subsequent analysis of treatment effect on water quality indicators was carried out using the Wilcoxon signed-rank test. Further, relative percent reduction was calculated ([FBM-CCMT]/FBM) where positive values indicate reduction in treatment fields relative to control. All data analysis was carried out using program R (R Core Team, 2017). Hydrograph characteristics for paired events were also subject to statistical exploratory analysis for frequentist assumptions and analyzed using Wilcoxon signed-rank tests to compare discharge between control and treatment fields. All hypothesis tests were assessed at the α=0.05 significance level. Pearson's r was calculated to examine effect size; Cohen (1992) categorizes effect sizes into three groups, small ($r<0.3$), medium ($r = 0.3 - <0.5$), and large ($r>0.5$). Seasonal designations were assigned based on growing season of the prevailing crop rotation that is typical of the region. November through April were considered the fallow, or cover crop season. While corn is generally planted earlier than soybean, the average timeframe of May through October was considered the growing, or cash crop season.

2.4 Results

2.4.1 Numerical summary

Four hundred and forty-two EOF runoff water quality samples were collected between February 2018 and March of 2020. Of those, 316 samples were paired samples (i.e., both treatment sampling systems functioned to produce a composite sample in an event). This represents 158 unique site-events used in the Wilcoxon test. One hundred and thirty-four site-events produced actionable discharge data used in loading estimates (i.e., complete or estimable based on existing data). The data contained herein is inclusive of 104 paired site events produced in coordination with USDA-NIFA; see Badon *et al*. (2022) for results specific to those samples.

2.4.2 Sediment & Nutrient Concentrations

Treatment effects on water quality parameters demonstrated statistically significant improvements in 5 of 7 indicators when measured throughout the course of the entire monitoring period: TSS mg L^{-1} ($p<0.01$), TUR ($p<0.01$), NO_3^--NO_2^-- N mg L^{-1} ($p<0.01$), TN mg L^{-1} ($p<0.01$), TP mg L^{-1} ($p<0.01$). All of these indicators exhibited a moderate effect size ($r= 0.3$ - <0.5). Water quality indicators, TKN mg $L^{-1}$and OP mg L^{-1}, showed no improvements ($p=0.48$ and $p=0.37$, respectively and $r<0.1$). See Figures 2.3-2.9 for illustration of distribution of response variables and Tables 2.2 and 2.3 for numeric summary of observations and test results, respectively.

Seasonal variation with regard to effects of the treatment on water quality was considered by subsetting samples collected during the cover crop season and during the cash crop season. None of the water quality indicators showed a significant difference between treatments during the cash crop season (all $p>0.39$). Whereas the improvements resulting over the course of the entire monitoring period noted above (TSS mg L^{-1}, TUR NTU, NO_3^--NO_2^-- N mg L^{-1}, TN mg L^{-1}, TP mg L^{-1}) became even more pronounced during the cover crop season (each $p <0.001$). Further, effect size in these five indicators increased from moderate to large ($r>0.5$). Again, TKN and OP concentrations were not significantly improved during the cover crop season ($p=0.13$, $r=0.15$ and $p=0.72$, $r=0.04$, respectively).

Relative percent change of nutrient concentrations ranged from a 31% reduction in TUR, to an 8% increase in median OP concentrations. Median TSS concentrations were reduced by 30% from 970 mg L^{-1} to 688 mg L^{-1}. Nitrogen species, NO_3^--NO_2^-- N and TN concentrations were reduced by 31% and 20% respectively. TKN exhibited no meaningful reduction (1%). Finally, TP concentrations in effluent were reduced 24%, whereas OP concentrations increased by 8% relative to the FBM control.

2.4.3 Discharge

In paired runoff events throughout the year, significant ($p= 0.024$) increases in discharge volume were measured from the CCMT treatment fields relative to the FBM control fields. The median percent difference relative to control was a 16% increase. This difference became even more stark during the cover crop season only ($p=0.004$ and 37% median increase) whereas no difference in normalized discharge was measured during the cash crop season ($p=0.97$ and 1.9% median relative decrease). See Tables 2.4 and 2.5 for summary of discharge observations and Wilcoxon test results, respectively. See Figure 2.10 for distribution of observed and estimated runoff volumes. Time to peak discharge and time to base (i.e., zero flow) were calculated for storm-based runoff events occurring during the cover crop season. Of 38 paired events with actionable discharge hydrographs, peak discharge was delayed on CCMT field in 29 events, relative to FBM fields. Time to peak discharge from CCMT fields was retarded an average of 133 minutes (SE. 38.8 minutes) relative to runoff from FBM fields. Similarly, time to base discharge was extended following CCMT implementation by an average of 490 minutes (SE. 117 minutes). The length of runoff events was longer on CCMT treatment fields in 30 of 38 events.

2.4.4 Sediment & Nutrient Loading

Increases in discharge volume led to a varying impact on nutrient transport. When normalized for area, NO_3^--NO_2^-- N mass leaving the treatment fields showed a statistically significant reduction ($p=0.03$) with a small effect size ($r=0.19$). This reduction represents a 12% median improvement relative to the loading observed in the FBM control from 0.088 kg ha^{-1} to 0.076 kg ha^{-1}. Four of six analytes, TSS kg ha^{-1}, TKN kg ha^{-1}, TN kg ha^{-1}, and TP kg ha^{-1} demonstrated no statistical difference ($p>0.1$) in nutrient loading. Finally, OP kg ha^{-1} was significantly increased ($p=0.01$) in effluent leaving the CCMT treatment fields, albeit with a small effect size $r=0.23$. The change in OP transport is represented by a median increase of 45% from 0.0063 kg ha^{-1} to 0.0091 kg ha^{-1}. See Tables 2.4 and 2.5 for summary of nutrient loading estimates and Wilcoxon test results and Figures 2.11 – 2.13 for distribution of loading estimates.

Seasonal differences in nutrient loading followed a similar pattern to nutrient concentrations. There were no significant observed differences ($p>0.1$) between treatments during the cash crop season. Orthophosphate kg ha^{-1}exhibited a significant increase ($p=0.02$) when measured during the cover crop season only. Total Nitrogen kg ha^{-1}, TKN kg ha^{-1}, and

TP kg ha^{-1} showed no differences during the cover crop season. Statistically significant improvements were observed for TSS and NO_3^--NO_2^-- N loading ($p=0.037$ and $p=0.017$, respectively) when only considering the cover crop season samples. The median cover crop season relative reduction of TSS loading was 27% from 58.9 kg ha^{-1} to 41.4 kg ha^{-1}. Median transport of NO_3^--NO_2^-- N was reduced 12% from 0.087 kg ha^{-1} to 0.076 kg ha^{-1} during the cover crop season.

It should be noted that all differences were calculated on a per-event basis. Cumulative seasonal loading was not calculated as a result of incomplete sampling of runoff events that happened throughout the year. Extenuating circumstances, such as prolonged flooding or sampling equipment malfunctions, would occasionally produce a composite water sample without accompanying discharge data or vice versa.

2.5 Discussion

2.5.1 Sediment & Nutrient Concentrations

The present study sought to gauge the effect of CCMT practices on water quality indicators when measured at the field scale. Meaningful reductions in concentrations were realized, particularly during the fallow season, for TUR and TSS. Though sediment impaired waterways make up a small proportion of the state's 303d impaired waterways list, it is the second most cited cause for impairment (MDEQ, 2022). Using cover crop and reduced tillage to mitigate soil erosion and stream enrichment will prove a useful complement to other hydrologic engineering practices (e.g., check dams, slotted riser pipes) when outlining a path toward reaching total maximum daily load (TMDL) goals. This is particularly the case in watersheds that are dominated by agriculture, like the Big Sunflower and Yazoo rivers. Soil erosion is a salient concern to most farmers; whether lost to waterways or lost to the wind, once it leaves there is no recompense.

Results showed decreases to TP concentrations leaving treatment fields. These reductions are a logical consequence of lower suspended sediment concentrations, as the majority fraction of phosphates are sorbed to soil particles, particularly in the clay rich soils of the study sites (Thomas Sims and Kleinman, 2005). These improvements, while statistically significant, are only a modest step toward reducing large scale nutrient transport. Phosphorus concentrations at the levels observed in this study were generally observed above typical natural levels and would likely contribute to freshwater eutrophication. Take for example, in Lake Champlain waters which contain phosphorus concentrations in the 0.024 - 0.058 mg L^{-1} range are considered eutrophic; measurements are typically quoted in micrograms. In contrast, our median observed total P concentration was 3.3 mg L^{-1}. Though, according to the prevailing limiting nutrient paradigm, P concentrations are not driving hypoxia in marine ecosystems. Indeed, recent modeling would suggest that despite high levels of P in runoff, it is still dominated by N in terms of effect on Gulf of Mexico hypoxia (Fennel and Laurent, 2018). Regionally acceptable levels are such that only five waterways in the state are listed for this nutrient of concern, and these did not include any in the agricultural center of the state (MDEQ 2022). Waters in the Big Sunflower River at Sunflower, MS generally range around 0.25-0.75 mg L^{-1} total P concentration (USGS, 2016). High P concentrations from agricultural lands, even when consisting of a large proportion of the landscape as in the Big Sunflower, result in instantaneous and continuous stream concentrations that are deemed to be locally acceptable (MDEQ, 2022; USGS, 2016).

Outlining useful farm practices that are beneficial to both the practitioner and the downstream aquatic and marine ecosystems was the impetus of this research. The experiment demonstrated positive environmental outcomes in the form of reduced total N and Nitrate-Nitrite- N concentrations in effluent leaving treatment fields. While it is possible that longer periods of saturation attributable to the cover crop led to biochemical denitrification, the likely mechanism for these reductions is assimilation of soluble N leftover from production by the fallow season cover crop. These results concur with recent research that attribute immobilization of soil NO_3^- to fallow season cover crop (Christopher et al., 2021). However, that study took place in the Midwest where mitigating N leaching to tile drains is the principal consideration. Another potential explanation for the observed reductions in N effluent concentrations could be increased microbial assimilation resulting from increased levels of soil organic carbon realized by both BMPs (Blesh & Drinkwater, 2013; Moriasi et al., 2020). Whatever the mechanism, lower nutrient concentrations leaving the field are advantageous for marine and aquatic ecosystems.

2.5.2 Hydrologic Response

Changes to runoff dynamics were presumed, yet the present response to the experimental treatment was surprising. Fields where the CCMT treatment was implemented exhibited longer runoff patterns (i.e., time to peak and time to base) relative to their FBM counterpart, yet overall discharge was increased from CCMT fields. Cover crop on its own has been shown to increase saturated hydrologic conductivity (K_{sat}), as well as improved mean infiltration rate (Hao et al., 2023). Increased K_{sat} and infiltration arose from improvements to soil structure associated with cover crop implementation (Blanco-Canqui et. al., 2011). This could naturally lead to shorter runoff events where more water enters the soil profile rather than leaving as runoff. In contrast, disturbance to soil structure associated with tillage should, in the short term, increase infiltration and conversely the no-tillage approach has led to higher discharge volume (Locke et.al., 2013).

The present findings contrast other results, which showed implementation of CC in a no-till system decreasing total discharge (Singh et. al., 2018). The longer runoff hydrographs in the present findings were also characteristic of a longer time to peak flow, indicating water that fell on the CCMT fields stayed on the field longer and left more slowly. This could prove useful in systems which are prone to flash rainfall events and would benefit as a buffer to stream flooding. However, moisture retention on fields associated with CCMT present a potentially troublesome tradeoff in the present study area during spring planting season, where farmers strive to drain fields quickly to allow farm machine access. Fields where the FBM treatment was implemented exhibited lower total discharge, shorter time to peak flow, and shorter time to base.

2.5.3 Sediment & Nutrient Transport

Meaningful reductions in nutrient loading from agricultural landscapes will be an essential component of any strategy to mitigate ongoing nutrient enrichment to the Northern Gulf of Mexico hypoxic zone. Our results suggest these practices may prove useful only when considering NO_3^--NO_2^-- N transport and this improvement may come at the cost of increased transport of other dissolved nutrients, namely OP. Reduced concentrations of both sediment and nutrients were offset by increases in discharge volume leading to limited positive benefit to stream nutrient loading resulting from the treatment.

Observed increases in discharge volume stand in contrast to Blanco-Conqui's (2018) review, which found that various cover crop treatments led to significant decreases in discharge in 82% of cases. In fact, this review highlights reduction of runoff as one of the most likely outcomes of cover crop implementation. While the present study did not aim to specifically examine infiltration rates, increases in discharge from treatment fields relative to the control would likely be attributed to changes in soil structure associated with reduction of tillage rather than implementation of cover crop. Cover crop implementation has been shown to increase infiltration rates, even dramatically (Haruna et al., 2018). In contrast to the present findings, Locke et al. (2013) found a six-fold increase in infiltration when using a minimum tillage regime rather than a no till approach. It is assumed that the negative effect of reducing tillage on infiltration was sufficient to offset any improvements to infiltration that may have been realized by the cover crop. Changes to runoff dynamics were presumed but increases in discharge volume rather than simple changes to runoff event duration and time to peak was unexpected.

Increases in orthophosphate transport resultant of an effort to reduce nitrogen enrichment to the Gulf of Mexico could prove particularly troublesome for intermediate aquatic ecosystems. Median observed OP values in this study were already >2.5 times greater than EPA suggested levels (50 micrograms L^{-1}) for stream water to prevent nuisance algae growths (US-EPA, 1986). These findings also concur with prior research that suggests cover crop- reduced tillage conservation practices can lead to increased P stratification and further transport related to labile P fractions (Duiker & Beegle, 2006; Jarvie et al., 2017). The dynamics of reactive P transport, particularly during and after cover crop decomposition merits more inquiry. While maintaining cover crop residues at the soil surface post-senescence is desirable, perhaps there may be a solution to slow the losses of soluble P that does not include residue integration via tillage.

Finally, of note is the lack of demonstrable reductions in sediment transport. This stands in stark contrast to the literature, where the authors were able to find only one non-significant result from a study that was considering fertilizer placement with or without cover rather than simple implementation of cover crop. Both practices independently should improve sediment transport and at worst act additively. Reductions to sediment transport are nearly universal

(Grabber & Jokela, 2013; Siller et al., 2016; Smith et al., 2015); yet, again, here it was found that increases in discharge volume led to increases in sediment transport.

The mixed effects on the nutrient transport indicate that combined cover crop-reduced tillage conservation practices on their own will provide an insufficient strategy for mitigating nutrient enrichment for the present study area. Alternative approaches, such as integrated nutrient management, may benefit from the inclusion of these practices, where the positive effects on soil health that cover crops are recognized for may synergize with other inputs or aspects of the approach.

2.5.4 Conclusion

Present nutrient concentration data suggest that CCMT management practices show potential in assuaging enrichment concerns. Yet, the observed effect of these stacked practices on discharge volume served to undermine these promises during the first two years of on-farm implementation. Consideration of discharge or infiltration management would benefit future research on using these management techniques, which specifically targets reducing discharge during the fallow season. Present findings regarding increases in discharge stand in contrast to most cover cropping research. The interaction between the present management techniques (i.e. CCxMT) and their impact on discharge would benefit from a complete-block experimental examination to assess potential for reducing nutrient loading. Further, soil structural and compositional changes which affect hydrologic conductivity may only be realized after relatively long-term application of the present practices.

2.6 Tables and Figures

Table 2.1 Cover crop blend and seeding rates for CCMT treatment

Common Name	Scientific Name	Planting rate (kg ha^{-1})				
		2017	2018		2019	
		Corn/Soy	Corn	Soy/Cotton	Corn	Soy/Cotton
Cosaque black oats	*Avena sativa* L.	23	17.8	20.5	18	20.25
Cereal ry	*Secale cereal*.	23	-	-	-	-
Winter triticale	*Triticosecale rimpaui* C. Yen & J.L. Yang [*Secale cereale* × *Triticum aestivum*]	-	17.8	20.5	18	20.25
Balansa Clover	*Trifolium michelianum* Savi *(ssp. balansae* (Boiss.) Ponert	-	3.7	3.7	3.6	3.6
Tillage Radish	*Raphanus sativus* L.	-	-	0.9	-	0.9
Hairy Vetch	*Vicia villosa* Roth	4	5.4	-	5.4	-
Austrian Winter Pea	*Pisum sativum* (subp. Arvense) L.	4	-	-	-	-

Cover crop seeding ratios and blend varied based on subsequent cash crop. Prior to corn crop, mixes contained higher ratio of legume. All values are mass of seed used in kilograms per hectare (kg ha^{-1}).

Table 2.2 Runoff nutrient concentration summary statistics

Analyte	Treatment	Minimum	Q1	Median	Q3	Max	sd	n
TSS (mg L^{-1})	CCMT	3.56	213	489	1.24 E+3	1.11 E +4	1.83 E +3	158
	FBM	19.0	350.0	836	1.94 E+3	1.12 E +4	1.66 E+3	158
TUR (NTU)	CCMT	15.7	232	670.0	1.43 E+3	9730	2.17 E+3	158
	FBM	9.23	407	951	2.13 E+3	1.03 E +4	2.06 E+3	158
NO_3^--NO_2^- -N (mg L^{-1})	CCMT	0.174	0.792	1.37	2.74	36.5	4.20	158
	FBM	0.133	1.20	2.02	3.69	16.3	2.89	158
TKN (mg L^{-1})	CCMT	1.00 E-4	0.730	1.12	2.03	169	14.4	158
	FBM	1.00 E-4	0.707	1.33	2.49	45.5	4.72	158
TN (mg L^{-1})	CCMT	0.522	1.77	2.77	5.18	181	16.3	158
	FBM	0.360	2.33	3.73	6.05	48.6	6.08	158
OP (mg L^{-1})	CCMT	5.10 E-3	0.0720	0.133	0.266	1.95	0.240	158
	FBM	4.90 E-3	0.0680	0.133	0.225	2.07	0.280	158
TP (mg L^{-1})	CCMT	0.154	1.70	3.00	4.42	19.4	4.22	158
	FBM	0.200	2.07	3.86	6.55	21.2	4.18	158

Summary statistics of nutrient concentrations for all paired event samples separated by treatment. Concentrations are measured in milligrams per liter (mg L^{-1}) and nephelometric turbidity units (NTU).TSS, total suspended solids; TUR, turbidity; NO_3^--NO_2^-- N, nitrate-nitrite nitrogen; TKN, total kjeldahl nitrogen; TN, total nitrogen; OP, orthophosphorus; TP, total phosphorus

Table 2.3 Nutrient concentration Wilcox test results

Method	**Alternative**	**Analyte**	**p.value**	**Effect Size (*r*)**	**Season**
Wilcoxon signed rank test	two sided	TSS (mg L^{-1}) by treatment	2.26E-05	0.339	annual
		TUR (NTU) by treatment	1.50E-07	0.418	annual
		NO_3^--NO_2^--N (mg L^{-1}) by treatment	8.55E-07	0.394	annual
		TKN (mg L^{-1}) by treatment	0.484	0.056	annual
		TN (mg L^{-1}) by treatment	1.04E-04	0.311	annual
		TP (mg L^{-1}) by treatment	1.50E-06	0.384	annual
		OP (mg L^{-1}) by treatment	0.372	0.071	annual

Statistical analysis of paired event nutrient concentrations was carried out using the Wilcoxon signed rank. Wilcox effect size of <0.3 is considered small, 0.3 - 0.5 considered moderate, and >0.5 is considered large. Direction of change indicated in preceding table (2.2). Concentrations are measured in milligrams per liter (mg L^{-1}) and nephelometric turbidity units (NTU). TSS, total suspended solids; TUR, turbidity; NO_3^--NO_2^-- N, nitrate-nitrite nitrogen; TKN, total kjeldahl nitrogen; TN, total nitrogen; OP, orthophosphorus; TP, total phosphorus

Table 2.4 Runoff volume and nutrient loading summary statistics

Analyte	Treatment	Minimum	Q1	Median	Q3	Max	sd	n
Runoff (L ha^{-1})	CCMT	1.26 E +3	2.75 E+4	8.44 E+4	1.91 E+5	9.19 E+5	1.48 E+5	134
	FBM	158	1.66 E+4	7.39 E+4	1.72 E+5	8.20 E+5	1.45 E+5	134
TSS (kg ha^{-1})	CCMT	0.124	9.63	37.5	116	3.60 E +3	391	134
	FBM	0.418	10.2	41.6	130.0	2.84 E+3	429	134
NO_3^--NO_2^- -N (kg ha^{-1})	CCMT	1.00 E-3	0.034	0.0980	0.336	5.56	0.650	134
	FBM	3.00 E-4	0.0280	0.128	0.380	4.08	0.720	134
TKN (kg ha^{-1})	CCMT	0.000	0.030	0.085	0.227	22.6	1.99	134
	FBM	0.000	0.013	0.073	0.258	7.15	0.800	134
TN (kg ha^{-1})	CCMT	3.10 E-3	0.072	0.171	0.606	23.3	2.22	134
	FBM	1.10 E-3	0.051	0.257	0.697	10.1	1.34	134
OP (kg ha^{-1})	CCMT	1.00 E-4	3.00 E-3	0.010	0.0350	0.438	0.0600	134
	FBM	0.000	1.00 E-3	6.00 E-3	0.0250	0.400	0.0600	134
TP (kg ha^{-1})	CCMT	1.20 E-3	0.073	0.186	0.542	12.5	1.24	134
	FBM	1.10 E-3	0.056	0.214	0.556	8.06	1.14	134

Summary statistics of runoff volume and nutrient loading estimates for all paired event samples separated by treatment. All values are normalized for area to account for unequal paired field sizes. Normalized runoff volume is measured in liters per hectare (L ha^{-1}) and loading estimates are measured in kilograms per hectare (kg ha^{-1}).

Table 2.5 Runoff and nutrient loading Wilcox test results

Method	**Alternative**	**Analyte**	**p.value**	**Effect Size (*r*)**	**Season**
Wilcoxon signed rank test	two sided	Discharge (L ha^{-1}) by treatment	0.0240	0.195	annual
		TSS (kg ha^{-1}) by treatment	0.141	0.127	annual
		NO_3^--NO_2^- -N (kg ha^{-1}) by treatment	0.0280	0.190	annual
		TKN (kg ha^{-1}) by treatment	0.199	0.111	annual
		TN (kg ha^{-1}) by treatment	0.424	0.069	annual
		OP (kg ha^{-1}) by treatment	0.009	0.226	annual
		TP (kg ha^{-1}) by treatment	0.382	0.075	annual

Statistical analysis of paired event runoff volumes and nutrient loading estimates was carried out using the Wilcoxon signed rank test. Wilcox effect size of <0.3 is considered small, 0.3 - 0.5 considered moderate, and >0.5 is considered large. Direction of change indicated in preceding table (2.4). Normalized runoff volume is measured in liters per hectare (L ha^{-1}) and loading estimates are measured in kilograms per hectare (kg ha^{-1}).

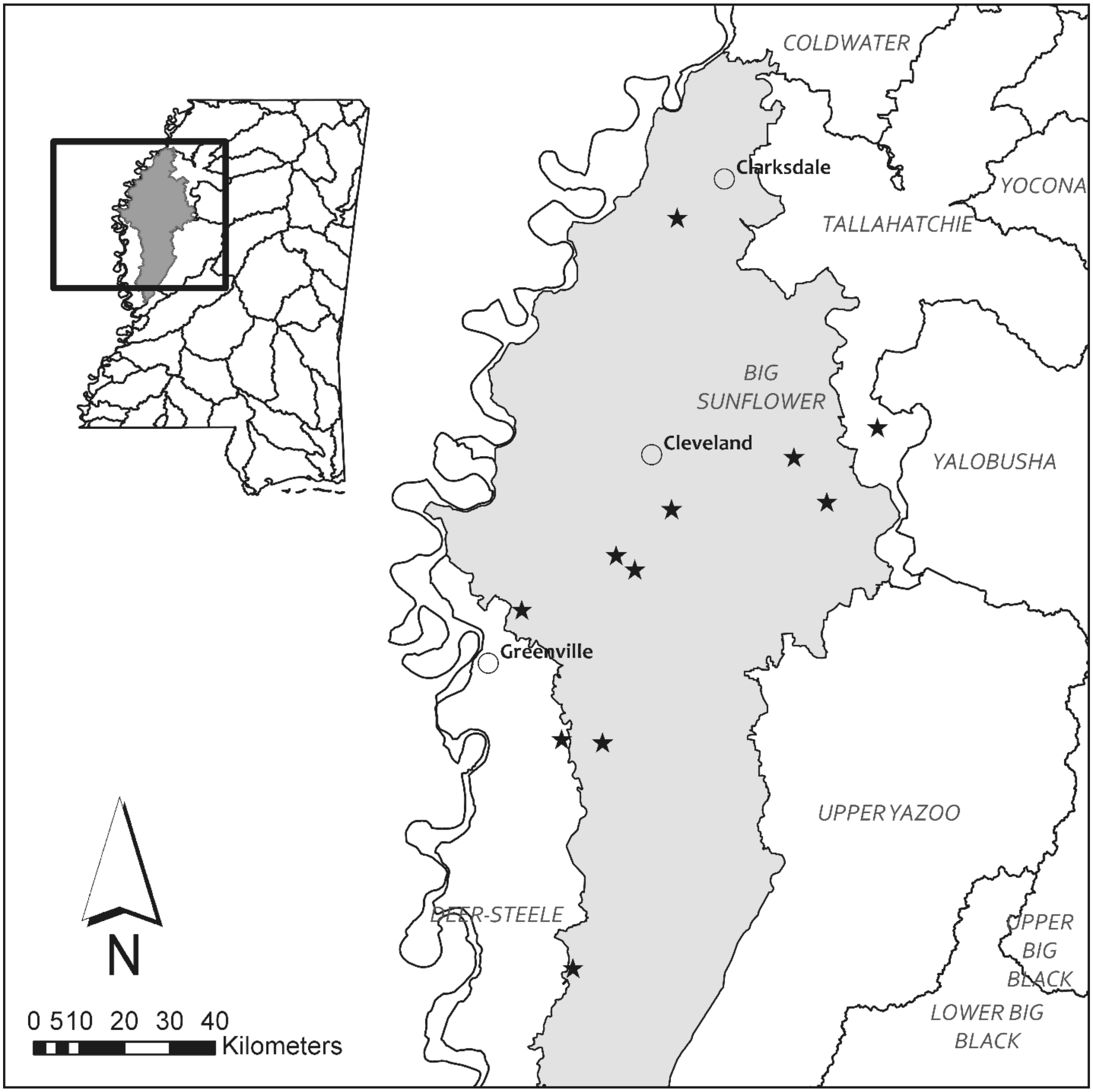

Figure 2.1 Map of sample sites

Inset highlights the Big Sunflower River watershed. HUC 8 watersheds are delineated. Stars indicate paired treatment-control sample sites spread across the Mississippi "Delta" ecoregion.

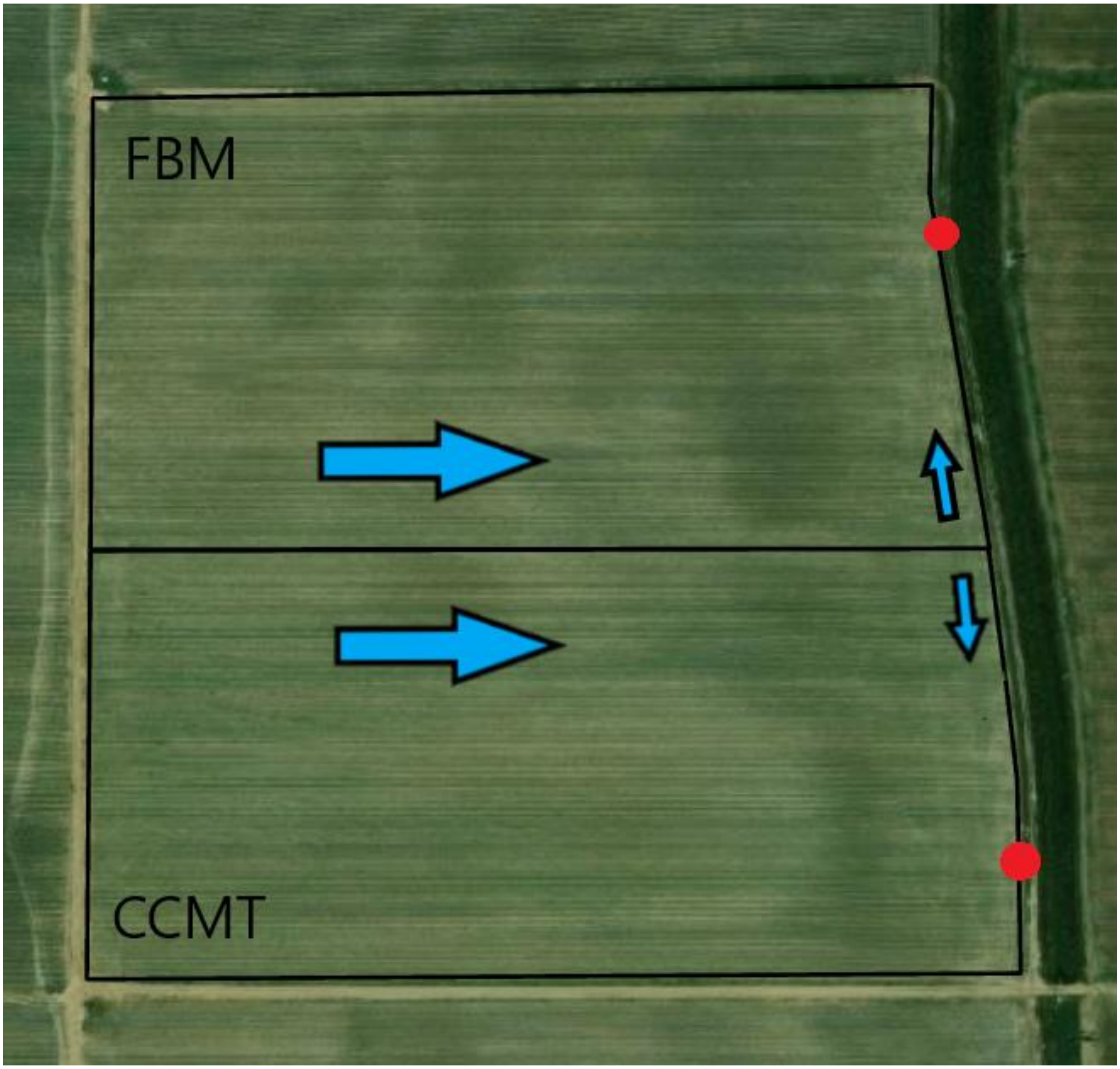

Figure 2.2 Diagram of split field design

Diagram of split field design where water leaving the field would be directed to two different outflow points (in red) using a simple earthen berm to split the tail ditch. Blue arrows indicate direction of runoff flow.

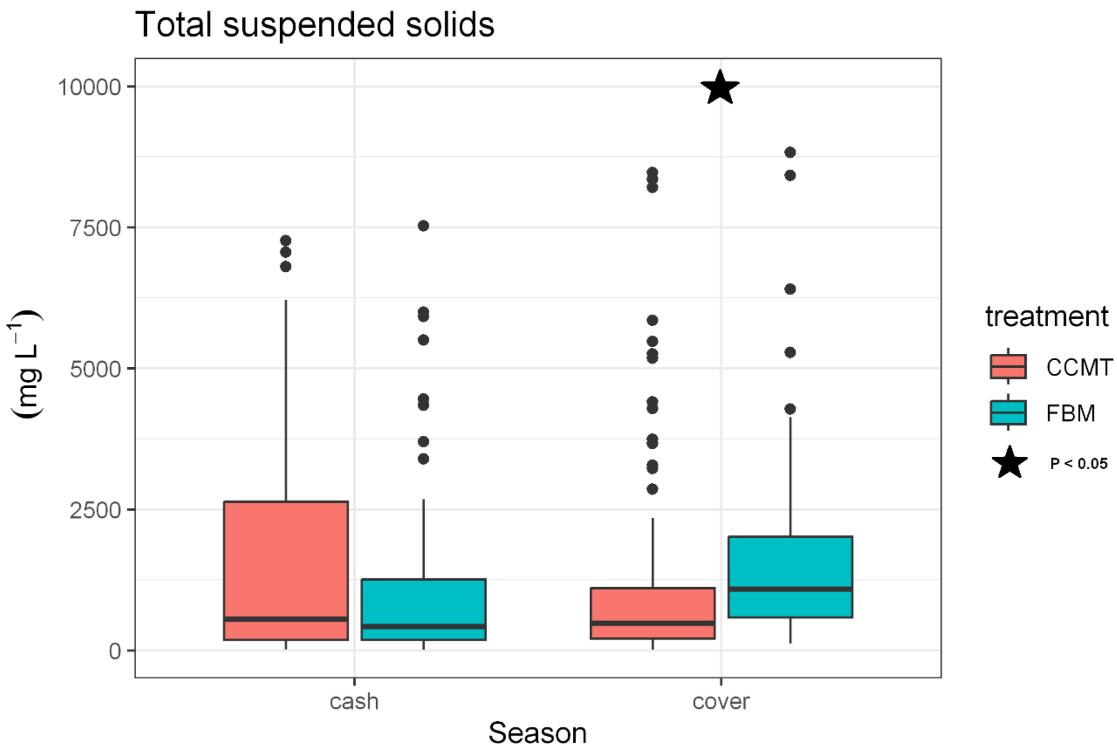

Figure 2.3 Distribution of total suspended solids concentration observations

Observed total suspended solid concentrations considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Runoff nutrient concentrations are measured in milligrams per liter (mg L^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

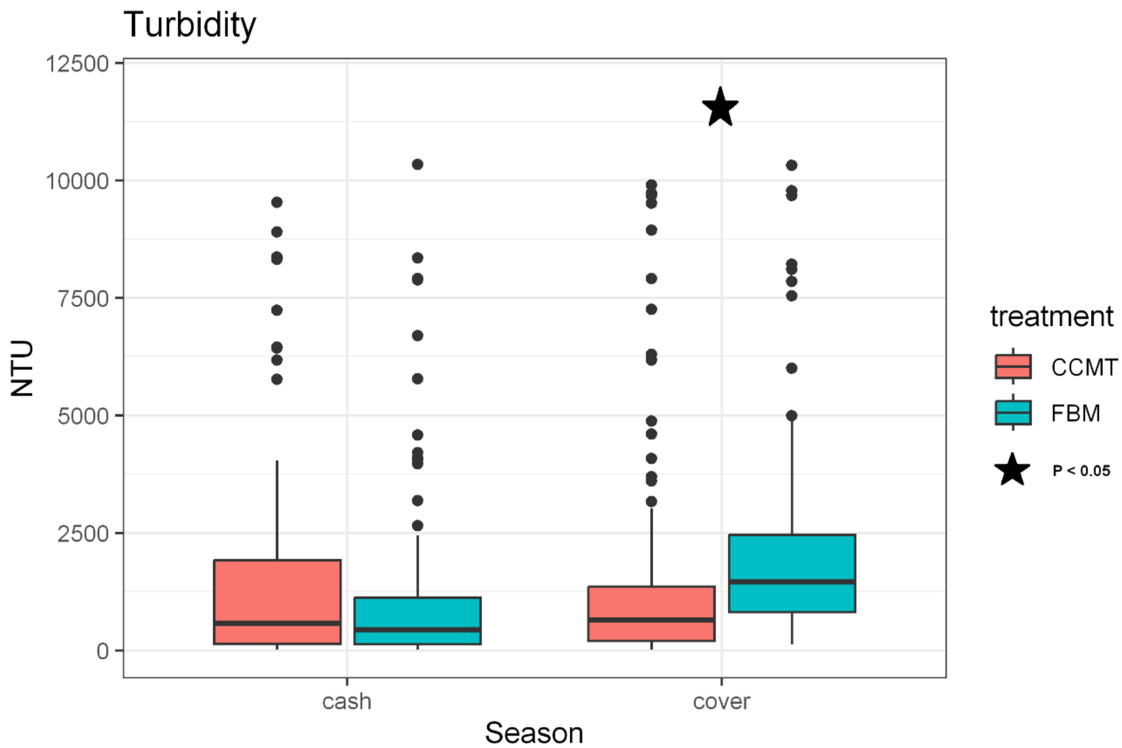

Figure 2.4 Distribution of turbidity observations

Observed turbidity values considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Turbidity is measured in nephelometric turbidity units (NTUs). Cash crop season is considered (May-October) and cover crop season (November–April). Statistically significant differences ($p<0.05$) are noted with a star.

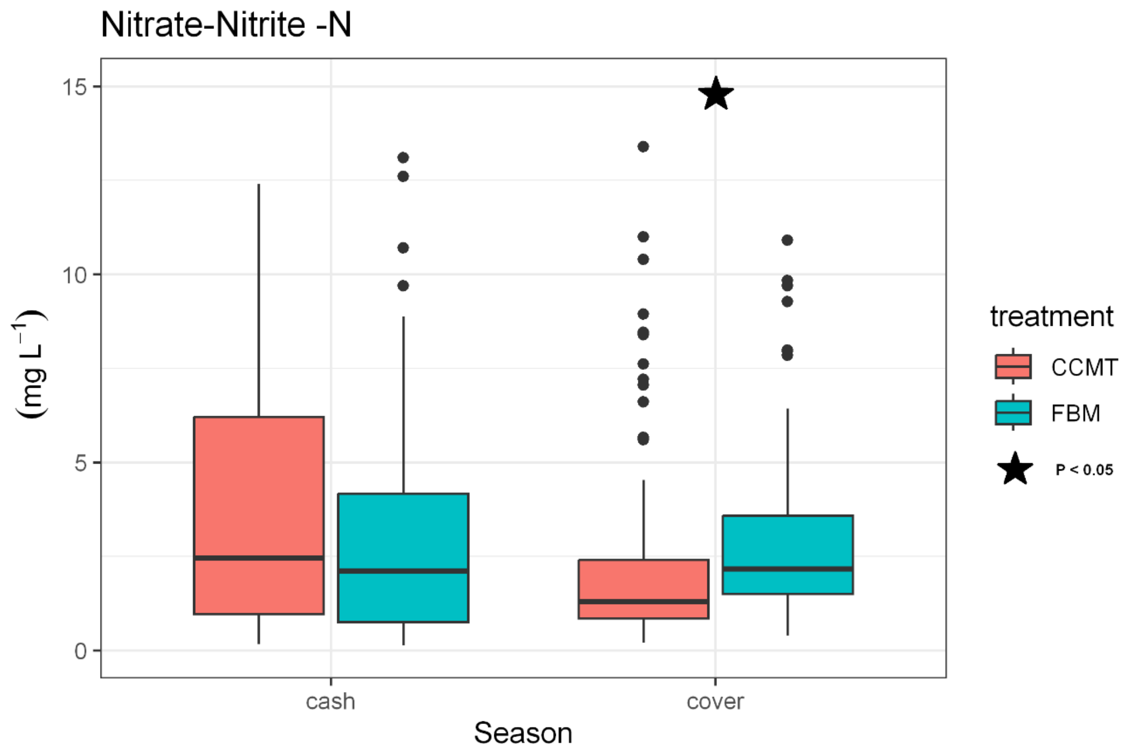

Figure 2.5 Distribution of nitrate- nitrite -N concentration observations

Observed NO_3^--NO_2^-- N concentrations considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Runoff nutrient concentrations are measured in milligrams per liter (mg L^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

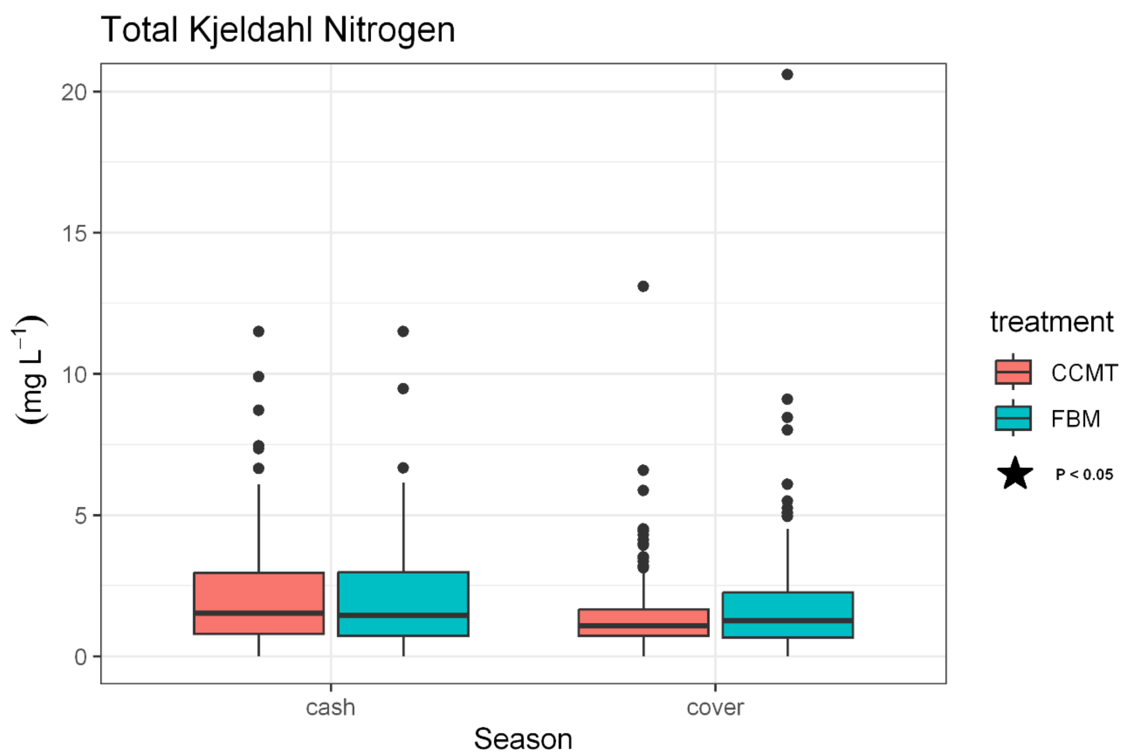

Figure 2.6 Distribution of total kjeldahl nitrogen concentration observations

Observed total kjeldahl nitrogen concentrations considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Runoff nutrient concentrations are measured in milligrams per liter (mg L^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

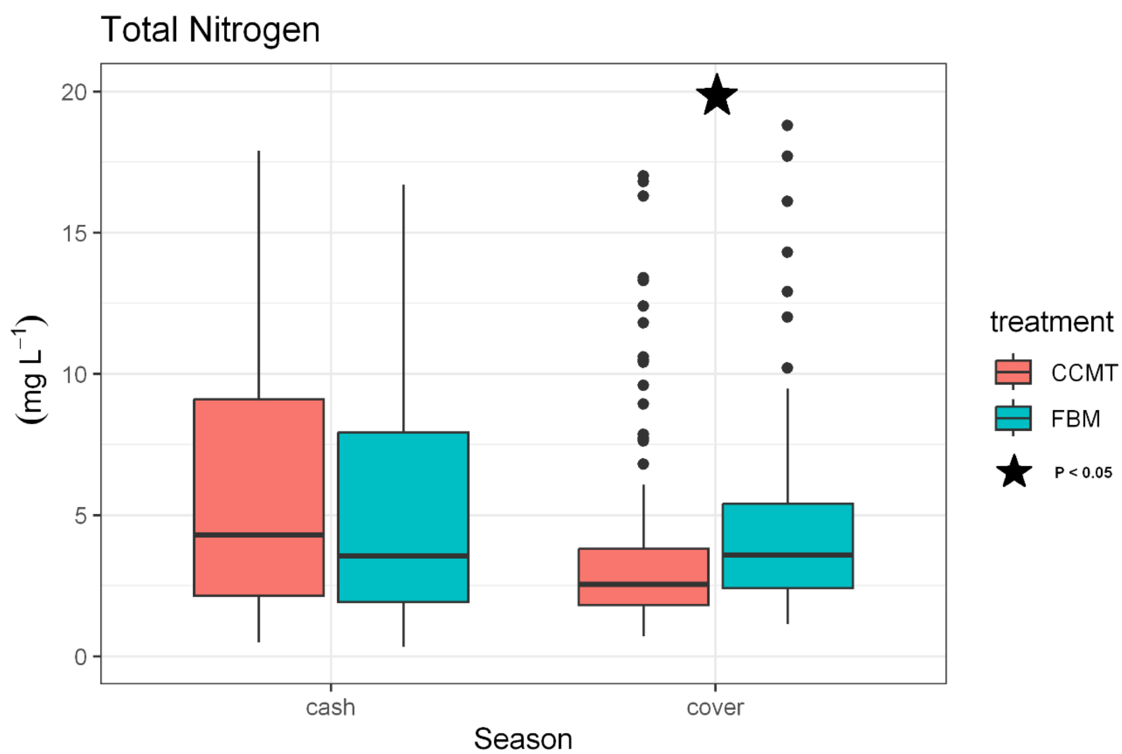

Figure 2.7 Distribution of total nitrogen concentration observations

Observed total nitrogen concentrations considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Runoff nutrient concentrations are measured in milligrams per liter (mg L^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

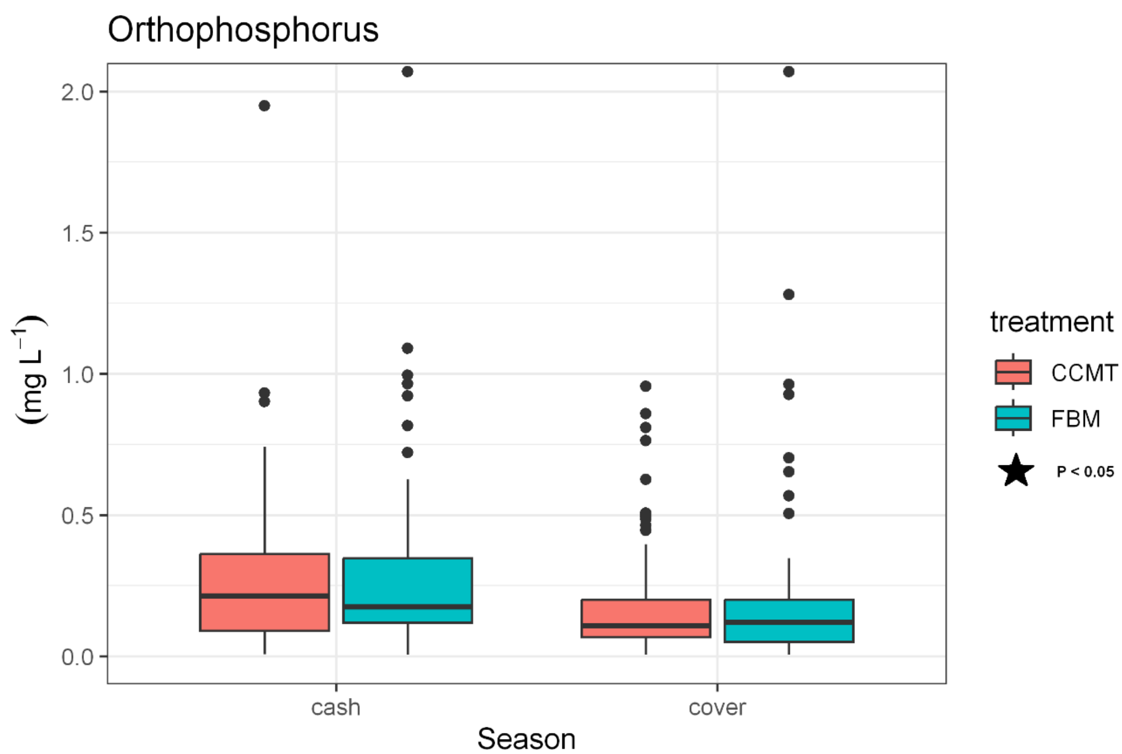

Figure 2.8 Distribution of orthophosphorus concentration observations

Observed orthophosphorus concentrations considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Runoff nutrient concentrations are measured in milligrams per liter (mg L^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

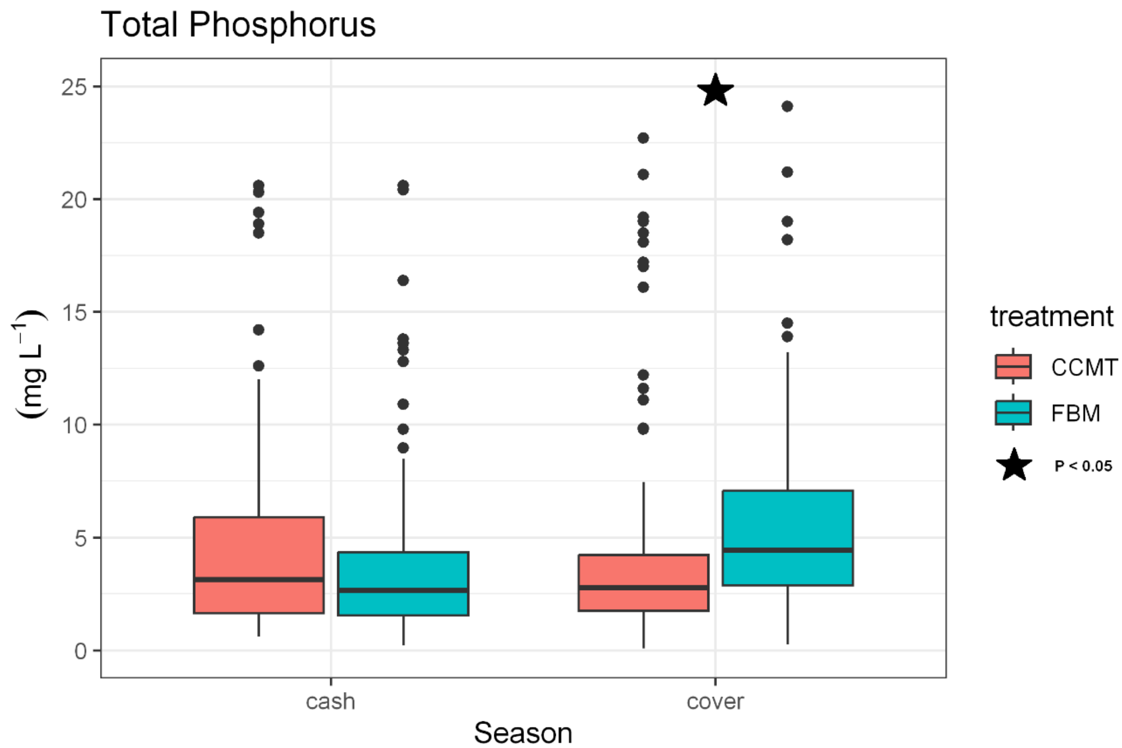

Figure 2.9 Distribution of total phosphorus concentration observations

Observed total phosphorus concentrations considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Runoff nutrient concentrations are measured in milligrams per liter (mg L^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

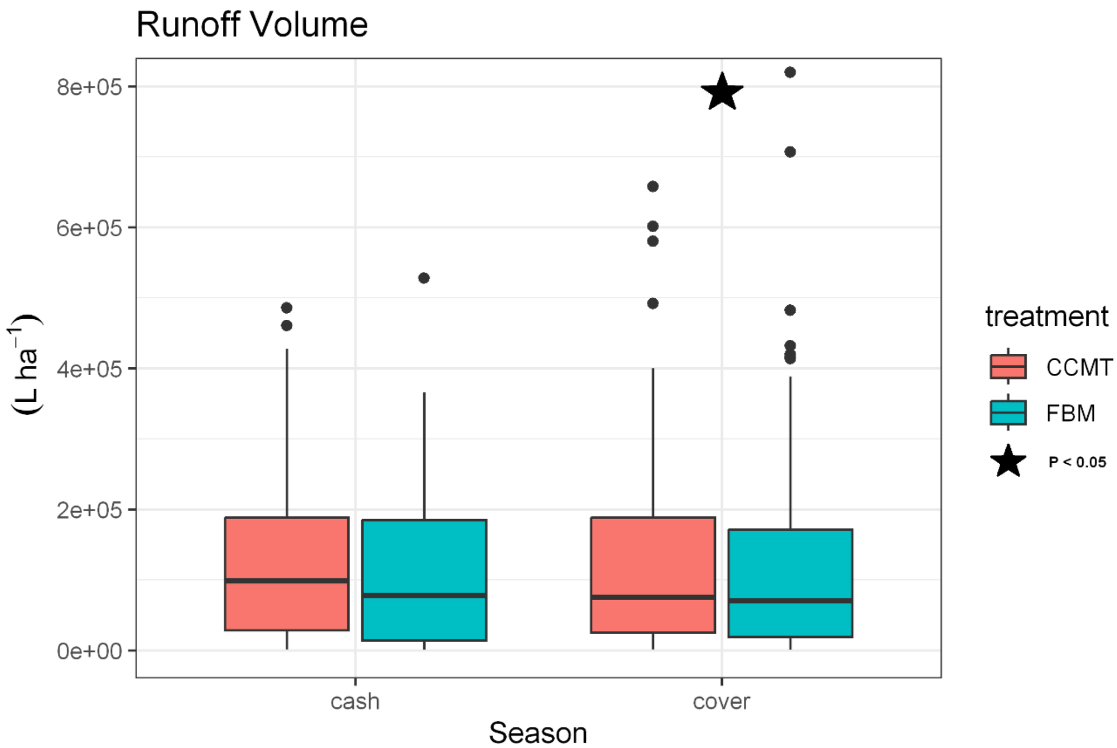

Figure 2.10 Distribution of effluent volume measurements

Observed & estimated event-wise discharge volumes considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Normalized runoff volume is measured in liters per hectare (L ha^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

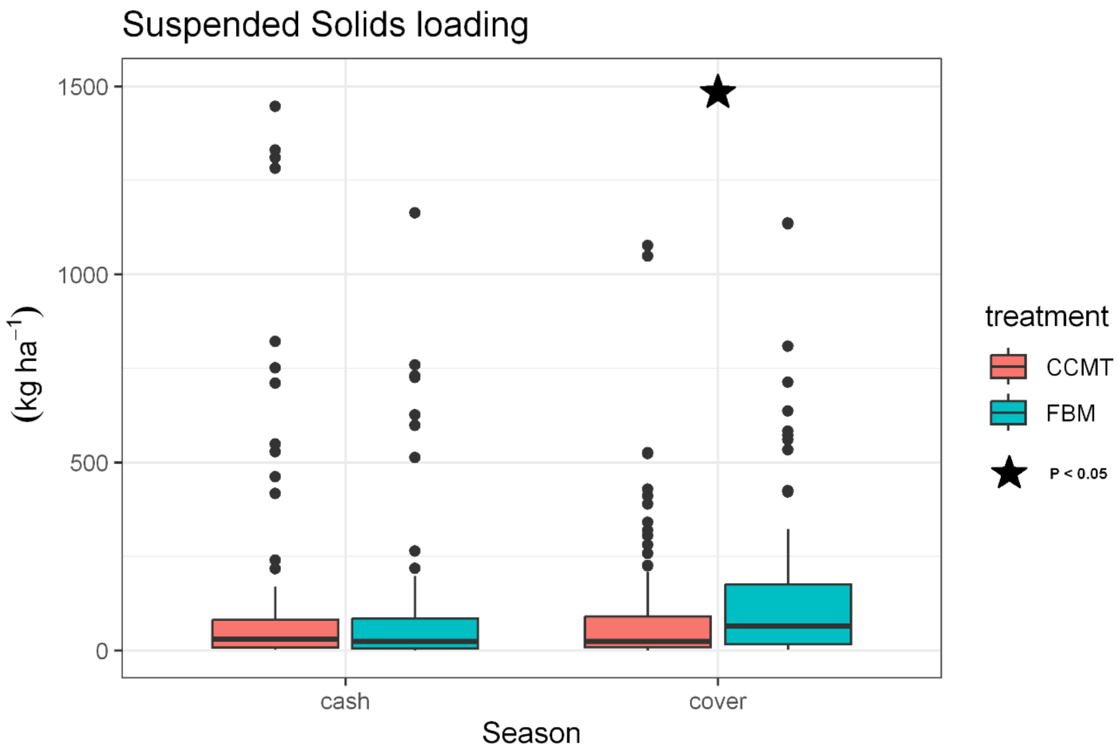

Figure 2.11 Distribution of suspended solids loads

Observed & estimated event-wise total suspended solids loads considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Nutrient loading mass is measured in kilograms per hectare (kg ha^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

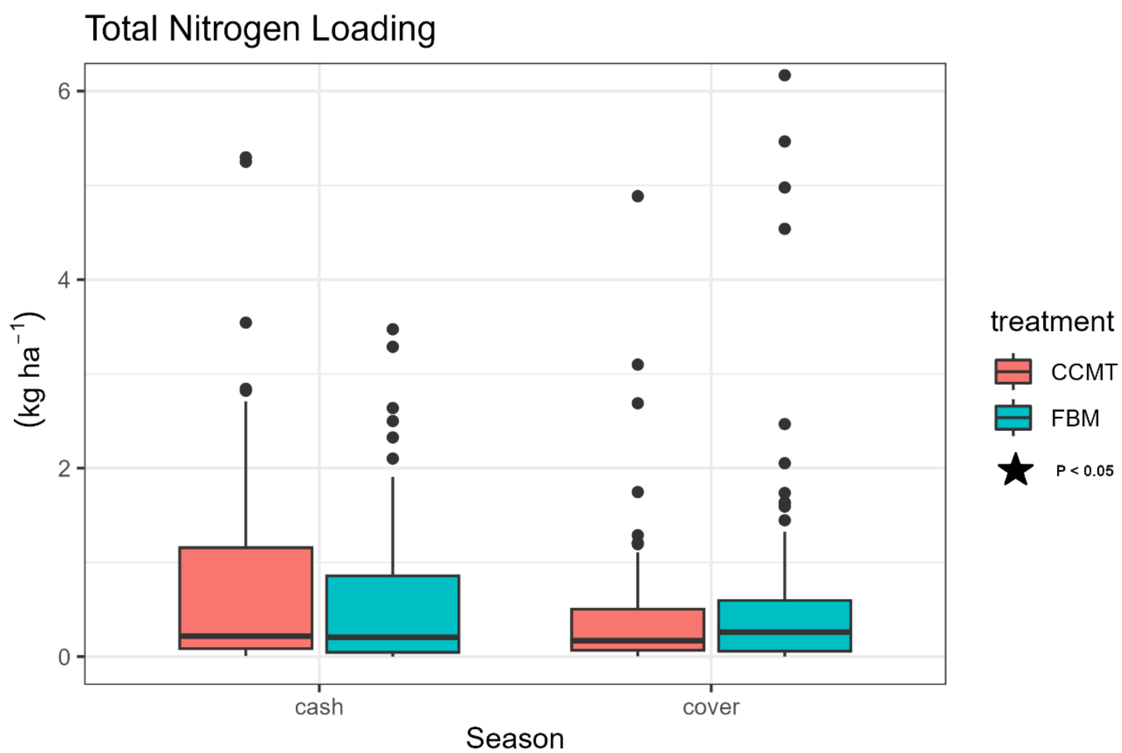

Figure 2.12 Distribution of total nitrogen loads

Observed & estimated event-wise total nitrogen loads considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Nutrient loading mass is measured in kilograms per hectare (kg ha^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

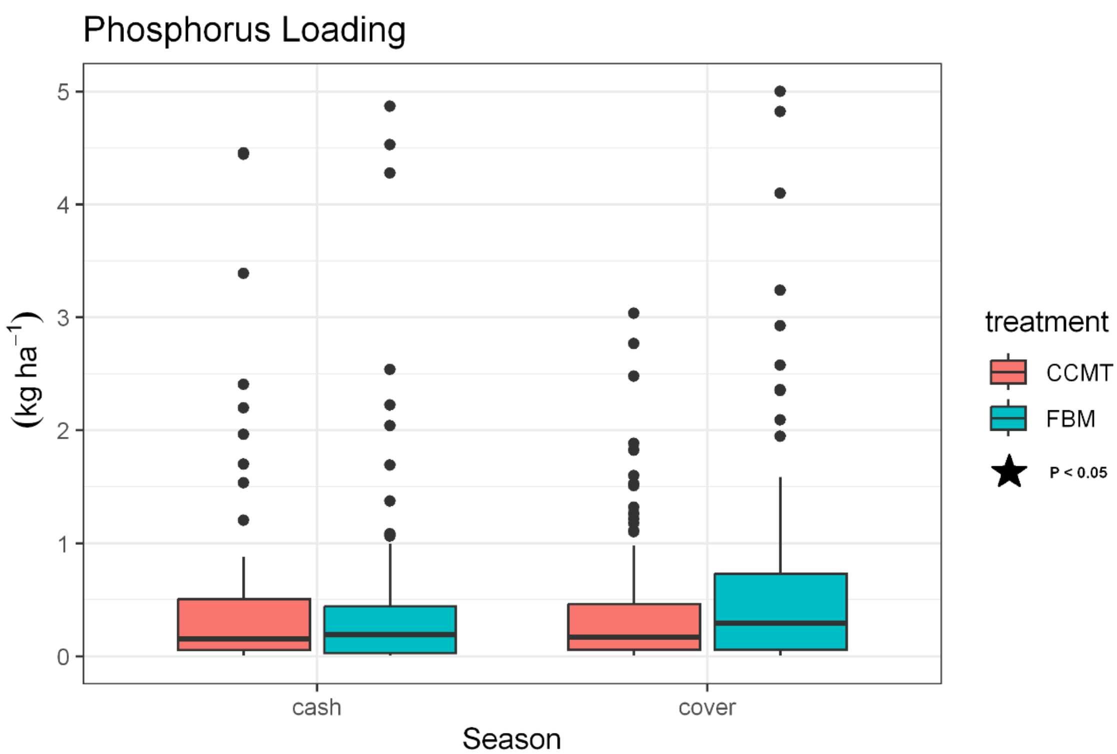

Figure 2.13 Distribution of total phosphorus loads

Observed & estimated event-wise total phosphorus loads considered by treatment and season. Experimental treatments included Cover Crop – Minimum Tillage (CCMT) and Farmer Best Management (FBM). Cash crop season is considered (May-October) and cover crop season (November–April). Nutrient loading mass is measured in kilograms per hectare (kg ha^{-1}). Statistically significant differences ($p<0.05$) are noted with a star.

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CHAPTER III

VALIDATION OF EDGE-OF-FIELD WATER QUALITY SAMPLING PROTOCOLS AND QUANTIFYING PROTOCOL EFFECTS ON RUNOFF NUTRIENT LOADING ESTIMATES FROM AGRICULTURAL NON-POINT SOURCES

3.1 Introduction

Much research has been carried out to investigate the effects of conservation best management practices (BMPs) and their ecological and economic implications (Baker et al., 2018; Christopher et al., 2021; Mausbach & Dedrick, 2004; Reba et al., 2020). Thus, water quality sample collection techniques that best represent actual impacts of best management practices (BMPs) are essential to developing an understanding of how or where practices would be most effective. Instream water sampling has a long history and well-established protocols developed to deploy standard practices that allow for confidence and continuity of observations to ascertain water quality indicators (Wilde, 2008). In agricultural landscapes, edge-of-field (EOF) monitoring practices are a recent advancement to track runoff nutrient concentrations and loading from agricultural landscapes to downstream aquatic ecosystems. Automated samplers, initially mechanical then electronic, were developed in the early 2000s to enhance EOF monitoring (Harmel et al., 2018). Researchers saw the need to complement practical knowledge gained through experience with empirical data to accurately assess and represent water quality impairments (Harmel et al., 2006; Mcfarland & Hauck, 2001). Guidance and sponsorship of water monitoring is available through the United States Department of Agriculture- National

Resource Conservation Service (USDA-NRCS) Environmental Quality Incentives Program (EQIP) practices 201 and 202.

Edge-of-field water quality sampling is typically achieved by using automated monitoring stations deployed at the field scale, as in the Arkansas Discovery Farms EOF monitoring program or in Conservation Effects Assessment Program sites (Aryal et al., 2018; Sharpley et al., 2015). The field, or an easily delineated section of a field, is drained to a single outflow where discharge is measured, and a composite water sample is collected during runoff events to determine non-point source pollution estimates in runoff water quality. Composite samples are used to estimate event mean concentration (EMC) which, when coupled with discharge, indicate nutrient and sediment loads conveyed downstream (Harmel et al., 2006).

The sampling protocol, or how the sampler is programmatically triggered, is predicted to influence estimated EMC. Sampling units are constrained by the size of collection container, thus the number of aliquots available to be collected in the composite. If nutrient and sediment concentrations change throughout a runoff hydrograph (Pierce et al., 2012), composite samples that fail to sample the entire event will yield inaccurate EMC and subsequent stream loading estimates. Further, if samplers only collect samples during the initial rising limb of the hydrograph, a “first flush” signature will be collected, typical of higher pollutant concentrations and not representative of the entire event (Bertrand-Krajewski et al., 1998; Cho & Lee, 2017). Both scenarios could lead to sub-optimal stream loading estimates used in understanding transport of nutrients and sediment from agricultural landscapes to aquatic ecosystems.

While runoff events typically exhibit a log normal shaped hydrograph, they can vary in magnitude. The variation in magnitude makes it difficult to design a sampling procedure that manages to cover all expected range in discharges, and therefore requires investigation of tradeoffs in sampler trigger schemes. The sampling system is limited in it's capacity to contain ongoing aliquots by a ten liter composite sample container. Flow-weighted -volumetric and time-series sampling designs often fill to capacity prior to the end of the event, whereas other sampling designs can fail to effectively capture smaller runoff events, such as irrigation driven runoff. Irrigation exhibits a markedly different nutrient and discharge character relative to rainfall events and can produce important ecological consequences (Merchán et al., 2013). It has been demonstrated that nutrient and sediment concentrations decrease over time across rainfall driven runoff hydrographs (Pierce et al., 2012; see Figure 3.2). Thus, a sampling design that accommodates a large range of possible events is essential for effectively estimating true EMC. Given the aforementioned hydrological complexities alongside the need to best estimate nutrient loading in non-point pollution sources, there is a critical need for research that examines the efficacy of various sampling protocols with regard to using EOF water quality sampling to estimate stream nutrient loading in agricultural landscapes.

This study is meant to compare water quality data collected with three common sampling procedures: two different flow-weighted designs and an additional time-series design. Edge-of-field water quality samples were collected with three different automated sampling units designed to collect and store water samples following rainfall events that produce measurable runoff. Individual events were sampled by the three different systems allowing for direct comparison of EMC and discharge in a paired manner. If the historically accepted methods of EOF water quality sample collection, flow-weighted - volumetric and time-series, both offer effective means of estimating EMC, then there would be little difference in stream loading estimates derived using these respective methods. A third protocol, flow-weighted - Δflow rate, was compared to the former to help guide future application of EOF sampling techniques.

Differences in EMC leading to over or under estimation of stream loading would suggest that protocols could be improved to better quantify BMP effects on water quality. A difference in nutrient and sediment concentration was expected, along with the associated stream loading estimates collected in runoff events which affected the sampler container full condition. Sampling protocols that would fail to sample the tail end of the hydrograph would disproportionately represent the nutrient/sediment rich rising limb of the event hydrograph, ultimately leading to overestimation of actual stream loading. Effective water quality sample collection techniques are an essential element to ascertain real-world impacts of BMPs being implemented by farmers.

3.2 Materials and Methods

3.2.1 Study Area

The sampling scheme was replicated on three farms from April 2021 until June 2022 in an effort to collect 30 unique runoff site-events. The farms were under intensive row-crop rotations and were located in the Lower Mississippi Alluvial Valley (LMAV). Sites were located in Bolivar, Sunflower, and Coahoma counties, Mississippi. Control plots on three of the paired-field cover crop-reduced tillage sites outlined in Chapter II were chosen to compare the sampling methodologies. Farmer best management plots were chosen to prevent variable management strategies of the cover crop treatment from influencing results. All three fields were managed using prevailing farmer best management practices typical of the region.

3.2.2 Equipment

The automated sampling units comprise custom-built configurations of two or three main components, respectively. They consist of an automatic sampler (Hach SD900 or Hach AS950) that collects and houses a water sample using a peristaltic pump and a device that will trigger the sampler given the correct conditions (Hach, Loveland, CO, USA). In the first flow-weighted design and the time-series design, the device used to trigger the sampler was an ultrasonic velocity meter (Unidata Starflow 6526) equipped with depth gauge (Unidata, O'Connor, WA, ASTL). The third design used a different ultrasonic velocity meter (Unidata Starflow-QSD) coupled with telemetry (KTS Wireless ASR) to calculate changes in flow-rate (Unidata, O'Connor, WA, ASTL; KTS Wireless, Lake Mary, FL, USA). Here the computer-radio activated the sampler based on the predefined criteria. Each design used the same 10-liter sample container that is typical of those used when collecting composite samples.

All three sampling units are a complex electrical machine constructed of hydrophobic components and as such, are sensitive in extreme weather and climates, which are routine with regards to humidity and moisture in the MS Delta region. Regular maintenance is required for the samplers to function. Additional parts included a large plastic enclosure, power system consisting of solar panel regulator and marine battery, and an air and waterproof electrical junction box. The automatic sampler and electrical junction box are maintained with desiccants for absorption of any excess moisture to protect sensitive electronics.

These units were placed adjacent each other at the outflow of control plots discussed in Chapter II and collected composite samples from the same outflow culvert during each runoff event. The sensor and inlet of the sampling units was arranged at each location to minimize interaction effects of the sensor and inlet on the other instruments in the outflow pipe. This includes keeping them as far apart from each other as feasible, as well as changing the relative order of sensor placement at each of the three replicates (see Figure 3.1).

3.2.3 Sampling Protocols

Automated samplers contributed 100 ml aliquots to the composite sample based on user defined criteria. The aim of this study was to see how these criteria may influence EMC and loading estimates. The three defined triggers were:

1. Volumetric: every 1000 L of measured discharge triggered the sampler to activate. This value is somewhat arbitrary and was fashioned to capture small runoff events like small storms and irrigation runoff. Being constrained by the 10 L composite container meant this scheme would only sample the first 100,000 L of any runoff event in 100 ml increments.
2. Time-series: sampler was activated every 5 mins conditional on depth and non-zero flow. Flow greater than zero and depth greater than 25 mm were used to define the beginning of a runoff event. The sampler would continue to activate at this interval for as long as these conditions were met, and the composite sample container was less than full. This scheme would completely sample runoff events that were less than 8 hours and 20 minutes long based on the 100 ml aliquot size.
3. Change in flowrate: sampler was activated on every change of 1 L/s in flow rate. The sampling protocol would always sample the rising and falling limbs of runoff hydrographs. While this scheme does not contribute aliquots proportionally to the volume of runoff similarly to time-series, it was designed to capture a large range of event magnitudes.

3.2.4 Sample Collection

Composite water quality samples were retrieved from each site within 24 hours of each runoff producing event. Refrigerated transport of samples from the field was carried out by MS State personnel. Analysis of samples was carried out at the MS State Water Quality lab. Sample holding period was no more than 72 hours between collection and analysis.

3.2.5 Water Sample Analysis

Water quality indicators included turbidity (TUR), total suspended solids (TSS), total nitrogen (TN), nitrite-nitrate nitrogen (NO_2^--NO_3^--N), and total phosphorus (TP). All methods meet standards outlined in the Code of Federal Regulations title 40 section 136 concerning analysis of environmental pollutants. Turbidity was measured with Hach 2100Q portable turbidimeter (Hach, Loveland, CO, USA). Hach method 8195 compares the intensity of light scattered by sample with that of a standard reference in suspension. Turbidity is reported in nepholometric turbidity units (NTU). Total suspended solids concentrations were determined following American Public Health Association 2005 method 2540 D. Samples are filtered through prepared fiberglass filters under vacuum. The sediment and filters are dried to constant weight and weighed. Subtracting the initial weight of the washed and dried filter multiplied by the sample volume yields total suspended solid concentration (equation 3.1).

$$(final\ weight - initial\ weight\ (mg)) * \left(\frac{1000}{sample\ volume\ in\ ml}\right) = TSS\ mg/l \tag{3.1}$$

Nitrogenous species TN and NO_3^--NO_2^--N assay was performed with Hach simplified TKN TNTplus tests kits using USEPA approved Hach method 10242 (Hach, Loveland, CO, USA). Total nitrogen is measured by acid digestion to nitrate then indicated spectrophotometrically. This value is compared to an undigested sample to measure the amount of N that is oxidized. This difference indicates the amount of total kjeldahl nitrogen present in samples (equation 2.2).

$$Total\ N = TKN + (NO_3^- - N) + (NO_2^- - N) \rightarrow Total\ N - TKN = (NO_3^- - N) - (NO_2^- - N) \qquad (3.2)$$

Total phosphorus assay was performed using Hach TNT843-845 chemistry kits which follow USEPA approved Hach method 10209 (Hach, Loveland, CO, USA). This uses the ascorbic acid method followed by spectrophotometry. Dilute P solution is first treated with sulfuric acid hydrolysis to break down inorganic polyphosphates then reacted with ammonium molybdate and potassium antimony tartrate in an acid medium to form a complex that is then reduced with ascorbic acid. This reduction indicates OP concentration with a blue color that is measured colorimetrically with a spectrophotometer at 650nm.

Discharge hydrographs using data from Starflow and QSD ultrasonic velocity meters were characterized using Microsoft Excel (Unidata, O'Connor, WA, ASTL). Length of runoff event, time to peak discharge (Q), and total discharge was measured and normalized by the field area. Total nutrient loading was calculated with effluent concentration and total measured discharge.

3.2.6 Data Analysis

Nutrient concentrations in effluent and nutrient loads were compared as discussed in Chapter II. Initial exploratory data analysis confirmed non-normal distribution of response variables. To test for differences between treatments, the complete cases, or events where all three samplers collected a sample, were subjected to the Friedman test, a non-parametric alternative to ANOVA (Friedman, 1937). A second approach, the Skillings-Mack test, that used incomplete cases as well was also used to test for treatment effects (Skillings & Mack, 1981).

To understand drivers of any observed differences, a linear mixed effects model was used to examine the effect of treatment, farm, and sampler full condition on response variables (Bates et al., 2015). All these effects were considered fixed in the models. Farm, or the field site, would have been included in the model as a random effect; yet here, owing to there only being three sites, it is included as fixed effect for model performance. The final predictor of interest was the sampler full condition noted when samples were retrieved, indicative of incomplete sampling of the runoff event. Finally, site-event was incorporated into the model as a random effect, as the observed runoff events represent a sample of the variance one would expect from all possible storm events. Data were log transformed prior to linear modeling. Further, the linear mixed effects model acknowledges the repeated measures nature of sampling and is robust to incomplete cases, or events where only two of the three sampling systems worked. The modeling procedure used an AIC model selection to select the logical and best performing model effect structure (Akaike, 1998; see Equation 3.3).

$$\log(Response) \sim treatment + farm + full + (1|event) \tag{3.3}$$

The series of response variables evaluated were TUR, TSS, NO_3^--NO_2^--N, TN, and TIP concentrations as well as TSS, NO_3^--NO_2^--N, TN, and TIP loads. The effectiveness of sampling protocols was reviewed with regard to how adequately they capture aliquots across the entire hydrograph to represent an EMC. This was captured by the proportion of runoff events ending before the sampling equipment filled to capacity.

3.3 Results

3.3.1 Numerical Summary

Forty-six unique site events were sampled during the monitoring period. Of those, 21 produced a composite sample from all three sampling systems and 25 site-events produced at least 2 of the 3 sampling regimes. Statistical summary of observed nutrient, discharge, and loading estimates are presented in Table 3.1 and 3.2.

3.3.2 Statistical Analysis

The Friedman test indicated significant ($\alpha = 0.95$) differences among treatment groups in four of five nutrient concentrations: TUR ($p < 0.01$), TSS ($p < 0.01$), NO_3^--NO_2^- -N ($p < 0.05$), and TP ($p < 0.01$). The final analyte, TN, indicated no significant differences among treatment groups ($p > 0.1$). The Skillings-Mack test offered support for these findings using the larger dataset inclusive of incomplete cases: TUR ($p < 0.01$), TSS ($p < 0.01$), NO_3^- -NO_2^- -N ($p < 0.05$), TP ($p < 0.01$). Further, it offered no support for differences among treatment groups with regard to N concentrations ($p > 0.1$). A visual summary of nutrient concentrations regarding treatment is offered in Figure 3.2. Post-hoc pairwise testing indicates the delta flowrate sampling protocol as the outgroup with the other two protocols not exhibiting significant differences when considering any of the nutrient analyte concentrations. In all cases, the median concentrations observed were lower when collecting composite samples using the delta flowrate protocol.

Measured discharge was not consistent across treatment groups despite measuring the same runoff events. The Friedman test on only complete cases indicated at least one difference between groups and further analysis showed the delta flowrate protocol, and associated velocity meter, measured significantly less runoff than the other two treatments ($p < 0.05$; see Figure 3.4). This led to all four measured analytes (TSS kg ha^-1, NO_3^--NO_2^-- N kg ha^-1, TN kg ha^-1, TP kg

$ha^{-}1$) of nutrient loading to show at least one significant difference among groups ($p < 0.01$). In all cases the delta flowrate group was reduced relative to the other two treatments (see Figure 3.5).

Observed nutrient concentrations were across the board influenced by the treatment protocols, particularly the delta flowrate sampling regime ($p< 0.001$ in all five models). Concentrations were lowest when using the delta flowrate sampling protocol, followed by incremental steps up to the time series protocol, then another to the volumetric protocol. This trend was true for all five nutrient concentration models and the standard error interval did not include zero for any of the treatments. Site had various impacts on response variables. One of three farms had site as a non-significant effect on the response variables, the other two exhibited the lowest observed concentrations and highest, respectively; both of these latter farms had significant model coefficients for the TSS and soil bound macronutrient P constituent concentrations. Nitrogenous species TN and NO_3^--NO_2^-- N were not higher in the farm which exhibited higher soil and P concentrations ($p > 0.1$). The sampler full condition had a contrary effect on nutrient concentrations to previously predicted. While it was non-significant in all five nutrient concentration models, it was inversely correlated with concentrations, meaning full sampler would typically exhibit lower concentration than those that were not full. Finally, all four nutrient loading models indicated that treatment was a significant driver of variation in the response variable (all $p< 0.05$). Here though, the bottle full condition had a positive coefficient in all 4 models, indicating that loading estimates would increase whenever the bottle full condition was met (all $p< 0.05$). See Table 3.3 for an exhaustive list of model coefficients and standard error estimates.

3.4 Discussion

Understanding nutrient and sediment transport at the field scale is valuable to accurately assess stream nutrient loading from non-point sources. Accurately representing this information is crucial, especially when using EOF water quality data as inputs for watershed-scale models that assess the effects of various suites of BMPs. The present results suggest that both choice of sampling protocol and choice of equipment can have an influence on measure of nutrient concentration and loading. While the present experimental design cannot deduce which element, sampling protocol or equipment or both, is responsible, it does offer evidence that simple choices made while constructing sampling systems can have a profound effect on estimations of nutrient transport. Two of the sampling systems used the same model of ultrasonic velocity meter and both were in accord when measuring discharge across the observed runoff events. The third system used a different model of the same type of instrument, which measured ~50% less cumulative discharge. This disparity in measured discharge would have an outsize effect on loading estimates, and thus those significant loading treatment effect results should be attributed to that. This choice of specific equipment, albeit of the same type, having such a profound effect on estimates indicates there is cause for standardization, and at the very least calibration of individual instruments, when constructing EOF monitoring stations where data would be used independently, i.e., data collected from a single field used to inform landscape models rather than used in paired field treatment-control scenario. While the present study did not use other methods of measuring discharge (e.g., flume and level logger), it did indicate that means of measurement can lead to potential variations in measured discharge and nutrient runoff. The data indicates the two instruments that agreed are more likely to reflect discharge patterns; yet even these measurements are called into question in the absence of calibration. Starflow velocity meters have been demonstrated to consistently overestimate discharge in a laboratory setting, ranging from 18% to 35% error relative to laboratory measurements, despite their quoted factory depth and velocity accuracy of ±0.25% and ±2%, respectively (Vermeyen 2000; Unidata 1998). Indeed, Blake and Packman (2008) encourage ongoing data post-processing that can help identify sensor problems through changes to the depth-velocity relationship, such as changes to stream bed morphology or drift in depth sensor zero (Watt & Jefferies 1996). Finally, potentially erroneous discharge measurements would confound the flow-weighted sampling protocols, vis-à-vis the way they contribute aliquots to the composite sample, even if a correction factor could be used to enhance discharge measurements.

The present study was conceived under the auspices of different systems (both equipment and protocol) producing different results. Unfortunately, the experimental design failed to illuminate which of the design choices is responsible for observed differences. Further investigation of the influence of EOF collection method is merited. However, given the prohibitive costs associated with equipment, collection, and sample analysis, limited opportunities may present themselves for an additional evaluation. The results do appear to concur with prior experience which saw delta flowrate sampling protocol coupled with QSD type velocity meter produce samples with comparatively lower nutrient concentrations and loads relative to volumetrically weighted composite samples produced using a Starflow velocity meter (Badon et. al, 2022). Thus, the need for comparison was validated; choice of instrument and sampling regime influenced loading and concentration estimates when measuring the same effluent. However, it does little to ascertain which approach yields the most accurate estimates.

Monitoring goals are case specific. Ecologically significant flows may vary greatly relative to what is significant from the on-farm perspective. Losing one to two pounds of N per acre in a single event may not be considered agronomically significant, yet this may prove significant from an environmental perspective when coupled with insufficient discharge. While this study aimed to assess methodological differences in measured stream loading, it does not provide a clear answer as to what may be the best approach to water quality monitoring in agricultural landscapes. The cost of implementing and maintaining EOF water quality monitoring equipment is prohibitive, with installation costs in excess of $10,000 and annual operating costs running even higher (Ribikawskis and VanRyswyk, 2015). If a pay for performance scheme were ever adopted for conservation practice subsidies, using in-situ collection equipment and offsite sample analysis would prove intractable on the wider scale. Alternatively, it would be more feasible to develop and calibrate regionally specific rating curves for assessing the effectiveness of practices by using a readily measurable proxy, such as cover crop biomass. This approach, as suggested by Cattaneo et al. (2005), could potentially simplify the process. Nonetheless, measuring conservation practice efficacy is fundamental to learning how to be good stewards of our land and resources.

3.4.1 Conclusion

Results of this study and others suggest the following best practices are warranted to obtain the most accurate discharge results when using automated flowmeters: careful site selection, ongoing data post-processing, and validation of measurements using an alternative stream gauging method. Laminar flow with minimal turbulence is desirable for the most accurate readings, thus the recommendation to locate the sensor near the tail end of outflow pipes, while being cognizant of measuring drawdown due to hydraulic drop. Ultrasonic velocity meters provide an excellent tool for measuring discharge in situations, such as backwater conditions, which would confound typical measurement techniques like weir and flume. Ongoing data processing and correction will allow users to identify site specific problems with discharge measurements. Automated techniques for post-processing data can offer the user better error correction while at the same time alerting to changes in state-discharge relationship which may indicate problems. Finally, in-situ site specific calibration, or validation, of device discharge measurements is necessary. An alternative gauging method should be applied, wherever possible, to assuage concerns over instrument accuracy and stability. Gauging stream flow should be carried out often enough to ensure device quality standards of measurement. Coupled with device measured stage and velocity, and alternative measure allows for better error correction, as well as definition of a more accurate stage-discharge relationship.

3.5 Tables and Figures

Table 3.1 Numerical summary of nutrient concentrations

Analyte	Treatment	Minimum	Q1	Median	Q3	Max	sd	n	NA's
TUR (NTU)	Delta Flowrate	79.1	172.0	652.0	1935.0	9640.0	2014.3	27	9
	Volumetric	100.0	475.0	1105.0	3042.5	10271.9	2960.2	33	3
	Time-series	44.0	285.0	1011.4	1795.0	7535.0	1914.0	33	3
TSS ($mg\ L^{-1}$)	Delta Flowrate	85.0	189.5	442.5	1522.5	5720.0	1308.0	27	9
	Volumetric	58.0	624.0	1500.0	3230.0	18500.0	4184.5	33	3
	Time-series	27.0	192.0	1200.0	2970.0	9720.0	2725.3	33	3
NO_3^--NO_2^-- N ($mg\ L^{-1}$)	Delta Flowrate	0.4	1.4	3.1	5.8	17.4	4.2	27	9
	Volumetric	0.4	2.1	4.3	7.5	24.2	5.3	33	3
	Time-series	0.3	1.7	3.3	5.5	17.5	4.4	33	3
TN ($mg\ L^{-1}$)	Delta Flowrate	1.2	2.6	5.9	10.7	25.2	6.8	27	9
	Volumetric	1.9	3.9	6.6	12.1	61.0	11.9	33	3
	Time-series	1.5	3.6	6.5	10.3	42.7	8.3	33	3
TP ($mg\ L^{-1}$)	Delta Flowrate	0.7	2.6	3.6	8.1	31.3	7.7	27	9
	Volumetric	1.0	3.9	7.3	15.3	383.0	66.1	33	3
	Time-series	1.0	3.4	6.2	12.5	353.0	60.5	33	3

Observed nutrient concentrations considered by treatment. Concentrations are measured in milligrams per liter ($mg\ L^{-1}$) and nephelometric turbidity units (NTU). TUR, turbidity; TSS, total suspended solids; NO_3^--NO_2^-- N, nitrate-nitrite nitrogen; TN, total nitrogen; TP, total phosphorus.

Table 3.2 Numerical summary of discharge and nutrient loading estimates

Analyte	Treatment	Minimum	Q1	Median	Q3	Max	sd	n	NA's
Q (L ha^{-1})	Delta Flowrate	1245.7	85295.5	272539.0	585604.5	6526839.0	1324703.7	27	9
	Volumetric	5479.0	134642.5	849530.5	1161187.3	11816893.0	2300335.6	32	4
	Time-series	7128.0	109472.0	1006233.0	1756025.0	11978914.0	2662300.0	33	3
TSS (kg ha^{-1})	Delta Flowrate	0.3	4.6	12.6	25.9	444.4	93.0	25	11
	Volumetric	0.4	16.1	34.6	227.7	5846.9	1044.2	32	4
	Time-series	0.2	13.8	32.3	203.9	1965.3	464.5	33	3
NO_3^--NO_2^-- N (kg ha^{-1})	Delta Flowrate	0.0	0.0	0.1	0.2	4.5	0.9	25	11
	Volumetric	0.0	0.0	0.2	0.6	13.8	2.6	32	4
	Time-series	0.0	0.1	0.2	0.8	11.3	2.4	33	3
TN (kg ha^{-1})	Delta Flowrate	0.0	0.1	0.1	0.5	6.6	1.3	25	11
	Volumetric	0.0	0.1	0.3	1.1	34.7	6.3	32	4
	Time-series	0.0	0.1	0.5	1.4	17.6	4.1	33	3
TP (kg ha^{-1})	Delta Flowrate	0.0	0.1	0.1	0.2	2.2	0.5	25	11
	Volumetric	0.0	0.1	0.3	1.0	36.0	6.4	32	4
	Time-series	0.0	0.2	0.5	1.5	12.9	2.8	33	3

Discharge and nutrient loading estimates considered by treatment. Normalized discharge (Q) is measured in liters per hectare (L ha^{-1}) and nutrient loads are measured in kilograms per hectare (kg ha^{-1}). Q, discharge; TSS, total suspended solids; NO_3^--NO_2^-- N, nitrate-nitrite nitrogen; TN, total nitrogen; TP, total phosphorus.

Table 3.3 Fixed effect coefficients for linear mixed effects models

Model	Term	Estimate	std.error	Statistic	df	p.value	Significant
TUR (NTU)	(Intercept)	6.159442	0.398319	15.4636	47.34457	3.91E-20	***
	trmtTimeseries	0.375492	0.199614	1.881095	77.54644	0.064	
	trmtVolumetric	0.599297	0.207481	2.888435	77.80236	0.005	**
	siteMOS	0.492087	0.492478	0.999206	42.71924	0.323	
	siteSKE	1.122377	0.497686	2.255189	42.68156	0.029	*
	fullTRUE	-0.11199	0.196702	-0.56931	83.77034	0.571	
TSS (mg L^{-1})	(Intercept)	5.889011	0.345167	17.06132	50.03604	1.69E-22	***
	trmtTimeseries	0.450674	0.204458	2.204241	83.15139	0.030	*
	trmtVolumetric	0.739442	0.21242	3.481029	83.52885	7.97E-4	***
	siteMOS	0.467183	0.421422	1.108587	43.11379	0.274	
	siteSKE	1.357581	0.425857	3.187881	43.11559	0.003	**
	fullTRUE	-0.22687	0.199307	-1.1383	91.8183	0.258	
NO_3^{-}-NO_2^{-} N (mg L^{-1})	(Intercept)	1.056152	0.263654	4.005827	47.50676	2.16E-4	***
	trmtTimeseries	0.263082	0.124529	2.112625	76.63436	0.038	*
	trmtVolumetric	0.369705	0.129452	2.855927	76.85404	5.51E-3	**
	siteMOS	0.20102	0.327055	0.614636	43.45476	0.542	
	siteSKE	0.161086	0.330525	0.487363	43.41176	0.628	
	fullTRUE	-0.13182	0.123061	-1.07119	82.03055	0.287	
TN (mg L^{-1})	(Intercept)	1.65103	0.222239	7.429089	49.8748	1.30E-09	***
	trmtTimeseries	0.167797	0.126457	1.326914	82.09938	0.188	
	trmtVolumetric	0.284524	0.131399	2.165348	82.43945	0.033	*
	siteMOS	0.239116	0.272305	0.878121	43.58761	0.385	
	siteSKE	0.345406	0.275171	1.255241	43.57517	0.216	
	fullTRUE	-0.09705	0.123649	-0.7849	90.04054	0.435	

Table 3.3 (Continued)

Model	Term	Estimate	std.error	Statistic	df	p.value	Significant
TP (mg L^{-1})	(Intercept)	1.111374	0.28596	3.886466	46.54458	3.2E-4	***
	trmtTimeseries	0.313872	0.126939	2.472625	74.84912	0.016	*
	trmtVolumetric	0.459522	0.131971	3.481983	75.04035	8.33E-4	***
	siteMOS	0.479253	0.35578	1.34705	43.0339	0.185	
	siteSKE	1.30086	0.359567	3.61785	42.98853	7.76E-4	***
	fullTRUE	-0.10898	0.125765	-0.86652	79.59389	0.389	
TSS (kg ha^{-1})	(Intercept)	1.922643	0.570037	3.372838	44.10376	1.56E-3	**
	trmtTimeseries	1.235835	0.303729	4.068869	69.24889	1.23E-5	***
	trmtVolumetric	1.115687	0.317789	3.510776	68.21924	7.97E-4	***
	siteMOS	0.302718	0.71033	0.426166	40.76477	0.672	
	siteSKE	0.601368	0.715419	0.840582	40.28664	0.406	
	fullTRUE	0.701159	0.305172	2.297588	75.60221	0.024	*
NO_3^--NO_2^--N (kg ha^{-1})	(Intercept)	-2.93932	0.564907	-5.20319	43.28328	5.11E-06	***
	trmtTimeseries	1.299124	0.249208	5.213016	63.30976	2.17E-06	***
	trmtVolumetric	0.921718	0.260342	3.540407	62.62919	7.60E-4	***
	siteMOS	-0.11836	0.708804	-0.16699	41.22218	0.868	
	siteSKE	-0.56576	0.714713	-0.79159	40.84508	0.433	
	fullTRUE	0.552551	0.252751	2.186147	67.45191	0.032	*
TN (kg ha^{-1})	(Intercept)	-2.35619	0.537737	-4.38168	43.0397	7.43E-05	***
	trmtTimeseries	1.159873	0.23562	4.922646	62.93327	6.48E-06	***
	trmtVolumetric	0.768316	0.246137	3.121501	62.26086	2.73E-3	**
	siteMOS	-0.06286	0.674837	-0.09315	41.01458	0.926	
	siteSKE	-0.40332	0.680487	-0.59269	40.64157	0.557	
	fullTRUE	0.691097	0.239032	2.891229	67.0251	5.168E-3	**
TP (kg ha^{-1})	(Intercept)	-2.88068	0.505398	-5.69983	41.53936	1.11E-06	***
	trmtTimeseries	1.287297	0.23596	5.455563	63.19506	8.67E-07	***
	trmtVolumetric	1.006269	0.2466	4.080575	62.39919	0.000130	***
	siteMOS	0.238267	0.633065	0.376371	39.19036	0.709	
	siteSKE	0.569818	0.638144	0.89293	38.78761	0.377	
	fullTRUE	0.614828	0.238752	2.575175	68.08835	0.012	*

Table 3.3 (Continued)

All individual analyte models used the same effect structure, with treatment, site, and bottle full condition treated as fixed effects. Runoff event was considered in the models as a random effect. TUR, turbidity; TSS, total suspended solids; NO_3^--NO_2^-- N, nitrate-nitrite nitrogen; TN, total nitrogen; TP, total phosphorus. Turbidity measured in nephelometric turbidity units (NTU), nutrient concentrations in milligrams per liter (mg L^{-1}), and nutrient loading in kilograms per hectare (kg ha^{-1}). Model terms are treatment: deltaflowrate, timeseries, and volumetric; site: HUN, MOS, and SKE; sampler full condition: true and false. Model intercept consisted of a combination of deltaflowrate treatment, site HUN, and sampler **not full** condition. ***, <0.001; **, <0.01; *, <0.05

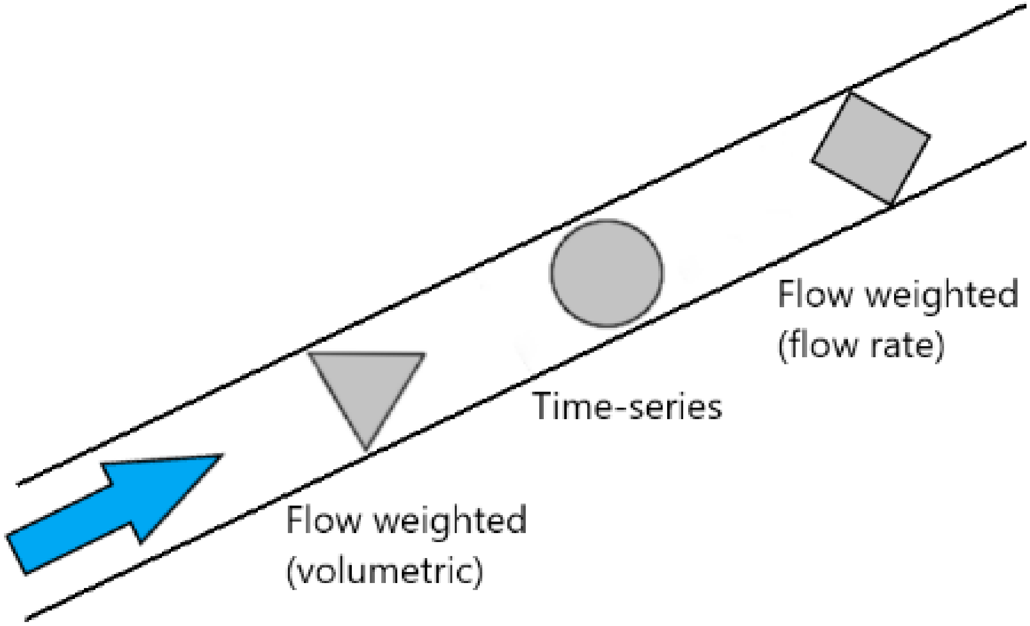

Figure 3.1 Diagram of sensor arrangement

Velocity sensor and sampler intake were arranged at least 18" apart and reordered at each location. Blue arrow indicates direction of effluent flow.

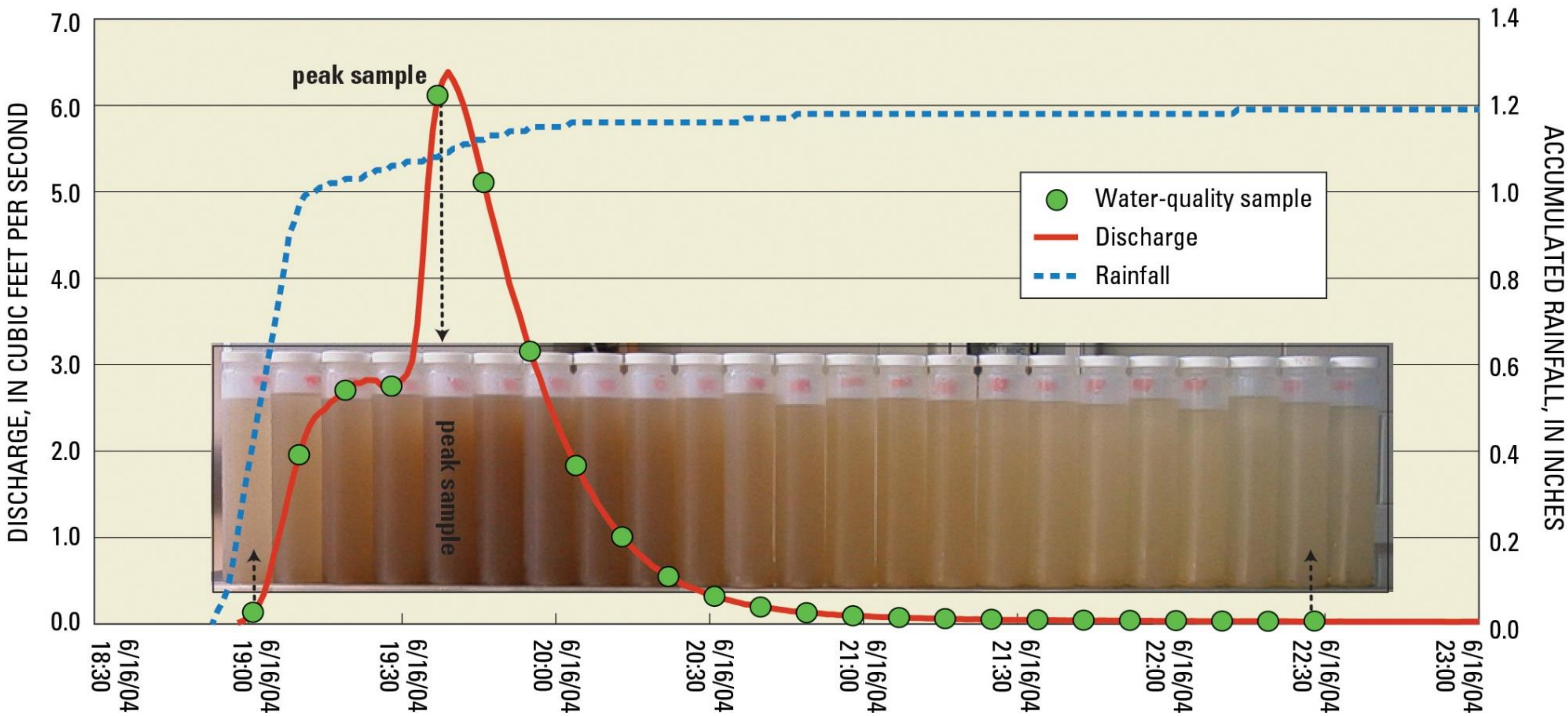

Figure 3.2 Example hydrograph with discrete water quality samples

An example hydrograph that illustrates turbidity changes over time across a runoff event when measured using discrete samples. Red line indicates discharge over time (y-axis #1), the blue line indicates a cumulative rainfall curve over time (y-axis #2). Green dots indicate when discrete samples were collected across the runoff hydrograph. Credit: USGS Upper Midwest Science Center

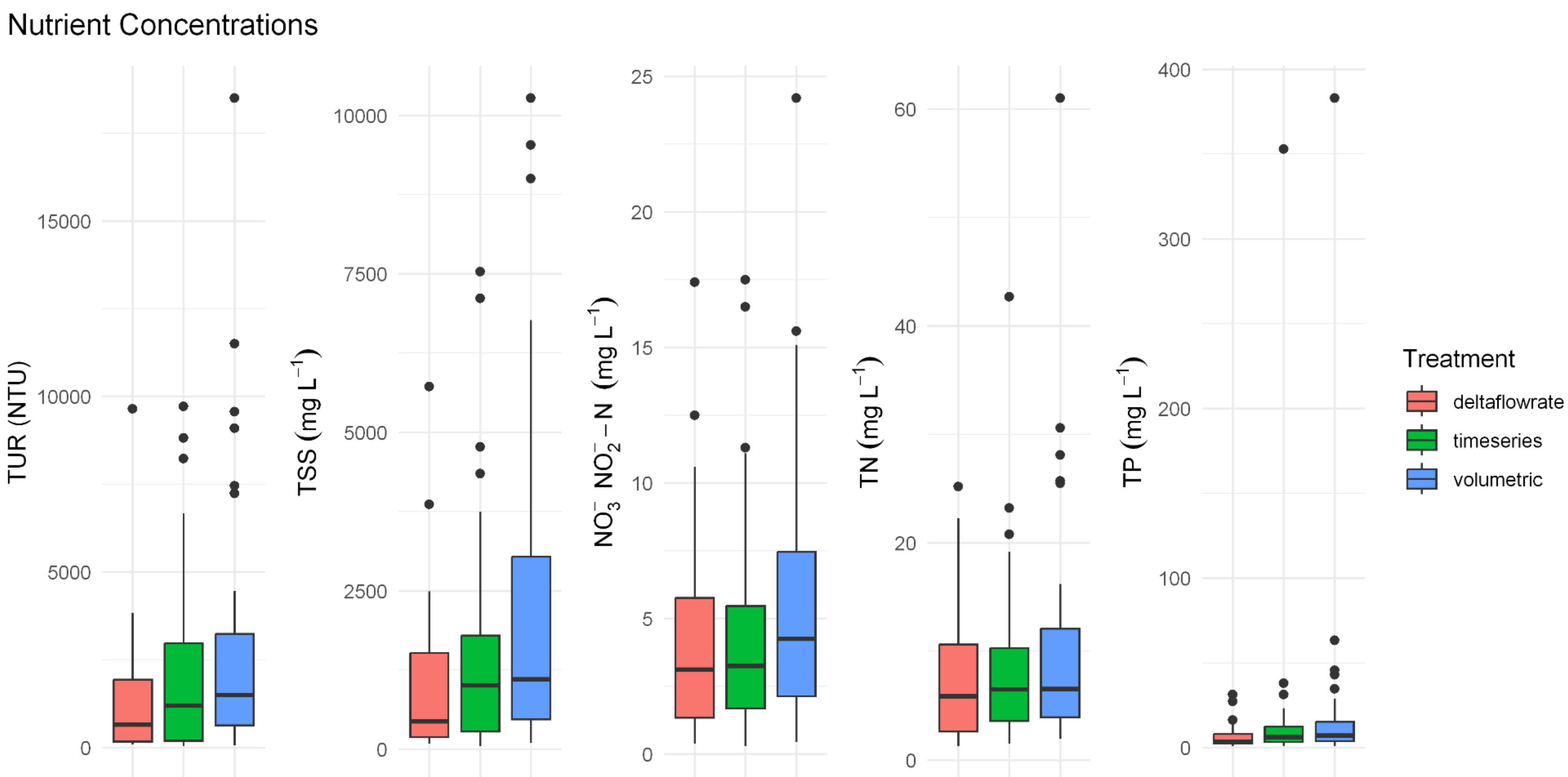

Figure 3.3 Nutrient concentration observations considered by sampling protocol

Distribution of event mean concentration observations in events which produced samples from at least 2 of the 3 sampling systems. Turbidity (TUR) is measured in nephelometric turbidity units (NTU) and nutrient concentrations are measured in milligrams per liter (mg L^{-1}). TUR, turbidity; TSS, total suspended solids; NO_3^--NO_2^-- N, nitrate-nitrite nitrogen; TN, total nitrogen; TP, total phosphorus.

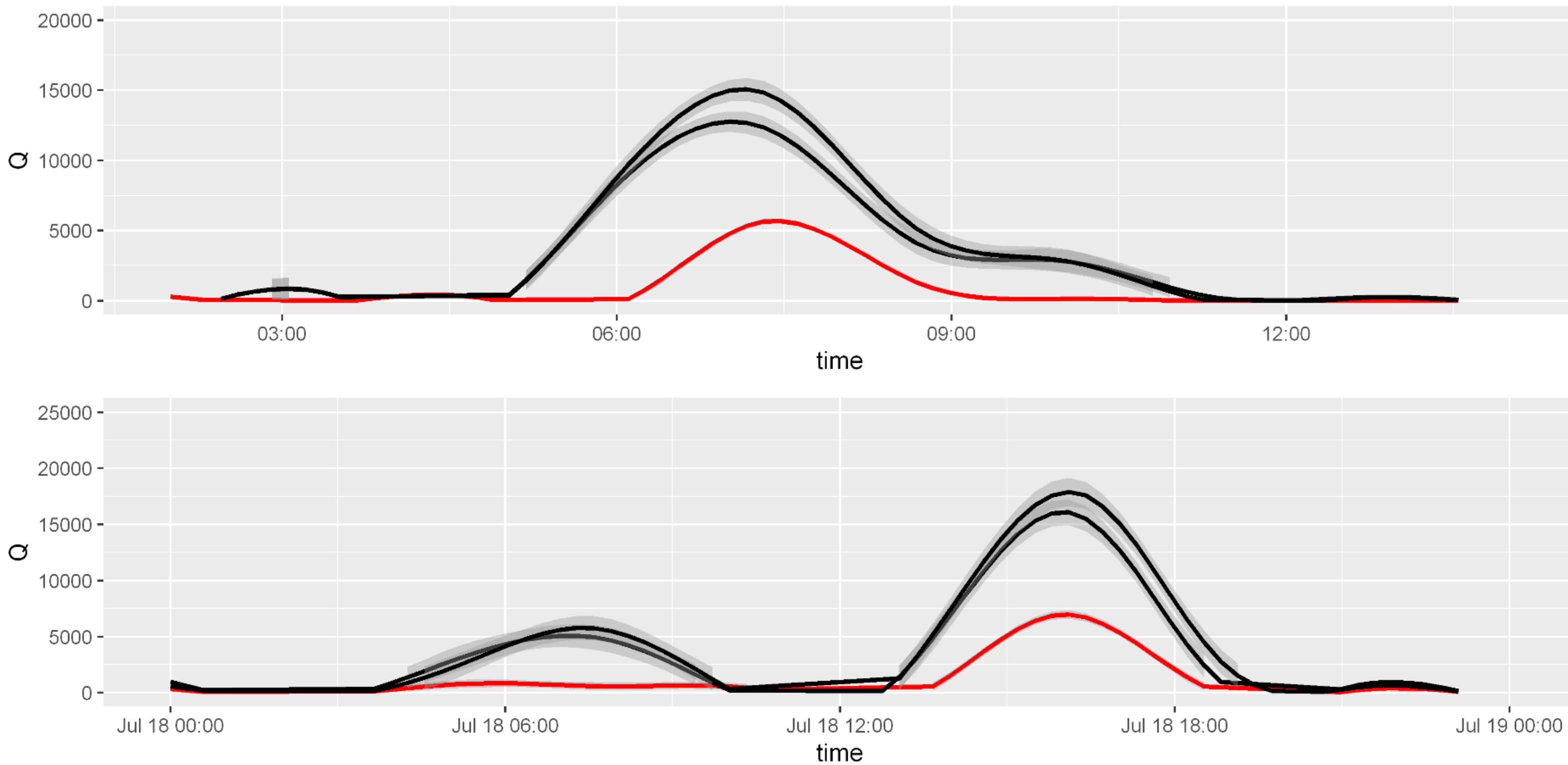

Figure 3.4 Hydrographs of runoff observations

Example of runoff hydrographs illustrating the disparity between velocity meter measurements. Black lines indicate runoff measured using Starflow velocity meter. Red line indicates runoff measured using QSD velocity meter. Here cumulative runoff measured using QSD was < 50% of volume measured using Starflow velocity meters.Q, discharge volume (L).

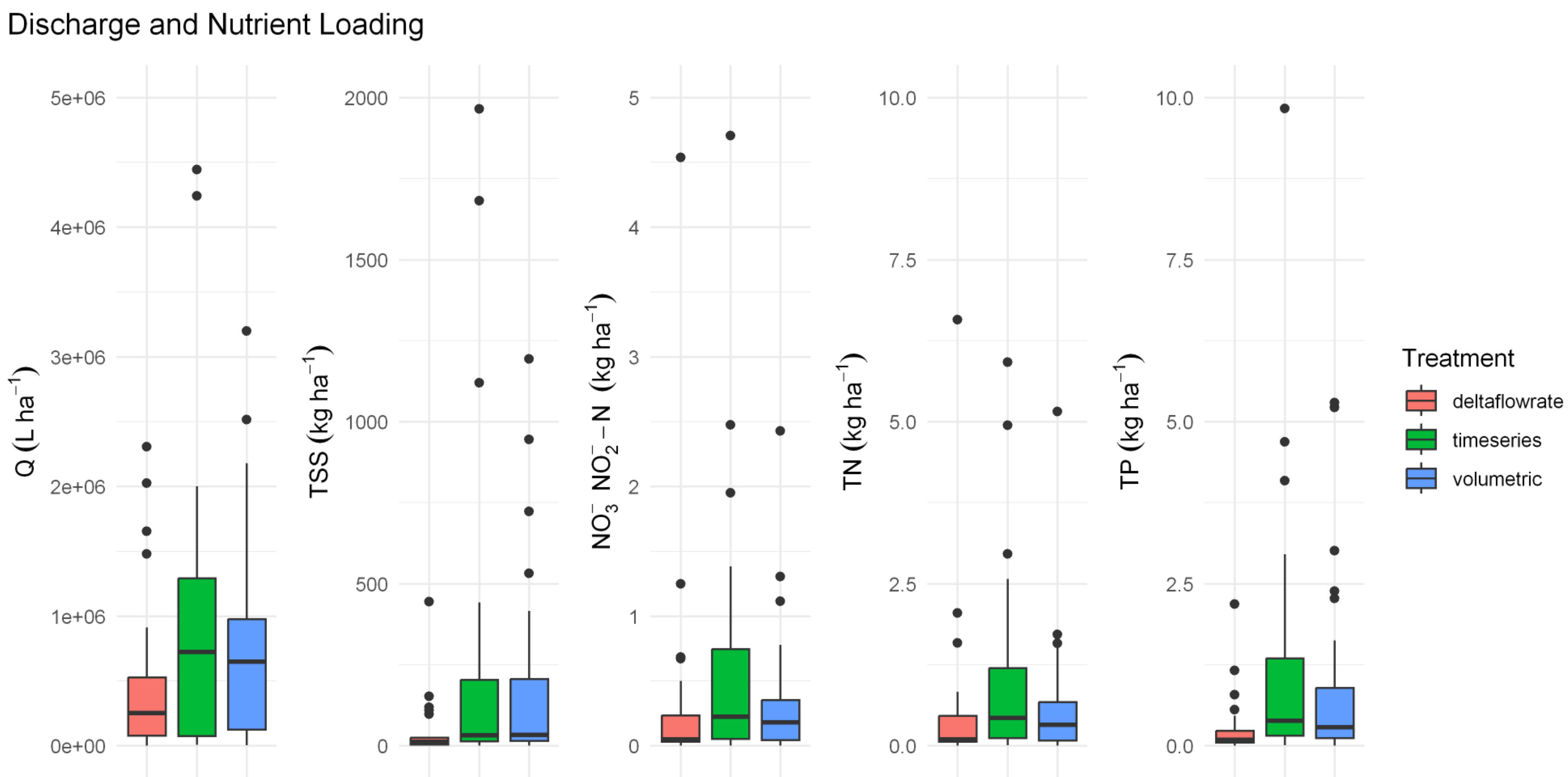

Figure 3.5 Discharge and loading estimates considered by sampling protocol

Distribution of discharge observations and nutrient loading estimates in events which produced samples from at least 2 of the 3 sampling systems. Normalized runoff volume (Q) is measured in liters per hectare (L ha^{-1}) and nutrient loading mass is measured in kilograms per hectare (kg ha^{-1}). Q, discharge; TSS, total suspended solids; NO_3^--NO_2^-- N, nitrate-nitrite nitrogen; TN, total nitrogen; TP, total phosphorus.

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