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IMPACT OF AGRICULTURAL LAND USE ON STREAM NITRATE, PHOSPHORUS, AND SEDIMENT CONCENTRATIONS AT THE WATERSHED AND FIELD SCALE

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IMPACT OF AGRICULTURAL LAND USE ON STREAM NITRATE, PHOSPHORUS, AND SEDIMENT CONCENTRATIONS AT THE WATERSHED AND FIELD SCALE

by

Brittany A. Kirsch

A THESIS

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Major: Agronomy

Under the Supervision of Professors Andrea D. Basche and Jessica R. Corman

Lincoln, Nebraska

May, 2020

IMPACT OF AGRICULTURAL LAND USE ON STREAM NITRATE, PHOSPHORUS, AND SEDIMENT CONCENTRATIONS AT THE WATERSHED AND FIELD SCALE

Brittany A. Kirsch, M.S.

University of Nebraska, 2020

Advisors: Andrea D. Basche, Jessica R. Corman

Water quality is directly impacted by the landscape through which it travels. As such, land use, including summer annual and winter annual/perennial agriculture, has dramatic influence on the water quality of downstream aquatic and terrestrial ecosystems. I examined the impact of agricultural land use on water quality through two projects, one at a watershed scale and one at a field scale. In my first project, I investigated the impact of agricultural land use and climate on water quality in 13 HUC10 watersheds across Nebraska using public data from US Geological Survey (USGS), US Department of Agriculture National Agricultural Statistics Service (USDA-NASS), and National Oceanic and Atmospheric Administration (NOAA). I focused on spring concentrations of nitrate, phosphorus, and suspended sediment in streams from 1980-2017. Results showed that each of the pollutants is impacted differently by agricultural land use and climate. Watersheds with higher percentages of summer annual (corn and soybean) acres generally had higher and more variable concentrations of pollutants. Additionally, watersheds with lower percentages of summer annual acres and higher percentages of grassland/pasture were found to have consistently lower pollutant concentrations across

flood and drought conditions. In the second project, my main objective was to create a field scale sampling protocol using rainfall simulators to investigate the impact of riparian area runoff on stream chemistry. Using a conservative tracer in the "rain" water, I was able to confirm the effectiveness of the proposed rainfall simulator protocol as a method for investigating riparian runoff impact on stream chemistry and pilot the protocol in the riparian areas of summer annual and grassland fields. Results of water quality analysis found that stream chemistry constituents (nitrogen, phosphorus, and sediment) increased during the rainfall simulation, indicating that the runoff generated carried additional nutrients and sediment into the stream. Overall, these results from both the field and watershed scale suggest that variability in water quality under summer annual is higher than in perennially-based land uses.

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CHAPTER 1: INTRODUCTION

Description of Nebraska

The state of Nebraska is found in the Great Plains region of the United States. Nebraska is unique as it encompasses a variety of agricultural regions and cropping systems. Corn-soybean rotations are now ubiquitous across much of the state, but most predominantly in the Eastern regions (USDA NASS, 2020). Winter wheat acreage has declined over the last several decades and is most widely grown in the southern and western regions of the state (USDA NASS, 2020). In North Central Nebraska, the "Sand hills" ecoregion is dominated by perennial grasses utilized for livestock grazing.

The variety of agricultural practices within the state is largely driven by the precipitation gradient found across Nebraska. This gradient is characterized by more humid Eastern regions to semi-arid Western regions (Hiller et al., 2009), with annual precipitation ranges from approximately 860-mm in the East to approximately 430-mm in the West (Frankson et al., 2017). As corn-soybean rotations require more rainfall, these crops are better suited for the Eastern regions, while wheat requires less rainfall and is better suited for the Western regions of the state. Recently, however, agricultural land use in the state has seen a shift to corn and soybean acres and an increase in irrigation, in part due to an increase in the demand for biofuel production (Hiller et al., 2009).

Water quality and land use

Poor water quality has a substantial cost to society through health, environmental, and economic damages. Individual health impacts include blue baby syndrome and an increased risk of colon cancer (Sobota et al., 2015), while one of the most well-known

environmental health impacts of water pollution related to U.S. agriculture is the hypoxic zone in the Gulf of Mexico. This is an area of little to no oxygen which leads to habitat change and detrimental health effects to aquatic organisms (Rabalais et al., 2010). High nutrient inputs from water sources (e.g. rivers entering the Gulf of Mexico) can also cause algal blooms (Allan and Castillo, 2007) which result in economic losses in the form of lost revenues to beachfront businesses (Morgan et al., 2009) and fisheries (Park et al., 2013). Additionally, it can be expensive for both larger and smaller municipalities in agricultural regions to remove water quality impairments via water treatment plants (Vedachalam et al., 2019). For example, Hastings, Nebraska (approximate population of 25,000 (U.S. Census Bureau, 2019) spent nearly \$46 million dollars to create the "Aquifer Storage and Restoration Project" in which the community will use water from the top of the aquifer, which is high in nitrates, for irrigation purposes, and use the water from lower in the aquifer, which is lower in nitrates, for drinking water (City of Hastings, 2020). This project was nearly \$29 million cheaper than building a new drinking water treatment facility (City of Hastings, 2020). With this vast potential for damages to society, it is imperative to understand how agriculture contributes to water pollution in order to reduce current negative impacts.

Scale in land use

Ecological scale is defined as "the spatial extent and temporal frequency, of a specific set of processes or structure" (Angeler and Allen, 2016). A change in study or experiment scale can change the bounds of the study and as such may include or exclude certain processes. The scale at which a study or experiment is done influences the interpretation of the results (Holling et al., 2002), making the choice of scale incredibly

important in order to properly interpret the results. Studies conducted at multiple scales may provide an opportunity to explore how the same processes behave at different scales. For example, Schoener and Stone (2019) investigated the correlation of runoff results from a plot scale and a catchment scale. The authors found that it was difficult to scale runoff predictions from the plot scale to the catchment scale as the runoff trends from the two scales were best fit by different prediction models (Schoener and Stone, 2019). However, results from both scales showed similar results regarding the importance of initial soil moisture in runoff (Schoener and Stone, 2019). Studies such as this highlight the need to choose scale carefully when describing a certain process.

Description of chapters

In my thesis, I seek to answer the question of how land use impacts water quality in Nebraska. Specifically, I focus on agricultural land use, including crops such as corn and soybean, the predominant annual crops grown in the state, as well as perennial grasslands. I address this question using two studies at different scales, including a watershed scale observational study of land use-precipitation-water quality interactions and a field scale experiment in which a new protocol is made to study riparian-water quality interactions.

In Chapter 2, "Nutrient and sediment loss across Nebraska's land use and climate gradient since 1980", I use public data for agricultural land use, drought or flood condition information , and water quality data from thirteen HUC10 watersheds to determine a relationship between the three factors. The watersheds used in the study expand across the state and cover a variety of agricultural land uses and climate gradients, allowing for a broad study comparison. Previous work has noted increases in

nutrient concentrations in the water in areas with more corn and soybean acres (e.g. Raymond et al., 2008; Schilling et al., 2009), however, few of these studies have been done in the Western Corn Belt or have included regions with high percentages of grassland acres. I use linear mixed model analysis to determine the relationship between land use, drought index, and water quality within these watersheds.

Within chapter 3, "Making it rain: using rainfall simulators to investigate land use effect on runoff composition in a stream", I propose a new protocol to study the impact of runoff on stream chemistry under differing land uses. The protocol uses rainfall simulators to create a runoff producing rainfall event in the riparian area of two small streams in Nebraska. The runoff is allowed to enter the stream, and changes in stream chemistry are monitored through stream water sampling. The success of the protocol is determined by the monitored changes in stream concentrations of a conservative tracer which was placed in the "rain" water before the experiment.

In the final chapter of the thesis, I summarize the outcomes of the study and the relationship of each outcome to the overall research question. I briefly discuss the relationship of the studies to reduction in water pollution.

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CHAPTER 2: NUTRIENT AND SEDIMENT LOSS ACROSS NEBRASKA'S LAND USE AND CLIMATE GRADIENT SINCE 1980

Abstract

The Upper Mississippi River Basin, which encompasses much of the eastern Corn Belt in the US, has been extensively studied to understand how agricultural land use impacts water quality. However, less is known about the relationship of agricultural land use and its impact on nutrient pollution in the Western Corn Belt. The state of Nebraska is located in the Western Corn Belt and is at the nexus of the more arid Great Plains cattle and wheat producing regions, providing a gradient of agricultural land uses and climate across the state. To determine the impact of land use as well as drought and flood conditions on water quality, analysis was performed on land use, drought and flood conditions, and water quality data from 13 HUC10 watersheds throughout Nebraska using public data from US Geological Survey (USGS), US Department of Agriculture National Agricultural Statistics Service (USDA-NASS), and National Oceanic and Atmospheric Administration (NOAA). The focus was spring concentrations of nitrate, phosphorus, and sediment from 1980-2017. The selected watersheds encompassed a range of agricultural land uses and climate gradients across the state, including watersheds with >60% corn and soybean acres as well as watersheds with >80% grassland acres. Watersheds in the study also spanned from more humid to more semiarid climates within the state. Pollutant variability and concentrations generally increased as the percentage summer annual (corn and soybean) acres in the watersheds increased above 50%. Watersheds with lower percentages of summer annual (<20%) showed low pollutant concentrations and low variability, even in the presence of increasing flooding

conditions. Results confirm that each of the studied pollutants moves through the landscape in different mechanisms: nitrate is impacted by both climate and land use and the interaction between the two, total phosphorus and suspended sediment are impacted by both climate and land use, and dissolved phosphorus is impacted by climate. The results also suggest shifting from summer-annual crop based agriculture to perennialbased agriculture can improve water quality and create watersheds that are more resistant to disturbances such as drought and flooding conditions.

Introduction

Water pollution creates substantial cost and risk to society which are expected to increase with a changing climate (Lall et al., 2018). Several environmental factors can influence water quality such as vegetation and land use, weather, soil parent material, and terrain/slope, to name a few, as these factors impact how nutrients move through landscapes. Nitrogen in the form of nitrate $(NO₃)$ is highly mobile and moves readily in water (National Research Council, 1993) allowing it to move quickly through the soil profile and into streams, rivers, and potentially ground water (Exner et al., 1991). In nonagricultural areas, the $NO₃$ must filter through the upper portion of the soil profile before eventually joining groundwater and/or flowing into a stream or river (Exner et al., 1991). In some agricultural landscapes, subsurface drainage is heavily used. This subsurface drainage allows the water, and as such $NO₃$, a way to more quickly exit the field and enter the waterways (Strock et al., 2010). Many streams in the United States have $NO₃$ concentrations exceeding the 10ppm drinking limit set by the US Environmental Protection Agency (EPA).

Phosphorus (P) is transported via several mechanisms, including as a dissolved part of leachate, as a dissolved part of runoff, and with eroded sediment (Potter et al., 2006). The type of landscape P originates from will determine how it is lost. For example, P is more likely to be lost via eroded sediment in an agricultural setting versus being lost in its dissolved form in water in a non-agricultural setting (Potter et al., 2006). Increasing water flow across the landscape leads to an increase in phosphorous loss (Schilling et al., 2009). Sediment, known to be a very large contributor to water pollution (Johnson et al., 2009) and containing nutrients and other pollutants, is moved via water flow. At higher flow velocities, water has the potential to move sediment faster and further than at low velocities (Potter et al., 2006). The type of land use and land cover can have great impacts on the amount of sediment removed from a particular location (Vahabi and Nikkami, 2008). Areas with less dense or non-permanent vegetative land cover are more susceptible to sediment erosion than those with a greater density or more permanent vegetative land cover. Suspended sediment (SS) can create issues in water treatment plants and can prevent water from being properly treated.

As a result, landscape characteristics have an important role in regulating water filtration and quality; for example, in agricultural regions, cropping patterns play a major role in this regulation. Hatfield et al (2009) found that the loss of small grain and perennial crops, over the latter part of the $20th$ century, was the agricultural management most directly related to an increase in NO_3 in a Central Iowa watershed. Mittelstet et al. (2019) found that percent cultivated crops and precipitation during the growing season were among the top variables to predict NO₃ concentrations across Nebraska while Jones et al. (2018) found that $NO₃$ concentrations increased in Iowa watersheds with more

intensely row-cropped areas. The increasing risks associated with climate change and increased rainfall variability make it ever more imperative to understand interactions of agricultural land use and water quality.

Agricultural land use can be influenced by major socioeconomic, regulatory, and environmental events, many of which have happened in the last century. For example, combination of low commodity prices and high equipment costs led to production on marginal land and shifts away from soil conservation practices in the 1920's (National Drought Mitigation Center, 2020). When combined with severe droughts in the early 1930's, these conditions led to what is known today as the Dust Bowl (National Drought Mitigation Center, 2020). The post-World War II era saw an increase in the demand for U.S. commodities and increased commodity prices as well as the introduction of pesticides and manufactured fertilizer to the landscape (Hiller et al., 2009). The 1980's saw a farm crisis, which resulted in decreased numbers of farms and increased farm size, while the early 2000's saw the expansion of the ethanol market increased demand for corn and soybeans (Hiller et al., 2009). Lower farm profitability since the early 2010's (USDA Economic Research Service, 2020) and recent trade conflicts (e.g. Li et al., 2018), coupled with the COVID-19 pandemic has led to increasing uncertainty in the global markets. The results of the COVID-19 pandemic may drastically change the outlook of international trade, including agricultural trade (Kerr, 2020).

Humans tend to manage systems for disruptions in an attempt to reduce the uncertainty within a system. Low levels of uncertainty allow for ease of management as the system will remain at an average state with little variance in response during disruptions. Systems with low levels of uncertainty during disruptions are said to have

high levels of resilience, defined as "the broad ability of a system to cope with disturbances without changing state" (Angeler and Allen, 2016). Systems can have a variety of uncertain aspects. An example of uncertainty of water quality in a watershed is the response of $NO₃$ to rainfall events. Studies have found both increases (Rozemeijer and Broers, 2007; Tiemeyer et al., 2008) and decreases or mixed trends in NO_3 concentrations (Borah et al., 2003; Poor and McDonnell, 2007) during natural rainfall events. Studies which found decreases or mixed trends in $NO₃$ concentrations found NO3trends depended on differences in rainfall intensity (Borah et al., 2003), land use in a catchment, and wet or dry periods within that catchment (Poor and McDonnell, 2007).

The state of Nebraska, located in the Northern Great Plains, has a landscape dominated by agriculture and hosts a diverse range of agricultural land uses as well as climatology. Across the state, climate regions span from the more humid regions in the East to the semi-arid regions in the West (Hiller et al., 2009), with a gradient of approximately 860-mm per year in the east to approximately 430-mm per year in the west (Frankson et al., 2017). Approximately 91% of the state is cropland or grassland (predominately for livestock grazing) (Nebraska Department of Agriculture, 2019), where cropland has been dominated by row crops such as corn and soybeans (Hiller et al., 2009) which make up approximately 70% of harvested cropland acres (USDA-NASS, 2020). Previously, the landscape in Nebraska previously included more diverse winter annual and perennial crops such as wheat, sorghum, oats, and alfalfa (Hiller et al., 2009). Crop diversity in Nebraska increased from the mid 1890's until reaching its peak in 1950- 1965, after which point it declined to its present state (Hiller et al., 2009). Corn-soybean rotations are now prominent across the state, and even more so the Eastern regions

(USDA NASS, 2020). However, Nebraska encompasses a variety of agricultural practices: from corn-soybean rotations in the eastern regions, to winter wheat in the southern and western regions, to the north central "Sandhills" region where perennial grasses used for livestock grazing are abundant. Human influence on land use across the state ranges from the Tallgrass Prairie region in Eastern Nebraska which is nearly completely converted away from the natural landscape, to the Sandhills region which contains some of the most intact natural communities in the state (Schneider et al., 2005). This combination of land use and precipitation gradient is unique to Nebraska and provides an excellent study region.

Previous studies of agricultural regions have investigated relationships similar to those investigated in this study. For example, Broussard and Turner (2009) investigated the impact of land use on stream $NO₃$ concentrations at a national level using variety of sized watersheds in their study. Schilling and Libra (2000) determined the relationship between row crop land use and stream $NO₃$ concentrations in a total of 25 watersheds ranging from 47 to 2774 km^2 . Loecke et al. (2017) investigated the impact of weather patterns on stream $NO₃$ concentrations in the central Midwest, while Jones et al. (2018) described the impact of precipitation on stream NO₃ concentrations in eight watersheds of different sizes Iowa. In Nebraska, Mittelstet et al. (2019) explored the impact of land use and soil characteristics on stream NO₃ concentrations in multiple sizes of watersheds. Finally, Hansen et al. (2019) explored the relationship between weather, agricultural land use, and stream concentrations of NO₃ and atrazine across Nebraska.

Many of these studies have focused on two factors at a time, or in the case of Hansen et al. (2019) have only investigated $NO₃$ and atrazine as water quality indicators.

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These studies have worked on a variety of scales, from watershed to state level, often using different sized watersheds within a single study. This study uses HUC10 watersheds (18,591 to 90,687 ha or 45,940 to 224,092 ac) to provide consist comparisons across watersheds. This study seeks to enhance a watershed's resilience to water quality pollution in response to extreme events by determining the impact of agricultural land use and drought conditions on three important water quality indicators $(NO₃, P, and SS)$ within Nebraska from 1980 to 2017. I expect increased pollutant concentration variability across drought and flood conditions in watersheds with a higher percent of corn and soybean acres.

Data and Methods

Water quality indicators

All data sets used in this study originated from public sources. This study focused on NO3, TDP, TP, and SS data from surface waters in the state of Nebraska. These water quality contaminants were chosen for this study as they are closely related to agricultural practices within the state. Namely, nitrogen and P are plant macronutrients which are applied to the soil as fertilizer and which also occur naturally in the soil. Fertilizer is applied in both the spring (pre-planting) and the fall (post-harvest) and can be lost to surface water (Gowda et al., 2008). Sediments are often lost to surface water due to agricultural management practices such as leaving bare soil at key points during the year (National Research Council, 1993). The water quality data used in this study were collected at the United States Geological Survey (USGS) National Water Information System (NWIS) monitoring locations and was retrieved using the Water Quality Portal (WQP) (NWIS, 2019).

This study focuses on water quality monitoring sites within individual HUC10 watersheds in the state of Nebraska, where near- continuous water quality information was available. Monitoring stations were selected if they had at least twenty years of data for one or more of the water quality indicators between 1980 and 2017 for the spring season (April and May). Watershed scale was determined by the location of the monitoring location in relation to the bottom of the watershed. The year 1980 was chosen because it provides a 30+ year period over which to make comparisons and is considered to represent enough data for determining climate normal or average conditions (NOAA-NCEI, 2020). Season bounds were chosen as this is the period when some spring fertilizer is applied (Shapiro et al., 2003), but summer annual crops are not yet taking up the fertilizer, much of the soil is bare and vulnerable to erosion in a summer annual system, and insurance planting windows for corn and soybean occur (USDA Risk Management Agency, 2020). Irrigation is not generally applied during this period due to low crop requirements (Kranz et al., 2008). In total, thirteen water quality monitoring sites met my criteria and were included for analysis (Figure 1).

After applying these criteria, thirteen water quality monitoring sites were chosen. As not all watersheds had enough data to fit my criteria for each water quality pollutant, subsets of watersheds were used to study each pollutant based on the amount of data for each pollutant. Of the 13 chosen watersheds, six were used for $NO₃$ analysis, eight were used total dissolved P analysis, eight were used for total P analysis, and six were used for total SS analysis.

Land use and cropping history

Land use data for 1980-2017 was collected from United States Department of Agriculture-National Agricultural Statistics Service (USDA-NASS) annual agricultural survey data (USDA-NASS, 2020), which is available at a county level resolution. Total acres harvested of the crop in question (i.e. corn, soybeans, wheat, oats, and hay) were retrieved for each of the counties contained within the 13 watersheds. As analysis took place at a HUC10 scale, interpolation was necessary to analyze the county level data at the watershed level. USDA-NASS county level land use data from 1980 to 2017 was divided into watershed level data using a method adapted from Broussard and Turner (2009). The adapted equation is as follows (Broussard and Turner, 2009):

$$
F_{LU} = \frac{\sum_{i=1}^{n} L_i * C_i}{W}
$$

Where F_{LU} = fraction of watershed's total area in a particular land use type

 $n =$ number of counties within a watershed

 $L =$ reported total area (acres) of that land use practice in a specific county

 $C =$ fraction of the county area that lies within the watershed

 $W =$ total watershed area (acres)

As with Broussard and Turner, it was assumed that land use within a county was equally distributed throughout the county due to high prevalence of the land use types in the watershed.

The area of a county contained within the watershed, in acres, as well as the area of the watershed, in acres, was calculated using ArcGIS (ESRI, 2019). Four of the watersheds extended outside the state of Nebraska, into either Iowa or South Dakota.

Land use analysis was done on the entire watershed, including areas extending outside the state. I also calculated the percent change in crop acres as follows:

> % change in crop acres $=$ 2017 crop acres -1980 crop acres total watershed acres

In addition to cropping data, I evaluated percent irrigation acres in a watershed and dominant soil hydrologic groups in the watersheds to investigate patterns in the pollutants of interest. Irrigation data was collected at a county level from NASS 2017 Census of Agriculture data (USDA NASS, 2018) and was converted to watershed level using the adapted Broussard and Turner (2009) equation. Soil hydrologic group data was retrieved from the Geospatial Data Gateway portal (Soil Survey Staff, 2020)

Climatology

Drought indices were obtained from the National Oceanic and Atmospheric Administration's National Centers for Environmental Information (NOAA-NCEI). The Palmer Modified Drought Severity Index (PMDI) was chosen because it is a reasonable, real-time indicator of drought or flood conditions while taking factors such as evapotranspiration and monthly precipitation into account (Heddinghaus and Sabol, 1991). PMDI was retrieved on a monthly basis for 1980 to 2017 for each of the 8 climate divisions within Nebraska, as determined by NOAA (NOAA-NCEI, 2018). Watersheds were placed into each of these climate divisions based on the location of the monitoring location. A monthly PMDI value was then assigned to each water quality measurement. A PMDI value less than -3.00 or greater than +3.00 indicates severe drought and severe flood, respectively (Heddinghaus and Sabol, 1991). PMDI also acted as a standardizing factor across all watersheds as its monthly values are calculated relative to the long-term

average for the area, allowing for comparisons across watersheds in different precipitations regimes.

Statistical analysis

Mixed effect models were fit to each of the water quality metrics using the R (version 3.6.2) (R Core Team, 2019) and the package lme4 (Bates et al., 2015). The global model included a fixed term for the three-way interaction between percent summer annual acres (defined as the percent of corn and soybean acres in a watershed), percent winter annual/perennial acres (defined as the percent of oat, wheat, and hay acres in the watershed) and PMDI, the two-way interaction for each combination, a fixed term for each term percent summer annual acres, percent winter annual/perennial acres, and PMDI, as well as the fixed term centered year, defined as year measurements taken centered on the mean year of the study. Random effects included a random intercept by watershed and variation by centered year in each watershed.

As PMDI was calculated on a monthly basis, average monthly concentrations were calculated for each nutrient for each monitoring location-year. Nitrate, total P, and total SS were log_{10} transformed to achieve normal distribution, while untransformed data for dissolved P was normally distributed. Backwards stepwise regression was used on the global model to determine the best fit model for each of the pollutants $-\log NO_3$, dissolved P, log total P, and log SS. To ensure the best fit possible, Cook's distance was used on the initial best fit model to determine overly influential data points. A Cook's distance of 0.2 was used to determine influential points, a value which falls between the two recommended guidance of three times the mean of the data and four divided by the number of observations. Points with a Cook's distance larger than 0.2 were removed

from the data set with no more than 9 data points $(3%)$ removed from any dataset. Backwards selection was again performed to determine the best fit model for the reduced dataset. The result of this backwards selection was used as the final best fit model. Coefficients from the best fit models were examined to determine the effect each factor had on pollutant concentrations.

To determine differences between pollutant concentrations in the watersheds, the random effect of each best fit model was explored using the best linear unbiased predictors (BLUPs) for each pollutant (Stroup et al., 2018). In my models, there are two types of BLUPs: one for the estimates of the intercept for each watershed in all best fit models and one for the variation for centered year in each watershed in each best fit model. Examination was done by extracting the random effect values for the intercept for each watershed from each best fit model using the ranef() function in lme4 (Bates et al., 2015). The values were then plotted with the standard deviations for each intercept value to show the differences between the watersheds.

Results

Agricultural land use across watersheds

Overall, I found that agricultural land use varied by watershed, and that this directly impacted on water quality within the watersheds. Percent summer annual acres generally remained consistent in each watershed since the mid to late 1990's. Many watersheds showed almost no overall change in percent summer annual acres over the duration of the study (<5% change), however of these watersheds, some showed variability over the duration of the study, with a few years having uncharacteristically low percent summer

annual acres, such as Pigeon Creek-Missouri River and Indian Creek-Missouri River. Of the watersheds that saw larger changes in percent summer annual acres $(55%)$ increases were <14%, with the exception of Lower Salt Creek, which saw a 34% increase during the study period (Table 1). Percent winter annual/perennial acres had slight downward trends in most watersheds throughout the study period, with some watersheds reducing to 0% for both crops, while grassland/pasture acres remained nearly unchanged (Table 1). Although some watersheds increased in percent summer annual acres and many decreased in winter annual/perennial acreage in this time period, the generally consistent trend of summer annual acreage in the various watersheds throughout the study period provides a managed gradient across Nebraska, where there are typically low percentages in the west and high percentages in the east following the general climate gradient of the state.

Cropping pattern predictors of nitrate, phosphorus, and sediment movement

I developed best fit models for each pollutant to determine the impact of summer annual acreage, winter annual/perennial acreage, PMDI, year, and watershed on water quality (Table 2-2). Percent summer annual acres in a watershed was found to be a significant factor in the best fit model of all pollutants, except dissolved P. The regression coefficient for percent summer annual acres was positive in the best fit model for log total SS, indicating that pollutant concentrations increase as summer annual acreage increases in a watershed. The total SS model also showed percent summer annual acres as significant in all two- and three-way interactions (Table 2-2), indicating all factors in the model have a greater combined impact on total SS concentrations. The regression coefficient for percent summer annual acres in the log total P model was negative

indicating a decrease in log total P concentration as summer annual acres decrease, while the percent summer annual acres terms was not significant in the dissolved P model – indicating that percent summer annual acres in a watershed does not significantly impact dissolved P concentrations (Table 2). While the regression coefficient for percent summer annual acres was positive in the $log NO₃$ model, it was also in a positive interaction with PMDI in the log NO³ model. This indicates that percent summer annual acres and PMDI dually impact NO_3 concentrations, and the effect of one of these factors on NO_3 concentrations is directly dependent on the level of the other factor.

Percent winter annual/perennial acres was shown to be significant only in the total P and total SS models, but not in the $NO₃$ or dissolved P models. The total P model showed a positive coefficient for percent winter annual/perennial acres, indicating that total P concentrations increased as winter annual/perennial acres increased in a watershed. Total SS showed a negative coefficient for percent winter annual/perennial acres, although this term was again included in all possible interactions in the total SS model.

The results of the best fit models are generally consistent with the visual results of pollutant concentrations versus percent summer annual acres and revealed important trends about variability in pollutant concentrations across watersheds (Figure 2-2). Although a complete gradient of percent summer annual acres or winter annual/perennial acres was not available for my analysis, the concentration of $NO₃$ and total SS tended to increase as the percent summer annual acres increased. This relationship was negative or not significant for total P and dissolved P, respectively. I found that variability and overall concentration of $NO₃$ and total P tended to increase as the percent summer annual acres in the watershed increases, especially as watersheds reach >50% average percent

summer annual acres (Figure 2a and 2c). The Lower Salt Creek watershed, which had the largest percent increase in summer annual acres over my study period (34%) and the largest percent decrease in winter annual/perennial acres (20%), had consistently variable total P concentrations, even as the percent summer annual acres increased in the watershed (Figure 2c and 2g). I also found variable $NO₃$ concentrations within a few watersheds with similar percent summer annual acres (-55%) , specifically, the Buffalo Creek-Platte River, Indian Creek-Missouri River, and Rawhide Creek-Elkhorn River watersheds (Figure 2a).

Additional variability was seen in dissolved P data, where concentrations seemed to have the highest variability in two watersheds (Mira Creek and Messenger-Creek and North Loup River) with approximately 20% summer annual acres. Decreasing variability and decreasing average concentration were observed as percent summer annual acres increased (Figure 2b). Only watersheds with what I considered to be high percentages (>50%) of average summer annual crop acres fit my criteria and therefore could be investigated for total SS. Total SS concentrations had large ranges within each watershed, with the exception of Pigeon Creek-Missouri River which had a relatively smaller range of concentrations, even though this watershed had a wider range of percent summer annual acres throughout the duration of the study (Figure 2d).

Impact of cropping patterns and climate on water quality

Palmer Modified Drought Index was a significant factor in the best fit model for all pollutants, except total P (Table 2-2). This suggests the drought or flood patterns play a large role in pollutant concentrations, especially dissolved P. Watersheds tended to show differing trends when separated into categories by average percent summer annual acres,

with watersheds with a high percent summer annual acres (average >50%, seven watersheds) having higher variability than watersheds with lower percent summer annual acres (average <20%, three watersheds), with the exception of dissolved P, where watersheds with medium summer annual crop acres (average 20-50%, three watersheds) were most variable (Figure 2-3). Watersheds which fell into the low category of summer annual crop acres showed consistent pollutant concentrations regardless of PMDI value, specifically the Dismal River, Long Pine Creek, and Big Beaver Creek-Niobrara River watersheds.

From the best fit models, I found that PMDI was not significant in the log total P model. The models for dissolved P and log total SS had a positive PMDI coefficient, indicating that as conditions move from drought to flood, pollutant concentrations increase. Palmer Modified Drought Index was found to be the only significant factor in the dissolved P model. The PMDI term in the log total SS model was again included in all possible interactions in the model. While PMDI was shown to be significant in the log NO3 model, its presence in a positive interaction with percent summer annual acres showed the two factors to dually impact $NO₃$ concentrations. As such, the level of one factor influences the impact of the second factor on NO₃ concentrations.

Differences in pollutant concentrations between watersheds

To examine differences between watersheds, the random effects of each of the best fit models were explored. The results show the random intercept for watershed was significant in each pollutant, indicating each watershed has a different intercept within each model (Table 2-2). The random effect for the centered year was only significant in the total SS model and was not significant in any other best fit model. The significance of centered year in the total SS model was likely due to some watersheds in that analysis, namely Pigeon Creek-Missouri, having a large range of total SS concentrations at varying percent summer annual acres over the years, a trend which was not seen in other watersheds.

The BLUPs show the intercepts for the watersheds are generally different from each other in each of the best fit models for each pollutant, while variation with respect to centered year is the same for all watersheds in all best fit models except the model for log total SS, where they vary with respect to watershed (Figure 4). The BLUPs in the log NO³ and log total P models generally showed increasing intercept values as the percent summer annual acres in the watershed increased (Figure 4). In the $log NO₃$ model, watershed intercepts became positive near a 55% average summer annual acres, with the exception of Lower Salt Creek watershed which had a positive intercept value and ~43% percent summer annual acres. Log total P showed positive intercept values at >40% average summer annual acres, with the exception of Indian Creek-Missouri River watershed, which had a slightly negative intercept. The best fit models for dissolved P and log total SS did not show consistent trends with increasing percent summer annual acres in the watershed.

Discussion

In my analysis, I found that watersheds with lower percent summer annual acres have lower, less variable pollutant concentrations in their streams across a variety of drought or flood conditions. Of the 13 watersheds analyzed, three watersheds fell into the low percent summer annual category (<20% summer annual): Dismal River, Long Pine Creek, and Big Beaver Creek-Niobrara River. These watersheds showed high levels of

resilience, indicating the watershed nutrient response is highly predictable across drought and flood conditions. This predictability allows for better control of the system, such as in policy making and land management.

While I generally saw increasing variability with increasing percent summer annual acres, watersheds in the dissolved P model with average percent summer annual acres from 20-50%, Mira Creek and Messenger Creek-North Loup River, showed the greatest variability and highest concentrations of dissolved P. Upon inspection of the soil hydrologic groups for these watersheds, this difference in variability pattern is likely because the Mira Creek and Messenger Creek-North Loup River watersheds are the only watersheds in my study to be dominated by soils of moderate infiltration (Soil Survey Staff, 2020). Watersheds in the western portion of the study tended to have higher infiltration rates, and therefore lower runoff capacity (Soil Survey Staff, 2020). Watersheds in the eastern portion of the study tended to have slow infiltration rate, with small amounts of tile drainage in all watersheds (<10% of all watershed acres) (Supplemental table 2) (USDA NASS, 2017). Watersheds in the Eastern regions tended to have the most tile drainage (2-9%) while watersheds in the Western regions have <1% tile drained acres (USDA NASS, 2017). The moderate infiltration rate combined with a lack of tile drainage in the region, mean that the Mira Creek and Messenger Creek-North Loup River watersheds may produce more runoff and, as such, carry dissolved P with them. Because $NO₃$ data was not available for the Mira Creek and Messenger Creek-North Loup River watersheds, I cannot say if this impact of infiltration patterns on $NO₃$ concentrations holds true for these watersheds.

A primary source of $NO₃$ in the landscape is nitrogen fertilizer use (Good and Beatty, 2011). Fertilizer in Nebraska is applied mainly in the spring and fall, during which periods, summer annual crops such as corn and soybean are not actively growing to take up the NO₃ being applied (Shaver et al., 2013). Based on prior analysis of state level fertilizer data, I can assume with some level of confidence that nitrogen fertilizer use generally remained consistent during the time of my study (Ferguson, 2015), and was therefore not a likely reason for the increase in $NO₃$ concentrations seen in many of the watersheds.

An additional influence on $NO₃$ levels is irrigation. Irrigation is used throughout Nebraska and uses groundwater from aquifers as its source (Ferguson, 2015). This groundwater can be high in $NO₃$, which, when used for irrigation, can be added to the landscape, which can increase $NO₃$ concentrations (Ferguson, 2015). However, when irrigation is applied selectively, it can have a positive effect on increasing $NO₃$ use efficiency and prevent $NO₃$ loss (Ferguson, 2015). Percent irrigated acres in a watershed in the study ranged from <1% (Mira Creek and Dismal River) to 58% (Maple Creek) (Supplemental Table 1). Three watersheds had 49-58% irrigated harvested acres in the watershed: Rawhide Creek-Elkhorn River, Elm Creek-Platte River, and Maple Creek. All other watersheds had $\langle 20\%$ irrigated acres. While I did not have NO₃ data for the Elm Creek-Platte River watershed, the irrigation in the other two watersheds may have impacted the variability of nutrient concentrations in these watersheds. Watersheds high in percent summer annual acres and low in percent irrigated acres tended to show more variable NO₃ concentrations. Watersheds with similar percentages summer annual acres (~55%), specifically, the Buffalo Creek-Platte River (19% irrigated acres), Indian Creek-
Missouri River (11% irrigated acres), and Rawhide Creek-Elkhorn River (50% irrigated acres) watersheds, showed large variability of $NO₃$ concentrations (Figure 2a). This variability in watersheds with similar percent summer annual acres may be due to irrigation prevalence and higher average rainfall amounts.

Additional study results showed nutrients are impacted differently by percent summer annual acres, percent winter annual/perennial, and PMDI. These results follow the expected response, further reinforcing our understanding of the system. This finding is similar to similar studies. For example, Broussard and Turner (2009) found that watersheds with higher percentages of corn acres had higher concentrations of NO₃. Schilling et al. (2009) also found increasing corn acres in a watershed will increase the amount of $NO₃$, P, and SS lost from the watershed. They also found that reducing the amount of corn and increasing the amount of perennials in the watershed leads to a reduction of $NO₃$, P, and SS (Schilling et al., 2009). Raymond et al. (2008) found that as the percent of agricultural land use rises to approximately 60% and above, there is an exponential increase in discharge. This increase in discharge could account for the increase in $NO₃$, P, and SS in the water as water is one of the main methods of transportation for these contaminants.

Flood or drought conditions were found to play a key role in nutrient movement in my models. Related to my findings, Loecke et al. (2017) found that during years of drought, excess $NO₃$ is stored in the soil as a result of limited uptake from crops and plants. The authors found that when flood conditions immediately follow drought conditions (known as "weather whiplash"), this excess $NO₃$ enters surface waters (Loecke et al., 2017). They found a 118% increase from a 5 year average in cumulative

NO³ flux during the flood year as a result (Loecke et al., 2017). This is consistent with my findings of higher concentrations of $NO₃$ in surface water during wetter periods. Jones et al. (2018) found that increases in precipitation resulted in greater delivery of NO³ to the streams, which is again consistent with my findings. These findings are also consistent with findings in broader regions including research on the Hypoxic Zone in the Gulf of Mexico where it has been found that the size of the Hypoxic Zone during midsummer can be predicted using the $NO₃$ concentrations from two months prior (Loecke et al. (2017), Rabalais et al., 2010).

Finally, results of this study showed agricultural land use differs between watersheds. Across the Western Corn Belt, there has been a continual shift of agricultural landscapes from grassland to a landscape dominated by summer annual row crops (corn and soybean) (Wright and Wimberly, 2013). Summer annual crops have their peak crop water demand in July and August which is not aligned with peak rainfall patterns, which typically occur in the spring. Starting in the mid 1960's, Nebraska saw an increase in row crop acres due to an increase in corn and soybean acres and a decrease in wheat, oat, hay, sorghum, and alfalfa acres (Hiller et al., 2009). This change in land use is a shift away from ecologically designed agricultural landscapes, which "emphasize conservation of soil, water, energy, and biological resources" and "make more appropriate matches between cropping patterns and the productive potential and physical limitations of the farm landscape" (Gliessman, 2015). With the simplification of agricultural land use in Nebraska since the 1960's (Hiller et al., 2009; Hijmans et al., 2016) and an expected increase in variability of weather patterns, such as severe thunderstorms (Hayhoe et al., 2018), agricultural regions are becoming more vulnerable to flooding and water pollution (Schilling et al., 2009; Basche and Edelson, 2017). The results of my analysis suggests that a shift from more conventional summer annual agriculture centered on summer annual crops to more perennially-based systems, including more winter annuals or cover crops in addition to perennial crops, can result in improved water quality that is less impacted by disturbances, such as extreme weather events.

Conclusion

My area of study focused on the Western Corn Belt, which contains greater variability in land use relative to the Eastern Corn Belt. This variability allowed me to incorporate a more diverse range of watersheds and land uses in my analysis. The results of my study also showed that nutrients are impacted differently by percent summer annual acres, percent winter annual/perennial acres, and PMDI. This interaction is vital to understand in order to reduce the pollutants in my water systems. Additionally, my study found that watersheds with decreased percentages of summer annual acres tended to have lower, less variable stream pollutant concentrations across a variety of PMDI values. This result suggests a shift to more perennial agriculture may be needed to reduce water quality pollutants and increase the system's resilience to climate fluctuations, such as drought or flood. By moving to land use patterns which utilize available water and protect soil resources, I will help to improve water quality in Nebraska and beyond.

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Figures

Figure 2-1: Map of location of sites (red dots) and HUC10 watersheds overlaid on the 2017 Cropland Data Layer (USDA NASS cropland data layer, 2020).

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**Due to irregular data points for 2017 in these watersheds, data from 2016 were used.

Table 2-2: Estimate (SE) (fixed effect) or variance (SD) (random effect) for each effect in the best fit models, where PMDI is the Palmer Modified Drought Index and centered year is the year measurements taken centered on the mean year of the study. All terms listed are significant at the α =0.05 level.

Figure 2-2: Monthly pollutant values plotted against percent summer annual acres (a-d) and percent winter annual/perennial acres (e-h) in a watershed. Different watersheds are represented by different colors and symbols. As percent summer annual acres increase, log NO³ and log total P increased, while dissolved P and log TSS did not show an increase. Red line in the $NO₃$ graphs indicates EPA drinking limit of 10 ppm.

M w

 -2.5 0.0 2.5 5.0

 -2.5 0.0 2.5 5.0

PMDI

 -2.5 0.0 2.5 5.0

-
- Maple Creek
- XX Pigeon Creek-Missouri River
- Rawhide Creek-Elkhorn River

Figure 2-3: Monthly pollutant values plotted against PMDI. Different watersheds are represented by different colors and different symbols. Each pollutant is broken out by the average percent summer annual acres in the watershed, with the "Low" category having <20% average percent summer annual acres, "Medium" having 20-50% average percent summer annual acres, and "High" having $>50\%$ average percent summer annual acres. Moving from low to high average percent summer annual acres, variability within the watersheds increased in all pollutants except dissolved P, where the medium percent summer annual acres had the highest variability. There were no watersheds in the low and medium categories that fit my criteria in the total SS analysis. Red line in the $NO₃$ graph indicates EPA drinking limit of 10 ppm.

Nitrate as N

Figure 2-4: Best linear unbiased predictors (BLUPs) for the random effect for watershed from each nutrient's best fit model. The y-axis shows the watershed name with the average percent summer annual acres in that watershed over the study period. Because the random intercept for watershed was significant in all best fit models, the BLUPs show watersheds generally have different intercept values in the models. Nitrate and total P showed a general increase in intercept value with increases in percent summer annual acres in the watershed. Dissolved P and SS did not show intercept trends associated with percent summer annual acres in the watershed. Watersheds are generally different from each other.

Supplemental materials

equation from Broussard and Turner (2009) as discussed in the methods section.

CHAPTER 3: MAKING IT RAIN: USING RAINFALL SIMULATORS TO INVESTIGATE LAND USE IMPACT ON RUNOFF COMPOSITION IN A STREAM

Abstract

Rainfall simulators have been previously used to study the impact of land use on runoff by collecting runoff at the downslope side of the study plot in a trough. However, none of these studies have investigated the impact of simulated runoff on stream chemistry when the land surrounding the riparian area is under different uses. In this study, I assess the possibility of using rainfall simulators to explore the impact of riparian runoff on stream chemistry. The objective of this work was to create a sampling protocol for this novel type of study using a conservative tracer to track the "rain" water from the simulators through the riparian area of two small streams in Nebraska. The riparian area of the two sampling sites were surrounded by land under row crop and prairie land uses. I expected to see an increase in concentration of conservative tracer in the stream while the rainfall simulators were on, and a decrease in conservative tracer concentration after the simulators turned off. My results show the proposed protocol may be used to effectively study the impact of runoff on stream chemistry. Additional nutrient analysis also showed increases in stream chemistry constituents (nitrogen, phosphorus, and sediment) during the simulated rainfall event with nutrient input appearing more variable at the row crop site than the prairie site. These results show promise for future work in this area to determine how runoff from the riparian area impacts stream chemistry during rainfall events.

Introduction

While water flows downhill, the path it takes can be impeded by a number of natural and anthropogenic factors. As such, the flow path of water changes with landscape and these differences in flow paths can greatly impact the quality of water leaving the landscape. For example, flow paths through grasslands tend to depend more on the presence of highly dense vegetation, which breaks up the potential flow path of surface runoff from the landscape (Turnbull et al., 2010). These grassland flow paths also prevent rainfall from reaching the soil surface (Hlavčová et al., 2019). However, when highly porous soils in these areas can lead to high soil infiltration rates and water will instead be taken up by plants or added to the groundwater (Bentall, 1998). Agricultural landscapes tend to have more connected flow paths than grasslands, because the annual row-crop pattern leaves soil bare throughout the growing season and leads to faster overland flow due to the lack of vegetation to slow the water velocity. Rain or irrigation water either runs off the landscape into ditches or waterways or is infiltrated into the soil. Once in the subsurface, the water may enter the groundwater, and move via shallow subsurface flow to surface water. If a subsurface tile drainage system is present, the water may enter it (Dinnes et al., 2002). Regardless of the mode of movement, water that moves across the soil surface may transport dissolved nutrients and sediments to the final destination of surface or ground water (Potter et al., 2006). Compared to a subsurface flow pattern, this runoff has little retention time in the landscape and so there is little opportunity for local soils or vegetation to remove some of the nutrients via denitrification and sediment deposition (Vidon et al., 2010). These differences in water

movement through various land uses leads to differences in the water quality across land uses.

Consequently, areas with agricultural land use tend to have decreased water quality. Some studies have shown that greater amounts of agriculture in a watershed produce higher concentrations of nitrate $(NO₃)$ and phosphorus (P) in the water at a HUC 11 or HUC 12 watershed scale (e.g. Tong and Chen, 2002; Coulter et al., 2004). These higher concentrations are due to nutrient accumulation in soils due to artificial nutrient enrichment through agricultural fertilizer use (Bennett et al., 2001; Van Meter et al., 2016) and lower retention and infiltration rates within the landscape which can limit natural processes such as denitrification which would naturally remove $NO₃$ from the system (Helmers et al., 2008).

Other studies have shown the impact of buffer strips – areas of vegetation along waterways used to control water and nutrient movement – on water quality at the watershed, field, or even field plot scale, such as retaining nutrients and reducing sediment loss (e.g. Kreig et al., 2019; Rey Benayas et al., 2019). These studies highlight the impact that the riparian area surrounding stream banks can have on the overall water quality of the stream at a watershed or field scale by reducing nutrient and sediment load from runoff. Helmers et al. (2008) noted the addition of buffer strips such as grassed waterways, filter strips, and riparian forest buffer can improve agricultural water quality by increasing infiltration. Studies that compare the percentage of buffer strip acres throughout a catchment to the water quality of the catchment can provide insight to the interaction between land use and water quality at a large scale. For example, Schulte et al. (2017) investigated the impact of buffer strips (10-20% of the total catchment acres)

installed in a row crop dominated catchment catchments between 0.5 and 3.2 ha $\left(\sim 1.2-8\right)$ ac) in size. They found the addition of buffer strips decreased losses in $NO₃$ by 3.3-fold, P by 4.3-fold, and sediment by 20-fold, when compared to a catchment in full row crop (Schulte et al., 2017). While studies such as this investigate interaction between land use and water quality at a larger scale, they do not investigate the direct impact of runoff from the riparian area on water quality.

An alternate approach to investigate the interaction between land use and water quality is to use rainfall simulators. Rainfall simulators have been well researched as a way to mimic natural rainfall and provide a controlled manner to investigate infiltration and runoff from rainfall events (e.g. Loch et al., 2001; Humphry et al., 2002; Kato et al., 2009). Studies using rainfall simulators have worked to either verify the effectiveness of rainfall simulators (Loch et al., 2001; Humphry et al., 2002; Kato et al., 2009), or have used rainfall simulators to determine the effect a rainfall event has on various landscape types at relatively small scales (e.g. Iserloh et al., 2012; Praskievicz, 2016; Miller et al., 2017; Riddle et al., 2018; Hlavčová et al., 2019). These experiments range from small simulators, covering 25 x 25cm (Hlavčová et al., 2019), to large simulators covering a circular area of 181 m² (Sharpley and Kleinman, 1998). Each of these simulators has its own merits. However, each of these investigations was conducted in a way that runoff generated by the rainfall simulator was collected at the end of the plot, usually in a bucket or small trough at the downslope end of the plot. Furthermore, the scale of these experiments, from centimeters to meters, can make it difficult to scale up processes to a watershed level (e.g. Schoener and Stone, 2019). Despite this limitation, rainfall

simulators have an important advantage: they allow for effective simulation of rain. If these simulators are placed on a streambank, they could be effectively used to directly detect the impact of riparian areas on streams. To date, there have been no studies that investigate how runoff generated by rainfall simulators interact with water in a stream. If rainfall simulators provide utility for this line of research, I would expect:

- 1. An increase in bromide concentrations while the rainfall simulators are turned on and a decrease in bromide concentrations after the rainfall simulators are turned off with the majority of bromide applied reaching the stream.
- 2. Increases in nutrient and sediment concentrations due to simulated runoff at each sampling location.

I present findings on the results from the simulated rainfall experiment, discuss the potential opportunities for expansion of this approach, and the challenges associated with this experimental design for pollution-based hydrological studies.

Methods

Simulator Design

Rainfall simulators were custom built based on a modified version of one designed by Kato et al. (2009). Each simulator (Conservation Demonstration, Salina, Kansas) covers a \sim 4.5 m x 2 m area and stands \sim 3m in height (Figure 1A). The tripod base of each simulator has adjustable legs with removable spikes on the end to allow for use in uneven terrain such as downgraded stream banks. Each simulator has a VeeJet

H1/2 U nozzle (Spraying Systems Co., Wheaton, IL) which is attached to a remote controlled motor which oscillates the nozzle across the plot area and operates at \sim 5 PSI. This oscillation mimics the variability of natural rainfall. Nozzles were attached to a solenoid to turn the water off when the oscillating motor is turned off.

Water was supplied to each simulator via 100 ft. of hose from a 275 gallon water tank using a 4.5 gallon per minute, 12 V battery operated pump. Rainfall gages were placed within the plot to verify the amount of rainfall during the event. Rainfall event size was determined based on limitations of the amount of water that could be transported to the site. The volume of water needed to run two simulators for 35 minutes was determined by finding the average discharge rate for one simulator, then multiplying the discharge by 35 min for a total of 235 gallons in 35 minutes. This volume produced a rainfall event of ~2 inches of rainfall in 35 minutes.

Simulator data analysis

In order to determine whether or not rainfall simulators can be used to investigate impacts of runoff on stream water quality, a conservative tracer, an inert compound used to track water movement was used. Common conservative tracers include bromide, chloride, and isotopes (Davis et al., 1980). The conservative tracer chosen for this experiment was sodium bromide due to the relatively high salt concentrations in Nebraska streams which would make the use of chloride less effective. Bromide does not naturally occur in high amounts in Nebraska streams, so any changes in bromide seen in the samples are assumed to be due to the addition of "rain" water into the stream.

To determine the extent of the "rain" water that entered the stream, and thereby the effectiveness of the simulators, analysis was done to determine the percent bromide recovered in the stream. This is defined as:

$$
\% \text{ bromide recovery} = \frac{bromide_{in\text{ stream}}}{bromide_{total}}
$$

Total concentration of bromide added to the stream was determined by plotting upstream-corrected concentrations of bromide, defined as the downstream concentrations minus average upstream concentration, against time and finding the area under the plotted curve.

Additional metrics investigated to determine the effectiveness of the simulators were time to peak and return time from each site. Time to peak was classified as the amount of time from when the simulators were turned on until the bromide concentrations in the stream peaked and was calculated to compare how quickly runoff generated by the rainfall simulators entered the stream. Return time was classified as the time taken to for bromide concentrations to return to background levels after shutting off the simulators and was calculated to determine the time frame in which the generated runoff continued to influence stream chemistry after the "rain" event was over. These metrics were compared between sites to determine any differences in trends in the two metrics. This comparison was done by first determining if the data was normally distributed using a Shapiro-Wilk test. As neither time to peak or return time was normally distributed, a Wilcox test was performed to determine differences between sites.

To determine the amount of nutrients the "rain" water moved into the stream, additional calculations were done to determine a nutrient to bromide ratio. This metric is an input weighted response, allowing for comparisons between experiments. In order to calculate these ratios, changes in upstream-corrected concentrations for each nutrient of interest were compared to upstream-corrected bromide concentrations over the duration of each experiment. The ratio between nutrient concentration and bromide concentration were calculated for each experiment at each location as follows:

$$
nutrient\ to\ bromide\ ratio = \frac{area\ under\ the\ curve\ of\ nutrient}{area\ under\ the\ curve\ of\ bromide}
$$

Due to analytical error, some concentrations at given time points may be negative when corrected for upstream and blank concentrations. These values were given a concentration of 0.

To determine the direct impact of runoff from a simulated rainfall event on stream water quality under different land uses, these nutrient to bromide ratios were compared between the two sites. Normality of the data was checked using a Shapiro-Wilk test for each of the nutrients and this varied by nutrient. For nutrients with normally distributed data (phosphorus species and total suspended sediment), a t-test was used to determine comparisons between sites. For nutrients with not normally distributed data (nitrogen species), a Wilcox test was done to determine comparisons between sites.

Average percent increases in concentration for each nutrient at each site were calculated as follows:

% nutrient increase

= background corrected downstream peak conc. -avg. upstream conc. avg.upstream conc.

Site Description

Two sampling locations were chosen in this experiment based on differences in vegetation/agricultural practices surrounding the stream and their ease of access due to the need to trailer water to the site and to have the water supply as near the stream as possible. Each sampling location was sampled three times during the summer of 2019 (June through August). The first sampling location was located at Spring Creek Prairie Audubon Center, in Denton, NE (40.683210, -96.852037). This tall grass prairie covers 344 ha (850 ac). Spring Creek runs through the property and is surrounded by trees and prairie grass. My site was on the southern edge of the property on the north side of the bridge (Figure 1B). On the south side of the bridge, upstream of the sampling locations, was a cattle pasture with cattle in it. Banks at this location were down-cut with heavy vegetation.

The second sampling site was located at University of Nebraska-Lincoln Rogers Memorial Farm (RMF) located ~10 miles east of Lincoln, NE (Figure 1B) (40.842125, - 96.466956). It covers ~300 acres and is a continuous no-till farm with controlled wheel traffic. Corn, soybeans, wheat, and grain sorghum are gown under a variety of crop rotations. My sampling location lies at the southeast side of the farm. This stream is surrounded by a riparian buffer with a wheat field to on the east and a grassy area on the west bordering the riparian area. Banks at this site were down-cut, with more sparse vegetation than at Spring Creek Prairie.

Field Method

To determine the impact of rainfall runoff on stream water quality, two rainfall simulators, as described above, were placed on either bank of a small stream, ~1 m from the stream edge and raised to \sim 3 m in height (Figure 1C). To characterize the initial soil moisture and bulk density, three soil core replicates were collected on each bank within the plot before the start of the experiment. Rain gages were then placed within the plot on each bank to verify the rainfall amount during the experiment.

A 275 gallon water tank was filled with deionized (DI) water and was transported to the field site. Sodium bromide was used as a conservative tracer in the stream. This tracer served as a check to ensure the water being applied to the soil via the simulators entered the stream. Stream discharge measurements were taken using the velocity-area method (Turnipseed and Sauer, 2010) using a Marsh-McBirney Flo-Mate Model 2000 flow meter (Loveland, CO). The stream discharge measurements were used to determine the amount of sodium bromide needed to achieve target instream bromide concentrations. To ensure adequate bromide concentrations in the "rain" in the event bromide was lost to the soil, an instream target of 1250 ug/L of bromide was used, well below the acute toxicity concentrations to freshwater organisms of 44 to 5800 mg/L (Canton et al., 1983).

To describe initial stream water conditions, basic physiochemical stream measurements were taken within the stream at the center of the study reach. Water temperature, dissolved oxygen, and conductivity were measured using a YSI multimeter 556 with a membrane dissolved oxygen sensor (Yellow Springs, OH).

To mimic a rainfall event, sprinklers were turned on simultaneously with a remote control and let to run continuously for the duration of the experiment. "Rain" water was allowed to run off the landscape and into the stream. To determine if the "rain" reached the stream and to characterize any changes stream water quality, stream water samples were collected during and after the rainfall simulation. Downstream of the sprinklers (approximately 4.5-6 m), water samples were collected within 5 minutes before the start of the experiment, and every 5 minutes for the first 60 minutes, and every 20 minutes from 60 minutes to 120 minutes. To track background water quality throughout the experiment, water samples were also collected upstream $\left(\sim 15{\text -}20 \text{ ft.}\right)$ of the rainfall simulators before the start of the experiment, every 10 minutes for the first 60 minutes, and every 20 minutes from 60 minutes to 120 minutes. Fewer upstream samples were collected than downstream samples based on preliminary trials which suggested water conditions were relatively stable throughout the 120 minutes of the experiment. The simulators were turned off at 35 minutes during the rainfall simulations. Three soil core replicates were again taken on each bank after the experiment to assess for changes in soil moisture.

Lab Analysis

After each experiment, stream water samples were returned to the lab and processed within 8 hours of collection for total, suspended, and dissolved constituents. For total nitrogen (TN) and total phosphorus (TP) analysis, unfiltered stream water

samples were collected. For dissolved constituents, stream water samples were filtered through a Whatman GC/F filter. The filtered stream water samples were used for bromide (Br), ammonium (NH₄⁺), nitrate (NO₃), total dissolved nitrogen (TDN), soluble reactive phosphate (SRP), and total dissolved phosphorus (TDP) analysis. A portion of the water in the initial sample bottle was used for total suspended sediment (TSS) analysis. Total suspended sediment analysis was done by filtering a known amount of water through a pre-combusted and pre-weighed GC/F filter using a vacuum pump. Clean filters were placed in a combustion furnace at 550° C for 4 h, cooled in a desiccator for at least 24 h, and then weighed. The filters were then used to filter the sample water. Used filters were then dried for at least 24 h at 65^oC, weighed, and combusted a second time as described above. Filters were weighed a third time after the final round of combustion. The difference between the initial weight and weight after being dried is the total amount of suspended sediments in the given volume of water. After initial processing, samples were kept frozen until analysis.

Soil moisture and bulk density were determined by weighing the moist soil after returning from the field, placing the soil cores in a drying oven at 105 °C until dry, and reweighing the soil. Soil moisture was determined as the difference between the wet soil weight and dry soil weight divided by the dry soil weight. Bulk density was determined as the oven dry weight of the soil core divided by the volume of the soil core.

The concentration of NH_4 ⁺ was measured using the OPA method with fluorometry on an AquaFlour 9000-010 fluorometer (Taylor et al., 2007; Holmes et al., 2011). Concentrations of $NO₃$ and Br were measured using ion chromatography with chemical

suppression of eluent conductivity using a Dionex ICS-1100 ion chromatography system (APHA, 2005). SRP concentrations were analyzed using the molybdate-ascorbic acid method on a Genesys 150 UV-Visible Spectrophotometer (APHA, 2005). Concentrations of TDP were measured using persulfate digestion, followed by the molybdate-ascorbic acid method, again on a Genesys 150 UV-Visible Spectrophotometer (APHA, 2005). TDN concentrations were determined using the ASTM D8083-16 method on a TOC-L CPN Shimadzu (Shimadzu Corporation, 2017). TN and TP concentrations were measured using persulfate digestion followed by the cadmium reduction method for $NO₃$ and the automated ascorbic acid reduction method for PO₄ on an Astoria Pacific autoanalyzer (APHA, 2005, Astoria Pacific).

Dissolved organic phosphorus (DOP) was calculated as the difference between TDP and SRP. Particulate phosphorus (PP) was calculated as the difference between TP and TDP. Dissolved organic nitrogen (DON) was calculated as the difference between TDN and DIN. Particulate nitrogen (PN) was calculated as the difference between TN and TDN. Due to the calculations required for DOP, PP, DON, and PN, concentrations for these values were some cases due to the concentrations used in the calculations being close in value. This negative value indicates the calculated value for DOP, PP, DON, or PN concentrations is smaller than the analytical error for the analysis used.

Statistics

Data were analyzed using R (version 3.6.2) (R Core Team, 2019). Initial stream characterization data analysis was done by determining differences between average upstream concentrations for each of the stream constituents of interest. In order to

calculate average upstream concentrations, overly influential data points needed to be removed to get an accurate description of the initial stream conditions. To determine overly influential data points, the data were fitted to a simple model with the upstream concentration as the response variable and the time the sample was taken as the explanatory variable. From this model, outlying data points were removed using a Cook's distance of 0.4 or 4 divided by the number of upstream observations, in this case 10 upstream observations, as these outliers may have been artificially altered during the sampling process. Averages of the remaining nutrient concentrations at each site were then used to determine differences in initial stream characterizations. A Shapiro-Wilk test was performed on the average upstream concentrations for each nutrient to determine normality. For normally distributed upstream nutrient concentrations (all constituents except NH₄⁺ and PN), a t-test was used to compare between sites, while a Wilcox test was used for non-normal data (NH₄⁺ and PN). For all other analysis, stream concentrations were corrected for the average upstream concentration, field blank, and background "rain" water concentrations.

In the case of TSS analysis, the first two downstream values at each site were not used as many were artificially high when compared to subsequent samples. This is likely due to artificial disturbance associated with the start of the project, so for the sake of consistency, the first 2 at each site were ignored.

To determine the effectiveness of the rainfall simulators in determining the impact of land use on water quality, I examined the bromide breakthrough curves from each site. Bromide breakthrough curves were shown by plotting the concentration of bromide in the

stream against time. Additional analysis information is discussed in the "Simulator analysis section".

Results and Discussion

Testing Expectation 1

To determine the effectiveness of the rainfall simulators in showing the impact of land use on water quality, I examined bromide breakthrough curves, percent bromide recovery, time to peak, and return time from each site. The bromide breakthrough curves showed that bromide concentration in the stream increased while the rainfall simulators were on, and then returned to background concentrations after the simulators were turned off (example shown in Figure 2A). This result provides validation for the proposed method as a potentially viable approach to study the impact of rainfall events on surrounding landscapes on small streams at a hyper-localized scale. There was between 11.5% and 65.8% bromide recovery at the sites with an average of 31.6% recovery, indicating that much of the bromide applied in the experiment was not captured in the sampling process (Supplemental Table 1). Percent bromide recovery was less than 100% likely due to in small part to the "rain" water being absorbed by the landscape and in larger part to the "rain" water not mixing properly with the stream water during sampling. Percent bromide recovery increased with each experiment, indicating my sampling process improved over time.

For all experiments, simulators were run for 35 minutes, with the exception of one run done at Rogers Memorial Farm, where the batteries operating the pumps ran out at 26 minutes. The time to peak occurred approximately 27 min after the simulators were
turned on. The fastest time to peak for any run was 20 min after the rainfall simulators were turned on, while the slowest time to peak was 35 minutes after the simulators were turned on (Supplemental Table 3-2). At Rogers Memorial Farm, the range of time to peak was between 20 and 30 min after the simulators were turned on. Only one of the time to peaks at Spring Creek occurred at 20 min, while in the other two experiments, the peak occurred at 35 min (the time the simulators were turned off) (Supplemental Table 3-2). There was no significant difference in time to peak between sites, indicating that the amount of time it took for the stream water to enter the stream was similar between sites. The observed range in time to peak may be due to the differences in the infiltration rates of the stream banks at the time of the experiment.

The return time was an average of approximately 57 minutes across all sites and ranged from 35 to 65 minutes, with 65 minutes being the most common return time (Supplemental Table 3-2). There was no significant difference in return time between the two sites, indicating that the streams returned to background conditions in similar time frames. These return times indicate similarities in flow paths between the two riparian areas during the simulated rainfall events.

Testing Expectation 2

When exploring differences in initial stream characterization between the two sites, I found significant differences in average upstream concentrations of SRP, TDN, and DON. All other initial nutrient concentration comparisons were non-significant. Concentrations of SRP, TDN, and DON at Rogers Memorial Farm were approximately 2.4-fold, 3.7-fold, and 10.7-fold higher than that at Spring Creek.

 Although initial concentrations of many nutrients in the streams were relatively high at both locations (e.g. TDP, DOP, SRP), I was still able to detect changes in nutrient concentrations at the sites when using the simulators (example in Figure 2 B-F). To determine if there was a difference in discharge weighted nutrient additions to the streams, nutrient to bromide ratios were compared. For all observed nutrient to bromide ratios, there was no significant difference (p>0.05) between locations (Figure 3 A-C) indicating that the proportion of nutrients entering the stream was not significantly different between sites. Thus, the methods by which nutrients leave the landscape and enter the stream with rain water was similar and moved at a similar rate whether the area surrounding the riparian region was under the agriculture and prairie land uses. Although there were no significant differences between the two sites, it is worth noting that the nutrient to bromide ratios at Rogers Memorial Farm were generally more variable than those at Spring Creek (Figure 3 A-C).

Average percent increases in concentration were calculated for each nutrient at each site and are shown in Table 3-1. Overall, percentages ranged from a 79% decrease (DON at Rogers Memorial Farm) to a 162% increase (TN at Rogers Memorial Farm) (Table 3-1). Decreases were seen at both study sites for DON and DOP concentrations, suggesting that these nutrients did not enter the water during the experiment and were instead diluted. Peaks used for the average percent increase calculations did not all occur at the same time (e.g. NO_3 may have peaked at 20 minutes while TN may have peaked at 50 minutes). As such, care should be taken when comparing the downstream results in

Table 3-1 as the values are not noted at the same time points due to differences in the experimental environment on a day-to-day basis.

Comparisons to natural rainfall studies

Rainfall simulators have the potential to increase the power and rigor of the scientific approach by allowing for controlled rainfall experiments, in contrast to the variability and unpredictability of natural rainfall trends. However, it is important to know how rainfall simulation experiments perform when compared to natural rainfall experiments to understand the ability of simulated experiments to describe natural processes. Previous studies have used natural rainfall events to investigate the impact of land use on stream chemistry. Many of these studies were performed in agricultural areas, usually under row crop managed grassland regions with a few being performed in non-agricultural settings (e.g. forests). As these studies were performed using real rainfall events, the studies often lasted much longer, with some seeing time to discharge peak as late as 25 hours after the rainfall event (Poor and McDonnell, 2007). However, the general trends discovered in such studies are relatable to the trends observed in my study.

For example, several studies have found increases in several phosphorus constituent concentrations during rainfall events in managed grassland catchments (Stamm et al., 1998; Heathwaite and Dils, 2000; Jordan et al., 2007) and agricultural catchments (Borah et al., 2003; Rozemeijer et al., 2010). Heathwaite and Dils (2000) found most of the phosphorus increases during rainfall events in managed grasslands to be in the dissolved fraction of phosphorus, which is similar to trends I observed at both sites. Additionally, my results for DOP are in agreeance with Stamm et al. (1998), who found DOP to be a

largely negligible portion of total P loses during rainfall events in managed a grassland catchment.

Studies have also found that $NO₃$ concentrations increased during rainfall events under agricultural land uses in the Netherlands (Rozemeijer and Broers, 2007) and Germany (Tiemeyer et al., 2008). This is similar to the results of my study at both sites (Figure 2 C). However, other studies have found decreases of $NO₃$ concentrations during a rainfall event due to a dilution effect in the stream. In a study done by Borah et al. (2003) , it was suggested that observed differences in NO₃ trends may be due to differences in the intensity of a rainfall event. The authors found weak trends of increasing $NO₃$ concentrations in small rainfall events, but strong trends of decreasing NO³ concentrations during heavy rainfall events in an Illinois agricultural watershed (Borah et al., 2003). As the rainfall event in my study was relatively small, this may explain why my study saw increases in NO₃. Poor and McDonnell (2007) found mixed trends in stream $NO₃$ concentrations in relation to precipitation events depending on the land use in a catchment. The authors showed forested and urban catchments showed increasing stream NO₃ concentrations with increased discharge, while the agricultural catchment only showed increasing $NO₃$ concentrations in the spring (drier period), but showed lowering NO³ concentrations in the fall and winter (wetter periods) (Poor and McDonnell, 2007). Additionally, my DON finding is in contrast with Jiang et al. (2010), who found increasing trends of DON during storm events in an mixed forest-agriculture watershed, while I observed a decrease in DON concentration at both sites. Finally, studies found sediment concentrations increased during rainfall and flow events in mixed land use watersheds (Nadal-Romero et al., 2008; Jiang et al., 2010), which is similar to my findings (Figure 2B).

Challenges for Rainfall Simulation Studies

While other studies have investigated the impact of rainfall simulators on runoff characteristics, this study differs by placing simulators directly on stream banks to achieve runoff directly into the stream. This study is currently conducted at a small scale, only a few square meters. The design has the potential to be scaled up, to a certain degree, to cover more stream bank area. One way to do this is to place multiple simulators in tandem with each other adjacent to the stream bank. This would allow a larger area to be under the simulated rainfall event, giving a more realistic look at the impact of a real rainfall event. Alternatively, simulators could be placed in tandem to each other perpendicular to the stream bank, allowing for a study of how the change in vegetation going away from the stream bank may impact water quality. A limitation to these suggestions is there may be problems with terrain that has too extreme a slope, or too much low, dense vegetation (e.g. bushes and trees) for the simulators to be effective. Simulators in tandem may also lead the simulators too far from the water source for full water pressure to reach the simulators.

Additionally, to use multiple simulators in tandem, or to scale the simulated rainfall event up to a longer event, a larger water supply would be required. For example, scaling the experiment up by running simulators in tandem on each stream bank (4 simulators total) would also require double the amount of water (235 gallons to 470 gallons). Alternatively, doubling the length of the rainfall event (35 minutes to 70

minutes), with the same water output as the current system would require a doubling of water needed (235 gallons to 470 gallons). In either case, it would require either a second water tank of the same size, or a significantly larger water tank than the one used in this experiment. In both cases, a larger truck and trailer system would be required to haul the water to the site.

Any further scaling, whether through longer experiment times, or running multiple simulators in tandem, would require even larger water supplies. A rainfall event of 5 hours long with two simulators, or with 17 simulators running at the same time for 35 minutes would require over 2,000 gallons of water, resulting in the need to use a tractor-trailer to haul the water, which in itself may pose a logistical concern with the weight limit on many of the bridges spanning the small streams of interest. This increase in water needed poses a logistical concern, though this may be worked around with the proper planning, equipment, and personnel.

An alternative to hauling a larger water source to the site would be to find a permanent water source near the site that can be used instead to fill up more permanent water tanks that are in close proximity to the site, for example, a large water tank sitting 50 ft. away from the stream bank that is able to be refilled via well water. If the permanent water source is not DI water, as was used in this experiment, it becomes even more crucial to test the water before the start of the experiment, as the well water will introduce higher background concentrations of nutrients, especially $NO₃$, into the study.

Conclusion

In this study, I was able to successfully create a protocol to study the impact of riparian area runoff on stream chemistry. I was able to pilot the protocol at two riparian locations, each surrounded by a different land use – agriculture and prairie. Of the two sites, Spring Creek Prairie is thought to be the most intact example of pre-agricultural land use in Nebraska while Rogers Memorial Farm is under extensive agricultural production. Such extremes in surrounding land use provided differing environments in which to test my experiment. Comparison between the two locations showed no difference in nutrient inputs to the stream between sites, however, inputs tended to be more variable at Rogers Memorial Farm than at Spring Creek.

My pilot study shows promise for future development and, when combined with similar future studies, can be used to fill the knowledge gap of the impact of the riparian area on water quality in the stream. Experiments such as the one proposed here can be used to show how differences in land use and stream banks can impact overall stream chemistry during rainfall events. When performed at a larger scale, this protocol can potentially be used to define a more specific relationship between the riparian area and water quality at a reach level and beyond.

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Figures

Figure 3-1: Rainfall simulators used to study runoff at two experimental sites. (A) Rainfall simulator design. The simulator stands ~3m tall, and when extended, it covers an area of approximately4.5 by 2 m. (B) Map of experiment locations relative to Lincoln, NE. The star represents UNL campus. The dot represents Rogers Memorial Farm

(agriculture dominated landscape). The triangle represents Spring Creek Prairie. (C): Example of the rainfall simulator experimental set up at Rogers Memorial Farm (Photo Credit: Fernanda Krupek). There is one simulator on each bank. Each simulator is set up so that the oscillation of the nozzle is perpendicular to the stream bank and the simulators are ~1 m from the edge of the stream.

Figure 3-2: Examples of nutrient breakthrough curves. (A) Background corrected concentrations of bromide downstream of the rainfall simulators at Spring Creek (SC2). Triangles (upstream points) indicate that bromide was added to the water through the experiment. Bromide was the only stream addition done during the experiment. (A-F) Green dots indicate upstream samples, red dots indicate downstream samples. (B-f) All concentrations increased during the time the simulator was on, decreasing sharply after the simulator was turned off (designated by the red line).

(B) Differences in P species between sites

Figure 3-3: T-test results of nutrient to bromide ratios. I found no significant differences (p>0.05) between sites in any of the nutrient to bromide ratios when using a Wilcoxon Rank Sum Test. Box plot upper and lower boxes show $25th$ and $75th$ percentile, respectively, with the whiskers showing the extremes of the range. RMF = Rogers Memorial Farm, $SC =$ Spring Creek Prairie, $n = 3$ at each site. (A) shows nutrient to bromide ratios for the nitrogen species. (B) shows nutrient to bromide ratios for the phosphorus species. (C) shows nutrient to bromide ratios for total suspended sediment.

Table 3-1: Average percent increase of each nutrient at each study site. Site average downstream concentrations are at the peak concentrations after the rainfall simulators were turned on. $RMF = Rogers$ Memorial Farm, $SC = Spring$ Creek. $* = Not$ available, initial concentration of 0.

Supplemental materials

Memorial Farm, SC = Spring Creek. Number after the location indicates the replicate

Spring Creek. Number after the location indicates the replicate

CHAPTER 4: CONCLUSION

The overall objective of my thesis sought to answer the question of how land use in Nebraska impacts water quality. I investigated this question by performing two projects, one at a HUC10 watershed scale and a second project at a field scale. In Chapter 2, I analyzed the resilience of a watershed to water quality pollution in response to extreme events by determining the impact of agricultural land use and drought conditions on nitrate, phosphorus, and sediment concentrations in watersheds across Nebraska. During the study period, I found agricultural land use varied by watershed, and remained fairly consistent within the watersheds, with the exception of Lower Salt Creek, which saw a 34% increase in summer annual acres. These differences in land use between watersheds impacted water quality. I confirmed each nutrient in the study is impacted differently by percent summer annual acres, percent winter annual/perennial crop acres, and Palmer Modified Drought Index values. This result was as expected and further reinforced the understanding of the way nutrients interact with the environment.

Additionally, I showed that watersheds with lower percent summer annual acres showed lower variability in nutrient concentrations across a variety of drought and flood conditions. The three watersheds in the study with <20% summer annual acres showed low nutrient concentration variability and thus showed high resilience of nutrient concentrations to changes in drought and flood conditions. This high level of resilience allows better management for disruptions in the system as the system will react to a disruption in a predictable way. From these results, a shift to more perennial based cropping systems will lead to more predictable systems with lessened water pollution.

In Chapter 3, I proposed a new protocol for a rainfall simulation study to detect the impact of runoff from the riparian area on stream chemistry. Through a field scale experiment, I showed validation for the study design by using a conservative tracer (sodium bromide) in the "rain" water. Study validation was shown through bromide breakthrough curves, which demonstrated increases in stream bromide concentrations downstream of the rainfall simulators while the simulators were turned on and decreasing bromide concentrations after the simulators were turned off.

After validating the study, I investigated the amount of nutrients which entered the stream with the "rain" water using nutrient to bromide ratios for each site. When comparing the nutrient to bromide ratios, I found the ratios at Rogers Memorial Farm tended to be more variable than those at Spring Creek, but the ratios between the two sites were not significantly different from each other. This is consistent with the results of Chapter 2 in that areas with more summer annual agriculture were found to have larger variability in nutrient concentrations than watersheds with more perennial cover. However, unlike the results in Chapter 2, there was no significant difference in the nutrient to bromide ratios between the two sites, indicating no significant difference in the methods or rates by which nutrients leave the riparian area at either site.

While both chapters sought to answer the same question, there are tradeoffs in the different approaches and methods used in the two studies. The long-term data set in Chapter 2 provides insight to nutrient trends over time, while the small, experimental scale of Chapter 3 provides a closer look at the mechanisms of nutrient movement, however, results at this scale may be hard to scale up to a watershed scale.

With the past and present events which have impacted land use (Dust Bowl, farm crisis, trade uncertainty), and an uncertain future ahead, knowing how future changes in land use and climate may impact water quality is important. Results of both studies as well as future related studies will provide helpful insight to this and to what efforts may be helpful from an ecological standpoint to reduce water pollution.