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NITRATE CONCENTRATIONS IN STREAMS AS A FUNCTION OF CROP COVER
IN MIDWESTERN AGRICULTURAL WATERSHEDS: ASSESSING
THE ROLE OF CORN AND SOYBEANS

JACOB TYLER PISKE

56 Pages

Increased availability and reduced cost of synthetic-nitrogen fertilizers have led to excess nitrogen being deposited in reservoirs. The accumulation of nitrogen (N) in reservoirs has negative effects, generating algal blooms, hypoxic zones, and poor drinking water quality. Corn and soybean utilize nitrogen at different rates, resulting in higher nitrogen fertilizer application to fields for corn than for soybean. This work examines whether the nitrate concentration in a stream may be correlated to the percentage of land devoted to growing corn or soybeans in the watershed. To investigate potential relationships, discharge (Q) and nitrate concentration data from ten USGS gauging stations across Indiana, Illinois, Iowa, Kansas, and South Dakota and agricultural land-use data from USDA were analyzed. Watershed areas ranged from 106 km² (Spoon River) to 154,767 km² (Kansas River). Corn was grown on between 14.3% (Kansas River) to 56.1% (Indian Creek) of the land, while soybeans accounted for 7.2% (Kansas River) to 45.4% (Spoon River). Crop percentages were compared to both weighted flow concentrations and nitrate loads per area from 2008 to 2017. For each system, weighted flow concentration equated to the total annual NO₃-N-load (kg) divided by the total annual Q. Nitrate load per area represented the quotient of annual NO₃-N-load (kg) to the watershed area (km²). The analyses indicated that as the percentage of corn cultivated in the watershed increased, both the weighted

flow concentration and nitrate load per area decreased for all watersheds, except for the Kansas River, which is the largest watershed with the least amount of corn. Collectively, analysis of the data indicated weighted concentrations increase as the percentage of land with corn increases.

Opposite trends were observed when the percentage of soybean cultivated in the watershed increased; weighted flow concentration and nitrate load per area all increased with respect to the percentage of soybean cultivated both for individual watersheds and collectively. The one exception being the North Raccoon River. The results imply soybean production has a more direct impact on nitrate concentrations, although corn fertilizer application and total cultivation rates are higher in each watershed.

KEYWORDS: CropScape, WaterWatch, stream gages, nitrate export, agriculture

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A Thesis Submitted in Partial
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J. T. P.

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CHAPTER I: INTRODUCTION

INTRODUCTION

The emphasis on studying long-term nitrate trends in the Mississippi River Basin stems from nitrate's central importance to the development of the Gulf of Mexico hypoxic zone and because of the changes that have taken place within the drainage basin (Stets et al, 2015). These changes within the basin include degradation of streams and reservoirs as a result of alterations associated with fertilizer application, subsurface drainage, and decrease in crop diversity in agriculture that have taken place within the last century within the basin (Gentry et al, 1998; Dinnes et al, 2002; David et al, 2010; Stets et al, 2015). Hypoxic conditions develop from a process called eutrophication, which is excess nutrients input in a body of water resulting in lost biodiversity and degradation of water quality (Stets et al, 2015). With an area of 16,700 km² at the outlet of the Mississippi River (Turner et al, 2008), the Gulf of Mexico hypoxic zone is the largest manifestation of anthropogenic pollution from synthetic nitrogen (N)-fertilizer application in the heavily cultivated Mississippi River Basin (MRB) in the United States (Stets et al, 2015). Hypoxia in the Gulf of Mexico is just one of the more than 400 hypoxic zones occurring in coastal waters that lie downstream of major population centers and agricultural areas across the globe (Diaz and Rosenberg, 2008; Hanrahan et al, 2018). Thus, it is important to understand the threats of excess N has on drinking water supplies (Kovacic et al., 2006; Hanrahan et al, 2018) and aquatic biodiversity (Carpenter et al., 1998; Stets et al, 2015; Hanrahan et al, 2018).

Agricultural regions have undergone specific environmental changes associated with land use decisions and crop practices, which has led to water quality problems (Dinnes et al, 2002). In the Midwest, artificially drained areas, increased use of synthetic fertilizers, and decreased diversity in crop rotation are among the most notable causes of agricultural nutrient contamination

of water resources (Dinnes et al, 2002). Less than 50 years ago, corn was grown in rotation with cereal crops and forage legumes, such as alfalfa, red clover, and sweet clover (Dinnes et al, 2002). These farming practices began to change with the increased availability of commercial nitrogen fertilizers that were introduced during the 1960s and 1970s; the need to incorporate legumes into a crop rotation was no longer needed for an optimal yield (Dinnes et al, 2002). The introduction of nitrogen-based fertilizers led to a rapid growth of application rates as well as nitrate concentrations in rivers and reservoirs concurrently increasing throughout agricultural regions during this period (Gentry et al, 1998). In 1964, the average N-fertilizer rate applied to corn in the United States was 64.25 kg ha^{-1} ; that rate had increased to $162.52 \text{ kg ha}^{-1}$ in 2016 (Figure 1). In central Illinois where the predominant cropping system is a corn-soybean rotation with extensive networks of subsurface drainage, corn receives nitrogen fertilization at an average rate of 196 kg N ha^{-1} (Gentry et al, 1998). On average, soybean yields of 50 to 80 bu/acre receive 0 to 35 kg ha^{-1} of N-fertilizer (Schmidt, 2016). When soybeans are in production, the addition of nitrogen fertilizer does not enhance soybean yield as soybeans accumulate 25 to 50% of utilized nitrogen through soil and atmospheric fixation (Gentry et al, 1998; Jones et al, 2016). Nitrogen-based fertilizer has become the most commercially used fertilizers, which is generally applied during spring and fall, in row crop production (Goswami and Kalita, 2010). Reported nitrate losses from plots growing corn are higher than those with soybeans (Keeney and Deluca, 1993; Powers, 2007; Randall and Mulla, 2001) and are higher on plots continually growing corn (217 kg ha^{-1}) than from corn-soybean rotations (204 kg ha^{-1}) over a four year period (Randall and Mulla, 2001; Weed and Kanwar, 1996). In areas where crop rotation is no longer practiced and corn has become the dominant crop, the loss of N has increased (Secchi et al., 2011).

Figure 1. N-Fertilizer application rate applied to corn and soybean from 1964-2016. Data retrieved from the United States Department of Agriculture – National Agricultural Statistics Service (USDA, NASS) (Last Updated 2/21/2018).

In addition to fertilizer application and crop changes, the land use in agricultural watersheds has undergone significant hydrological modifications. These modifications have been occurring for decades and include channelization of the headwater streams and installation of intensive subsurface tile drainage in fields that efficiently route water to nearby streams (David et al, 2010). A tiled field implies that there is inadequate natural drainage that has resulted in the installation of a subsurface drainage tile system to transport excess water and nutrients from the soil (Lemke et al., 2010). Draining excess water from the soil prevents the crops from flooding but rapidly transports excess nutrients not taken up by the crops to surface water bodies, which ultimately creates nutrient problems downstream. Tile drainage has been in place since the 1860s and continues being replaced and expanded each year, with plastic pipes instead of the original clay pipes being used since the 1950s (Baker et al., 2008; David et al, 2010). In Illinois, about

4,000,000 ha are tile drained, representing 35% of all Illinois cropland (USDA, 1987; David et al, 1997). Streams in agricultural areas have shown high concentrations of N in the form of nitrate (NO_3^-), at concentrations often greater than the EPA drinking water standard of 10 mg/L nitrate as nitrogen ($\text{NO}_3\text{-N}$) (David et al, 1997; Kladivko et al, 2004; Hanrahan et al, 2018). High concentrations come from a combination of agricultural runoff through tile-drainage and the use of nitrogen fertilizers in areas adjacent to streams (Miller et al, 2011; Lemke et al, 2011). With the help of tile drains, nutrient transportation is accelerated from fields to streams that are bound for the Mississippi River and ultimately the Gulf of Mexico (Sugg, 2007). Approximately 25% of the NO_3^- in the stream system will remain mobile and continue to the Mississippi River, where it is eventually discharged into the Gulf of Mexico (Arango et al., 2007; Christensen et al., 1990; Kovacic et al., 2006). Most $\text{NO}_3\text{-N}$ exported from tile-drained watersheds in the Midwest occurs from January to June, coinciding with seasonal patterns of increased precipitation, elevated stream discharge, and fertilizer application (Royer et al., 2006; David et al., 2010; Raymond et al., 2012; Hanrahan et al, 2018). Therefore, management strategies, including agricultural conservation practices that prevent $\text{NO}_3\text{-N}$ loss to adjacent waterways, have been suggested as potential solutions for reducing excess $\text{NO}_3\text{-N}$ export from the MRB (Dinnes et al., 2002; Hanrahan et al, 2018).

In an attempt to improve aquatic conditions and reduce the hypoxic zone in the Gulf of Mexico, the EPA has established a goal of reducing N loads by 45% in the Mississippi River by 2035, with an intermediate goal of 20% reduction by 2025 (United States Environmental Protection Agency, 2017). Approaches to reducing N losses from agriculture in the MRB have been grouped into three categories: (1) managing the fate of nitrate loss from agricultural fields, (2) adjusting N fertilizer management, and (3) ecologically based nutrient management practices

(Blesh and Drinkwater, 2013). In addition, the 12 states in the MRB created their plan to reduce N loads into the Mississippi River. Illinois set a goal of developing best management practices for reducing nitrate-nitrogen load by 15% by 2025, with an eventual target of 45% reduction (IEPA, 2017). The Iowa strategy, which was developed over a two-year period as a result of the Gulf Hypoxia Action Plan, follows the recommended framework provided by the EPA in the 2011 memo (Iowa Nutrient Reduction Strategy, 2017). Within each of the state's reduction plan, priority watersheds have been identified. In this study, seven (7) of the ten (10) watersheds that were analyzed are subwatersheds of the priority watersheds or the priority watersheds identified are subwatersheds of this study.

To understand the fate of nitrate loss from agricultural fields, a statistical analysis was conducted using USGS water quality data and USDA land classification data. The analysis incorporated data on an annual scale and seasonal scale to determine the effect of land cover changes on nitrate export in agricultural streams. The goal of this work was to answer the following two questions, (1) is there a relationship between crop type (corn or soybean) and nitrate export? (2) Is there a statistical difference in nitrate export among seasons?

HYPOTHESES

1. As the percentage of cultivated crops devoted to corn increases, the annual mean nitrate load in a stream will increase. This is because corn receives more nitrogen fertilizers than soybean.
2. As the percentage of cultivated soybean increases, the annual mean nitrate load will decrease. This is the initial thought since soybean fixes its own nitrogen for growth and receives a lower application of nitrogen fertilizers than corn.

3. When looking at the seasonal loads, the highest nitrate loads are expected in the spring and fall, while the lowest loads occur during the summer and winter months. Farmers apply most of the fertilizer in the spring and fall (Goswami and Kalita, 2010). With the potential to have bare soil and no crops taking up the nitrogen creates a higher chance for more runoff.

STUDY AREA

Table 1. Study Sites with agricultural statistics. Table sorted based on percent agriculture; pasture not included as percent agriculture.

USGS Station	River	Watershed Area (km ²)	Percent Agriculture (2017)	NO ₃ -N Availability
3336850	Spoon River	106	92.1%	2013 – 2017
5554300	Indian Creek	175	91.7%	2011 – 2017
5482300	North Raccoon River	1813	84.3%	2008 – 2017
5482500	Raccoon River	4195	84.0%	2008 – 2017
5447500	Green River	2597	81.5%	2015 – 2017
5524500	Iroquois River	1162	78.5%	2015 – 2017
5464420	Cedar River	16425	75.9%	2012 – 2017
5465500	Iowa River	32375	70.8%	2009 – 2017
6481000	Big Sioux River	10170	59.2%	2017
6892350	Kansas River	154767	44.4%	2013 – 2017

This study incorporated data from 10 watersheds that spanned across Midwestern United States, specifically the states of Indiana, Illinois, Iowa, Kansas, and South Dakota (Figure 2). In each watershed, land use were primarily row-crop agricultural production of corn and soybeans (Table 1). Each watershed was chosen based on the availability of nitrate concentration and discharge data available from the USGS (Table 1). Watershed areas ranged from 106 km² (Spoon River) to 154,767 km² (Kansas River), while land-use devoted to cultivated crops in 2017 ranged from 59.2 (Big Sioux River) to 92.2% (Spoon River). Historically, corn and soybean cultivation

dominated the land cover in each watershed, with the Kansas River being the only exception. Within the Kansas River watershed, pasture (40.3%) was the dominant land cover. Comparing the cultivation difference between corn and soybean, corn was grown on between 14.3% (Kansas River) to 56.1% (Indian Creek) of the land, while soybeans accounted for 7.2% (Kansas River) to 45.4% (Spoon River) of the land. The percentage of corn and soybean for each watershed is shown in Figure 3.

Figure 2. Locations of the watersheds within Midwest USA.

Figure 3. Annual percentage of agricultural land use devoted to corn (yellow) and soybean (green) for each watershed; a) Spoon River, b) Indian Creek, c) North Raccoon River, d) Raccoon River, e) Green River, f) Iroquois River, g) Cedar River, h) Iowa River, i) Big Sioux River, j) Kansas River.

CHAPTER II: METHODOLOGY

STREAM DATA

Continuous, 15-minute interval NO₃-N concentration (mg N/L) and discharge (Q in m³/s) data were downloaded from the USGS Water Science Center (<https://waterwatch.usgs.gov/wqwatch/>) for each of the ten watersheds. The timeframe of available data for each watershed varied between 2008 and 2017 from the USGS, but all watersheds had at least a one-year dataset.

The total annual NO₃-N load was the summation of the discharge (Q_i) multiplied by the concentration (C_i) for each 15 minute interval (i) (eq1), where D is the constant representing the conversion factors.

$$\text{Annual NO}_3\text{-N load (kg)} = \sum Q_i \times C_i \times 15 \text{ min} \times D \quad \text{eq 1}$$

Having multiple watersheds with different areas and potentially different climates, NO₃-N was normalized to discharge (discharge normalization) or to area (area normalization), removing potential bias introduced by variation of these parameters among the watersheds. For each system, weighted-flow concentration (discharge normalization) equated to the total annual NO₃-N-load (kg) divided by the total annual Q (eq 2).

$$\text{Weighted Flow Concentration} = \frac{\text{Total annual NO}_3\text{-N load (kg)}}{\text{Total annual Q (m}^3\text{)}} \quad \text{eq 2}$$

Nitrate load per area (area normalization) represented the quotient of annual NO₃-N-load (kg) to the watershed area (km²) (eq 3). These variables were used for linear regression analysis.

$$\text{Nitrate Load per Area} = \frac{\text{Total annual NO}_3\text{-N load (kg)}}{\text{watershed area (km}^2\text{)}} \quad \text{eq 3}$$

DATA CATEGORIZATION

The relationships between the percentage of crop and nitrate load expressed as weighted-flow concentrations or nitrate load per area were examined on an annual and seasonal basis. The annual timeframe of April 1 to March 31 was based on previous studies (King, et al, 2015; Williams et al, 2015; Pease et al, 2018; Hanrahan et al, 2018). On a seasonal scale, the categories were spring (Apr-Jun), summer (Jul-Sep), fall (Oct-Dec), and winter (Jan-Mar). These seasonal dates represent the planting season (spring), the growing seasons (summer), the harvest season (fall), and fallow season (winter) (Hanrahan et al, 2018).

GIS

Before analyzing crop cover, the watershed for each gauging station was created. The first step was downloading the 30-meter digital elevation model (DEM) of each of the states from USGS National Elevation Dataset. Using the ArcMap version 10.6 hydrology tools, individual watersheds were created using the steps presented in Figure 4. When snapping the pour point, GPS coordinates for each gauging station were used to accurately delineate the watershed.

Figure 4. Process of creating watersheds using hydrology tools in ArcMap.

Annual crop data in the form of the Cropland Data Layer (CDL) developed by the United States Department of Agriculture – National Agricultural Statistics Service (USDA, NASS) were used for evaluating large-scale agricultural change at annual intervals (Shao et al., 2016). Since 1997, the USDA has cataloged the type of crop grown by farmers throughout the entire United States at a resolution of 30 meters. As a raster, these data were imported into ArcMap and clipped

to their respective watershed. Once the land data were clipped to their respective watershed, then land use percentages were determined within the watershed.

In addition to the yearly crop data, the USDA provides crop frequency for corn and soybean through Cropscape. These data provide how many consecutive years an area was the same crop. Corn and soybean frequency data from 2008 to 2017 for each watershed were used. The mean weighted sum for each crop was calculated and compared to the mean weighted-flow concentration and the mean nitrate load per area.

REMOTE SENSING

The watersheds, along with the annual crop classification data, were exported from ArcMap to ENVI version 5.3 (Exelis Visual Information Solutions, Boulder, Colorado), an image analysis software, to determine crop rotation. Using ENVI, annual percent land cover change was determined by running a thematic change analysis. These tools show the percentage of land that stayed the same and what had changed classification on an annual scale. The results of the thematic change analysis showed the percent of crop changed, which gives the percentage of crop rotation between corn and soybean. Figure 5 shows the process of completing a thematic change.

Figure 5. Process of completing a thematic change using ENVI.

STATISTICS

Linear Regression

Linear regression analysis evaluates the relative impact of a predictor variable on a particular outcome (Zou et al, 2003). The independent variables used were percent of crop, corn or soybean, vs. the dependent variable, weighted-flow concentration or nitrate load per area. A

simple linear regression was used for each variable with an α of 0.05. In addition to the linear regression, a Pearson Coefficient Correlation analysis was conducted. The analysis provided the strength and direction of the linear relationship between two continuous variables (Zou et al, 2003). If the coefficient value is -1, then the strength of the correlation is perfectly negative. If the value is +1, then the strength is perfectly positive, and if the value is 0, then there is no association between the variables.

ANOVA

An ANOVA was run to determine any statically difference between the nitrate export and the season. An ANOVA is best used when comparing statistical significance among more than three groups. For this study, since the data were categorized into four season, an ANOVA was the best statistical test. If results show there is significance among the four seasons, then a Tukey Test was conducted to see identify seasons with significant differences between their nitrate loads.

CHAPTER III: RESULTS

To address the relationships between corn cultivation or soybean cultivation and nitrate load, the data were looked at on both a watershed scale and collectively, using all ten of the watersheds. To examine the seasonal influence, the relationship between crop type and nitrate export was broken down into seasons: spring (Apr-Jun), summer (Jul-Sep), fall (Oct-Dec), and winter (Jan-Mar).

Corn and soybean cultivation dominated the land cover in each watershed, with the Kansas River being the only exception. Within the Kansas River watershed, pasture (40.3%) was the dominant land cover and corn and soybean combined for 21.5% of the agricultural use. Comparing the cultivated difference between corn and soybean, corn was grown on between 14.3% (Kansas River) to 56.1% (Indian Creek) of the land, while soybeans accounted for 7.2% (Kansas River) to 45.4% (Spoon River) of the land. Within each of the watersheds, corn cultivation was always greater than soybean cultivation (Figures 3 and 6-15).

Crop rotation and crop frequency were used to determine any relationship between continuous cultivation in a single parcel and nitrate export. The crop rotation analysis showed that on average more soybean was rotated to corn, then corn rotated to soybean (Figure 16). While rotation did occur between corn and soybean crops, the corn or soybeans were grown on the same parcel for consecutive years throughout each watershed. The mean years for consecutive planting of corn ranged from 4.1 years (Kansas River) to 6.6 years (Green River). Mean years of consecutive soybean cultivation ranged from 3.1 years (Green River) to 4.6 years (Spoon River). Of the 10 years of data provided by the USDA, on average corn was planted consecutively in the same parcel for 5.3 years before it was rotated to a different crop, while soybean was planted in

the same parcel on average of 4.1 years before being rotated. There was no spatial evaluation of the cultivated crops, just the overall percentages of corn and soybean in each watershed.

Figure 6. Total cultivated corn (yellow) and soybean (green) within the Spoon River watershed 2013- 2017.

Figure 7. Total cultivated corn (yellow) and soybean (green) within the Indian Creek watershed 2011 – 2017

Figure 8. Total cultivated corn (yellow) and soybean (green) within the North Raccoon River watershed 2008 – 2017.

Figure 9. Total cultivated corn (yellow) and soybean (green) within the Raccoon River watershed 2008 – 2017.

Figure 10. Total cultivated corn (yellow) and soybean (green) within the Green River watershed 2015 – 2017.

Figure 11. Total cultivated corn (yellow) and soybean (green) within the Iroquois River watershed 2015 – 2017.

Figure 12. Total cultivated corn (yellow) and soybean (green) within the Cedar River watershed 2012 – 2017.

Figure 13. Total cultivated corn (yellow) and soybean (green) within the Iowa River watershed 2009 – 2017

Figure 14. Total cultivated corn (yellow) and soybean (green) within the Big Sioux River watershed 2017.

Figure 15. Total cultivated corn (yellow) and soybean (green) within the Kansas River watershed 2013 – 2017.

Figure 16. Crop rotation between corn and soybean for each watershed for the years in which NO₃-N data were available; a) Spoon River 2013 – 2017, b) Indian Creek 2011 – 2017, c) North Raccoon River 2008 – 2017, d) Raccoon River 2008 – 2017, e) Green River 2015 – 2017, f) Iroquois River 2015 – 2017, g) Cedar River 2012 – 2017, h) Iowa River 2009 – 2017, i) Kansas River 2013 – 2017.

Table 2. Mean years of consecutive planting of a single crop within each watershed.

Consecutive planting of each crop in years		
Watershed	Corn	Soybean
Spoon River	5.1	6.6
Indian Creek	5.5	4.4
North Raccoon River	5.4	4.3
Raccoon River	5.6	4.1
Green River	6.6	3.1
Iroquois River	5.7	3.5
Cedar River	5.6	4.0
Iowa River	5.5	4.0
Big Sioux River	4.2	4.0
Kansas River	4.1	3.2

ANNUAL NO₃-N WEIGHTED-FLOW CONCENTRATION

Corn

Examining the data among the watersheds collectively, mean weighted-flow concentrations ranged from $8.6 \times 10^{-4} \text{ kg/m}^3$ (Kansas River, 16.3% corn) to $1.07 \times 10^{-2} \text{ kg/m}^3$ (North Raccoon River, 48.8% corn). The data showed a statistically significant positive relationship ($p < 0.01$) between weighted-flow concentration and cultivated corn (Figure 17).

Figure 17. Mean weighted-flow concentration vs. mean cultivated corn for all ten watersheds. Points represent mean values and error bars represent one standard deviation (σ).

At the individual watershed scale, annual weighted-flow concentrations ranged from $1.37 \times 10^{-4} \text{ kg/m}^3$ (Kansas River, 2015) to $1.54 \times 10^{-2} \text{ kg/m}^3$ (North Raccoon River, 2013), which corresponded to 15.2% corn cultivation in the Kansas River watershed and 48.93% corn within the North Raccoon River watershed (Figure 18). At watershed scale, the data demonstrated negative relationships among the watersheds, with the exception of Kansas River and the Iowa River, which showed a positive to no relationship between weighted-flow concentration and cultivated corn within each watershed.

Figure 18. Weighted-flow concentration vs cultivated corn for each watershed on an individual scale. The Big Sioux River was not included because it only had one year of data; a) Spoon River, b) Indian Creek, c) North Raccoon River, d) Raccoon River, e) Green River, f) Iroquois River, g) Cedar River, h) Iowa River, i) Kansas River.

Soybean

Examining the data among the watersheds collectively, mean weighted-flow concentrations ranged from $8.62 \times 10^{-4} \text{ kg/m}^3$ (Kansas River, 7.9% soybean) to $1.07 \times 10^{-2} \text{ kg/m}^3$ (North Raccoon River, 36.2% soybean). The data showed a statistically significant positive relationship ($p < 0.01$) between weighted-flow concentration and cultivated soybean (Figure 19).

Figure 19. Mean weighted-flow concentration vs. mean cultivated soybean with one standard deviation for all ten watersheds. Points represent mean values and error bars represent one standard deviation (σ).

On an individual watershed scale, annual weighted-flow concentrations ranged from $1.37 \times 10^{-4} \text{ kg/m}^3$ (Kansas River, 2015) to $1.54 \times 10^{-2} \text{ kg/m}^3$ (North Raccoon River, 2013), which corresponded to 7.9% soybean cultivation in the Kansas River watershed and 34.8% soybean within the North Raccoon River watershed (Figure 20). At watershed scale, the data demonstrated positive relationships among the watersheds, with the exception of North Raccoon River between weighted-flow concentrations and cultivated soybean.

Figure 20. Weighted-flow concentration vs cultivated soybean for each watershed on an individual scale. The Big Sioux River was not included because it only have one year of data; a) Spoon River, b) Indian Creek, c) North Raccoon River, d) Raccoon River, e) Green River, f) Iroquois River, g) Cedar River, h) Iowa River, i) Kansas River.

Crop Frequency

Both corn and soybean experienced a positive relationship between the mean number of years for consecutive crop cultivation and the mean weighted-flow concentration in the watershed (Figure 21). Average consecutive corn cultivation ranged from 4.12 years (Kansas River) to 6.62 years (Green River). Average consecutive soybean cultivation ranged from 3.13 years (Green River) to 4.63 years (Spoon River).

Figure 21. Average consecutive corn (circles) and soybean (squares) cultivation vs mean weighted-flow concentration.

ANNUAL NO₃-N LOAD PER AREA

Corn

Examining the data among the watersheds collectively, annual mean nitrate load per area ranged from $2.8 \times 10^1 \text{ kg/m}^2$ (Kansas River, 16.3% corn) to $2.29 \times 10^3 \text{ kg/m}^2$ (North Raccoon River, 47.8% corn). The data showed a significant positive relationship ($p < 0.01$) between nitrate load per area and cultivated corn within the watershed (Figure 22).

Figure 22. Mean nitrate load per area vs. mean cultivated corn. Points represent mean values and error bars represent one standard deviation (σ).

On an individual watershed scale, nitrate load per area ranged from 3.99 kg/m^2 (Kansas River, 2015) to $6.31 \times 10^3 \text{ kg/m}^2$ (North Raccoon River, 2015), which corresponded to 15.2% corn cultivation in the Kansas River watershed and 48.9% corn within the North Raccoon River watershed (Figure 23). Spoon River, Indian Creek, North Raccoon River, and the Raccoon River each had a negative relationship between cultivated corn and nitrate load per area. All other watersheds exhibited positive relationship.

Figure 23. Annual nitrate load per area vs cultivated corn for each watershed on an individual scale. The Big Sioux River was not included because it only have one year of data; a) Spoon River, b) Indian Creek, c) North Raccoon River, d) Raccoon River, e) Green River, f) Iroquois River, g) Cedar River, h) Iowa River, i) Kansas River.

Soybean

Examining the data among the watersheds collectively, nitrate load per area ranged from $2.8 \times 10^1 \text{ kg/m}^2$ (Kansas River, 7.9% soybean) to $2.29 \times 10^3 \text{ kg/m}^2$ (North Raccoon River, 34.8% soybean). Collectively, the data showed a statistically significant positive relationship ($p < 0.01$) between nitrate load per area and cultivated soybean within the watershed (Figure 24).

Figure 24. Mean nitrate load per area vs. mean cultivated soybean with one standard deviation for all ten watersheds. Points represent mean values and error bars represent one standard deviation (σ).

On an individual watershed scale, nitrate load per area ranged from 3.99×10^0 kg/m² (Kansas River, 2015) to 6.31×10^3 kg/m² (North Raccoon River, 2015), which corresponded to 7.9% soybean cultivation in the Kansas River watershed and 34.8% soybean within the North Raccoon River watershed (Figure 25). Individually, the data demonstrated positive relationships among the watersheds, with the exception of Iroquois River and the Green River between nitrate load per area and cultivated soybean.

Figure 25. Annual nitrate load per area vs cultivated soybean for each watershed on an individual scale. The Big Sioux River was not included because it only have one year of data; a) Spoon River, b) Indian Creek, c) North Raccoon River, d) Raccoon River, e) Green River, f) Iroquois River, g) Cedar River, h) Iowa River, i) Kansas River.

Crop Frequency

Both corn and soybean exhibited a positive relationship between their respective consecutive cultivation and the mean nitrate load per area in the watershed (Figure 26). Average consecutive corn cultivation ranged from 4.12 years (Kansas River) to 6.62 years (Green River). Average consecutive soybean cultivation ranged from 3.13 years (Green River) to 4.63 years (Spoon River).

Figure 26. Average consecutive corn (circles) and soybean (squares) cultivation vs mean load per area.

SEASONAL NO₃-N LOADS

Both mean weighted-flow concentration and mean load per area were observed highest in the spring and then decreased as the year progressed; the lowest export occurred during the winter (Figure 27). An ANOVA determined that there was a statistical difference among the seasons ($p < 0.01$ between nitrate export and the seasons). Given a statistical difference among the seasons, a Tukey Test (Table 7) determined the significance among the individual seasons. Results showed that spring export were different than those in the summer, fall, and winter, all had a $p < 0.01$. None of the other seasons illustrated statistical differences ($p > 0.01$). This means, that the greatest difference in nitrate export occurred during the spring.

Table 7. Tukey Test p values between the seasons for nitrate export in both mean weighted-flow and load per area. Bold indicates statically significant correlations.

Tukey Results		
Season	Weighted-flow	Load per Area
Summer – Spring	<0.001	<0.001
Fall – Spring	<0.001	<0.001
Winter – Spring	<0.001	<0.001
Fall – Summer	0.552	0.530
Winter – Summer	0.099	0.391
Winter – Fall	0.759	0.996

Figure 27. Box and whisker plots of the weighted-flow average and the annual load per area for each season. The line in the box represents the median value, with the edge of the box corresponding to the 25th and 75th percentiles. The end caps are the 5th and 95th percentiles.

Seasonal $\text{NO}_3\text{-N}$ weighted concentrations ranged from $7.26 \times 10^{-5} \text{ kg/m}^3$ (Iowa River) in the fall of 2011 to $2.01 \times 10^{-2} \text{ kg/m}^3$ (North Raccoon River) in the spring of 2015. For corn, positive relationships between seasonal $\text{NO}_3\text{-N}$ weighted concentrations and cultivated corn were observed for each of the four seasons, with the highest concentrations observed during the spring,

then steadily decreased throughout the year (Figure 28). For soybeans, positive relationships between seasonal NO₃-N weighted concentrations and cultivated soybean were also observed for each of the four seasons, with the highest concentrations observed during the spring, then steadily decreased throughout the year (Figure 29).

Seasonal NO₃-N load per area ranged from 2.11×10^{-2} kg/km² (Indian Creek) in the summer of 2011 to 2.59×10^3 kg/km² (Indian Creek) in the spring of 2013. Positive relationships between NO₃-N load per area and cultivated corn were observed across all four seasons, with the highest export observed during the spring, and then gradually decreased as the year progressed (Figure 30). The same positive relationships were observed with cultivated soybean and the load per area where the highest load were observed in the spring, the decreased as the year progressed (Figure 31). These seasonal trends for both the weighted-flow concentration and the load per area were similar to the overall collective trend of cultivated crops and nitrate export on an annual level.

Figure 28. Seasonal $\text{NO}_3\text{-N}$ weighted-flow concentrations vs cultivated corn on a collective scale. Points represent mean values and error bars represent one standard deviation (σ).

Figure 29. Seasonal $\text{NO}_3\text{-N}$ weighted-flow concentrations vs cultivated soybean on a collective scale. Points represent mean values and error bars represent one standard deviation (σ).

Figure 30. Seasonal $\text{NO}_3\text{-N}$ load per area vs cultivated corn on a collective scale. Points represent mean values and error bars represent one standard deviation (σ).

Figure 31. Seasonal $\text{NO}_3\text{-N}$ load per area vs cultivated soybean on a collective scale. Points represent mean values and error bars represent one standard deviation (σ).

CHAPTER IV: DISCUSSION

RELATIONSHIP BETWEEN AGRICULTURE AND NITRATE EXPORT

Both the weighted-flow concentration (discharge normalization) and the nitrate load per area (area normalization) represent nitrate load, and both normalizations versus the type of crop (corn or soybean) generated similar relationships. Thus to avoid confusion, nitrate export will be used from this point rather than the individual reduced data type.

The analyzed data for all ten watersheds showed that as the percentage of either corn or soybean increased in a watershed, the nitrate export increased. Increases in the percentage of land devoted to soybean cultivation generated a higher nitrate export as compared to an equal increase in corn cultivation. Row crop production as a whole has been linked with increased nitrate surface water contamination over the last several decades (Keeney and Deluca, 1993); thus, a positive relationship between nitrate export and either corn or soybean for all ten watersheds comes from the fact that these areas have high-cultivated agricultural production. Even under optimal growing conditions, crop yield only accounts for 50% of the added N; the excess nitrogen remains within or is exported from the system (Oberle and Keeney, 1990).

Further analysis of the data revealed a positive relationship between the percentage of land-use devoted to row crop agriculture and nitrate export (Figure 32a, 33a). However, excluding corn and soybean land use from the data generated a negative relationship between agriculture and nitrate export (Figures 32b, 33b). The data suggest that corn and soybean contribute the most nitrate export than any other row crop in the Midwest. With corn and soybean accounting for more than 65% of the row crops in all the watersheds, except for Kansas, their importance regarding nitrogen management cannot be discounted.

Figure 32. Mean weighted-flow concentration vs. a) mean cultivated row crops and b) row crops excluding corn and soybean with one standard deviation for all ten watersheds. Points represent mean values and error bars represent one standard deviation (σ).

Figure 33. Mean nitrate load per area vs. a) mean cultivated row crops and b) row crops excluding corn and soybean with one standard deviation for all ten watersheds. Points represent mean values and error bars represent one standard deviation (σ).

The distribution of nitrate export to crop type was similar across all four seasons, with the highest export occurring during the spring and then decreasing throughout the year. Tile flow in the Midwest usually occurs primarily in April through June (Randall and Goss, 2008a), which coincides with seasonal patterns of increased precipitation, elevated stream discharge, and fertilizer application (David et al., 2010; Hanrahan et al, 2018; Raymond et al., 2012; Royer et al., 2006). Hanrahan et al (2018) reported that more than 70% of NO₃-N export occurred during high tile flow. This timeframe of increased tile flow is the same timeframe as the spring season in this study. A lack of tile flow during the winter prevents the rapid transport and export of nutrients from the soils, but as spring approaches and temperatures increase leading to snowmelt, the tiles will be flushed out and available nitrogen in the system would have been transported to the streams. It was also observed that spring had the highest nitrate export regardless of the crop, as any residual, regardless of crop, that was left on the fields after harvest is insignificant since overall crop rotation is minimum and seasonal trends are the same regardless of crop type (Figure 28, 29). In addition to crop residues showing up in the spring, spring fertilizer applications can also cause an increase in NO₃-N in streams with the help of precipitation and runoff. March through May precipitation causes the highest loss of N from fertilized fields before the crops growth and uptake of N starting in June (Balkcom et al, 2003).

THE ROLE OF CORN AND SOYBEAN WITHIN A WATERSHED

While the overall dataset showed a positive relationship between nitrate export and crop type, an opposite trend was observed on an individual watershed scale, with corn, a negative relationship occurred, and with soybean, a positive relationship occurred. A number of factors

including, percentage of crop cultivation, fertilizer rates, nitrogen uptake, residue breakdown, and denitrification rates of the crops can explain this relationship.

While corn receives more nitrogen fertilizer than soybean (Figure 1), the N fertilizer efficiency for corn was higher than N efficiency for soybean (Hesterman et al, 1987). Within the Raccoon River watershed, Jones et al. (2016) reported higher export of N after soybean cultivation, contributing the excess N to the decomposition of the soybean plant residue. In addition, the amount of runoff after harvest plays a role in nitrate export, even though it was not accounted for in this study. After harvest, soybean residual decomposes faster than corn, 68% of soybean residue decomposes over a 32-day period (Broder and Wagner, 1988), leaving behind bare soil that becomes exposed to direct rainfall (Laflen and Moldenhauer, 1979). Since corn residue is higher than soybean, corn residue provides surface cover to enhance rainfall capture and erosion control (Meki et al, 2013). David et al. (2009) evaluated six different watershed models in Illinois and each predicated lower denitrification rates for soybean than compared to corn, with an average rate of $9.35 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for soybean and $14.53 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for corn. Jones et al. 2016 also reported that more denitrification occurs in corn fields than in soybean fields, making less $\text{NO}_3\text{-N}$ available for loss through subsurface drainage.

The higher the cultivation of corn corresponding with, the higher denitrification rates, the more nitrogen uptake by corn, and longer residue residence time ultimately leads to lower nitrate export from agricultural fields. For example, Indian Creek experienced the highest cultivation of corn on an annual basis, with between 48.5% and 56.1% of growing corn (Figure 3). These land uses correspond with decreased nitrate export as corn percentage increased (Figure 18b and 23b). If the amount of corn production changes, then these rates will also change, leading to a change in nitrate export. The Kansas River serves as the lower bound in the overall trend of the data,

having the lowest production of corn between 14.3% and 18.4%. Within the watershed, a positive trend between corn and nitrate export was observed. Watersheds that exhibited greater than 47% corn cultivation had a negative relationship towards nitrate export. Watersheds with less than 47% corn cultivation generally exhibited a positive relationship as seen within the Kansas River and Iowa River. The data indicates there may be a threshold on percent corn cultivation, where further increases result in less nitrate export. Thus, increasing corn cultivation in Kansas River or Iowa River watershed will increase nitrate export from those watersheds until the threshold is reached. However, nitrate export will still be high collectively but the relationship on an individual watershed scale may show a decreasing trend between corn cultivation and nitrate export in these respective watersheds.

State nutrient reduction strategies have been implemented to reduce $\text{NO}_3\text{-N}$ export; Iowa has reported that the use of cover crops, buffer systems, reduced tillage, and increased crop rotation all helped reduced $\text{NO}_3\text{-N}$ export (Thompson et al, 2017). Data from this study speaks to the increased crop rotation to help reduce nitrate export. Previous research examining nitrogen use efficiency and crop rotation showed that a corn-soybean rotation had a 69% higher nitrogen use efficiency than a continuous corn cropping system (Attia et al, 2015). In addition, Attia et al (2015) indicated that planting corn and soybean on 2 to 3 year rotation systems could improve N usage between the crops. Among the examined watersheds, crop rotation occurred each year, but the amount of rotation on a year to year basis is minimal (Figure 16). Among the watersheds, the consecutive years of soybean cultivation in a field were lower than consecutive years of corn cultivation in a field. Average consecutive corn cultivation ranged from 4.12 years (Kansas River) to 6.62 years (Green River). Average consecutive soybean cultivation ranged from 3.13 years (Green River) to 4.63 years (Spoon River). Both corn and soybean had a positive

relationship between consecutive crop cultivation and nitrate export (Figures 21 and 26). The data align with those of Attia et al. (2015); during periods with less years of continuous crop cultivation, nitrate export is lower. As the time a crop was continuously grown in a field increased, the export of nitrate simultaneously increased. Iowa have reported that increased crop rotation on 3 to 5 years can help reduce nutrient loss, but this practice is uncommon. Survey results in 2014 showed that 65% of farmers did not use extended rotations nor did they plan to use it in the future, 18% reported they did not use it, but might consider it in the future, finally 17% reported they used extended rotations (Nowatzke and Arbuckle, 2016). The data presented in this study, show that as crop rotations increase, then nitrate export will decrease (Figures 21 and 26).

While the variables mentioned above were not looked at during this study, they do support and explain the trends between nitrate export and crop type within a corn-soybean cropping system. To meet the goal of the nutrient reduction plan, having best management practices in place in agricultural areas as well as understanding the relationships between corn and soybean is important to reduce the overall impact of nitrate leaching into nearby streams and affecting areas downstream.

CHAPTER V: CONCLUSIONS

The results of the collective data showed a positive relationship between percent corn or percent soybean and nitrate export, supporting the hypothesis as the percentage of cultivated corn increases, the annual nitrate load would increase; but arguing against the hypothesis as percentage of cultivated soybean increases, the annual nitrate load would decrease. Seasonal results both supports and argues against the highest nitrate loads are expected in the spring and fall, while the lowest loads occur during the summer and winter months. The data showed that spring had the highest export, while summer, fall, and winter all exhibited lower nitrate loads.

Conclusions can be made from the data in this study and data from previous studies. 1) Corn has a higher cultivation percentage, higher fertilizer application rate, higher denitrification rate, higher N uptake rate, and a lower residual breakdown when compared to soybean. These factors all influence the relationship between crop type and nitrate export within a watershed, which the data support with a negative relationship between corn and nitrate export and a positive relationship between soybean and nitrate export. 2) Rotation is a key in reducing nitrate export to nearby streams. The more frequent rotation between corn and soybean, the lower nitrate export to the streams. This has been stated by the Iowa Nutrient Reduction strategy as well and could be a factor in reducing nitrate in agricultural watersheds given the different characteristics between corn and soybean.

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